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MODELING MICROBIOLOGICAL AND CHEMICAL PROCESSES IN MUNICIPAL SOLID WASTE BIOREACTOR: DEVELOPMENT AND APPLICATIONS OF A THREE-PHASE NUMERICAL MODEL BIOKEMOD-3P

by

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Spring Term
2009

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ABSTRACT

The numerical computer models that simulate municipal solid waste (MSW) bioreactor landfills have mainly two components – a biodegradation process module and a multi-phase flow module. The biodegradation model describes the chemical and microbiological processes of solid waste biodegradation. The models available to date include predefined solid waste biodegradation reactions and participating species. In a bioreactor landfill several processes, such as anaerobic and aerobic biodegradation, nitrogen and sulfate cycling, precipitation and dissolution of metals, and adsorption and gasification of various anthropogenic organic compounds, occur simultaneously. These processes may involve reactions of several species and the available biochemical models for solid waste biodegradation do not provide users with the flexibility to selectively simulate these processes. This research work includes the development of a generalized biochemical process model, BIOKEMOD-3P, which can accommodate a large number of species and process reactions. This model is able to simulate bioreactor landfill processes in a completely mixed condition; when coupled with a multi-phase model it will be able to simulate a full-scale bioreactor landfill. This generalized biochemical model can simulate laboratory and pilot-scale operations which are important to determine biochemical parameters important for simulation of full-scale operations. To illustrate application of BIOKEMOD-3P, two sets of laboratory MSW bioreactors were simulated in this research work. The first demonstrated simulation of data from anaerobic biodegradation of MSW in experimental bioreactors. In another application, simultaneous nitrification and denitrification processes in
MSW bioreactors were simulated. The results from these simulations generated information about various modeling parameters that would help implement these processes in a full-scale bioreactor landfill operation.

Key Words: Biodegradation modeling, bioreactor landfill, multi-phase model.
To

my teachers and

my parents Chandraprabha and Anand Gawande
ACKNOWLEDGEMENTS

I am thankful to my adviser Dr. Debra R. Reinhart and I express my deep sense of gratitude to her for providing me with the opportunity to carry out this research work. Her valuable guidance throughout my Ph.D. program and the inspiration helped me achieve this goal. I am thankful to Dr. Gour-Tsyh Yeh for his valuable guidance for the development of the computer model and the course work. The guidance of Dr. C. David Cooper and Dr. Andrew Randall during the course work helped me in this research work, I am thankful to them. I thank Dr. Manoj Chopra and Dr. Alexander Katsevich along with other members of my Ph.D. dissertation committee for their time and help to accomplish this research work. I thank Dr. Morton Barlaz and Dr. Nicole Berge for allowing me to use their experimental data and valuable discussion. I am thankful to Dr. Vasily Vavilin for the valuable discussion on various aspects of biochemical modeling.

I am thankful to various funding agencies for sponsoring research projects of Dr. Debra R. Reinhart which funded me for the most of this research work. I am thankful to my parents Mrs. Chandraprabha and Mr. Anand Gawande who inspired me to come to the USA and providing me with funds when ever needed. I thank my friends, Manish Kothari, Dr. Pradeep Jain, Dr. Amaya Lobo, Dr. Vikram Pattarkine, Dr. Maria Rizou, Dr. Prashant Shrikhande, D.S.R.K. Srinivas, Jan Dybdahl, Mei-Ling Liu, the friends of yahoo group, VRCECIVIL92, brother Ashwin and sister Leena who stayed in touch during this research work.

Nitin A. Gawande
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CHAPTER 1:  
INTRODUCTION

1.1 Background Information

Municipal solid waste (MSW) bioreactor landfills aim to achieve rapid stabilization of waste with gains from space and biogas recovery (Pohland 1975; Reinhart and Townsend, 1998). Liquids are added to enhance biodegradation processes which produce methane and also cause reduction of waste volume. The bioreactor landfill is a complex system with physical, chemical, and biological processes occurring simultaneously. Numerical modeling could be employed as an effective tool to improve the understanding of these processes.

A full-scale bioreactor landfill can be numerically described as composed of large number of representative elementary volumes (REVs) as shown in Figure 1-1. With the help of REVs, the space geometry along with physical and chemical characteristics of a landfill can be described. Figure 1-2 shows a schematic of various processes in a bioreactor landfill. These processes could be broadly divided into two components, a physical component that describes the flow of liquids, gases and heat, and a biochemical component that describes the chemical and microbiological processes. A model required to simulate bioreactor landfill will have these two components coupled together. Application of such complex models have been extensively done to simulate processes in the subsurface under saturated and unsaturated conditions for site remediation (Brun and Engesgaard, 2002). Bioreactor landfills add complexity to simulating these processes because, unlike waste site remediation for soils, the solid matrix is biodegradable and changes over time. Additional processes may be required in a numerical model to describe
the dynamic changes in the solids matrix of a bioreactor landfill.

Figure 1-1. Bioreactor landfill represented by representative elementary volumes.

Figure 1-2. Biochemical and transport processes in bioreactor landfill operation.
The motivation for this research work was to develop a comprehensive model that could simulate a full-scale bioreactor landfill. To date extensive work has been done on the simulation of the physical processes of multi-phase flow in subsurface under saturated and unsaturated conditions; whereas the biochemical component describing the processes of solid waste biodegradation which causes changes in leachate quality and generates gas, has been over simplified. Unavailability of a robust model is the reason that simple models are used to describe the biochemical components of bioreactor landfill processes. A biochemical computer model needs to be computationally robust and allow user-specified species and reactions without the need to modify the computer code. Such a model would allow any user without computer programming knowledge to run the model for different applications.

The scope of the present research was restricted to the development of a robust model to simulate the biochemical processes in bioreactor landfills, boxed in Figure 1-2. This research work included the following objectives:

1. conduct a literature review on existing models currently used to simulate various chemical and microbiological processes in bioreactor landfills;
2. develop a numerical computer model to simulate these processes; and
3. apply the computer model to simulate processes of solid waste bioreactors.

The objectives mentioned above were met by completing tasks corresponding to these objectives.
1.2 Dissertation Organization

This dissertation comprises of five chapters. Chapter 2 presents the literature review of numerical models available to date to simulate the chemical and microbiological processes in bioreactor landfills. It also includes identification of processes for simulating anaerobic biodegradation of MSW in bioreactors. Chapters 3, 4, and 5 are written in journal paper format in order to facilitate submission to peer reviewed journals.

Chapter 3 describes the development of numerical computer model BIOKEMOD-3P, which includes the mathematical formulation of governing equations, the numerical implementation to solve these equations, and model verification by analytical solution.

Chapter 4 describes the application of the numerical model BIOKEMOD-3P to simulate experimental data from solid waste bioreactors (Barlaz et al., 1989). This work includes identification of various reactions and species that were necessary for the simulation and discussion of the model results.

Chapter 5 describes another application of the numerical model BIOKEMOD-3P to simulate experimental data from simultaneous nitrification and denitrification in laboratory microcosms (Berge 2006). This work includes identification of necessary reactions and species for the simulation and a discussion of the model results.

Chapter 6 includes conclusions and recommendations from this research work. Appendix A contains the analytical solution for the model verification exercise. Appendix B presents the manual for the use of numerical model BIOKEMOD-3P, the governing equations and mathematical formulation. Appendix C presents the input and output files for the simulation from Chapter 4. Appendix D presents the input and output files for simulations from Chapter 5.
References


CHAPTER 2:
LITERATURE REVIEW

2.1 Biochemical Models

The biochemical processes of municipal solid waste (MSW) biodegradation are similar to the processes of innovative technologies for subsurface site remediation such as biochemical degradation, vapor extraction, and natural attenuation. In spite of this similarity, the research on modeling solid waste biodegradation finds little collaboration with subsurface modeling for site remediation. The numerical models for simulation of landfill processes mostly evolved independent of research conducted in subsurface contaminant transport modeling.

The earlier landfill models were leaching type ranging from empirical models and simple water balances, to complex unsaturated flow models. Straub and Lynch (1982a) demonstrated the feasibility of using an unsaturated flow and contaminant transport model to predict leachate production and concentrations of dissolved inorganics in an experimental landfill. Their other work, (Straub and Lynch, 1982b) presented simulation of experimental landfill bioreactor with and without recirculation. Other hydrological models include the unsaturated flow model for moisture transport by Korfiatis and Demetracopoulos (1984), hydrological models like Hydrologic Evaluation of Landfill Performance (HELP) model by Schroeder et al. (1983), and generation and transport of solute contaminants through landfills by Demetracopoulos et al. (1986).

Halvadakis (1983) presented a simplified biochemical model for landfill processes that considered hydrolysis of solid waste, utilization of soluble carbon, growth and decay of
acidogenic and methanogenic biomass and finally methane and carbon dioxide production. More models were developed with the inclusion of simultaneous heat, mass and momentum transfer in multiphase systems (Young, 1992; Swarbrick et al., 1995; El-Fadel et al., 1996(a and b), Lethlean, 1998). A few models like those of Young (1992) and Swarbrick et al. (1995) used principles of chemical thermodynamics to model the landfill degradation processes and predict contaminant concentrations in leachate. Others (El-Fadel et al., 1996a) used Monod-type bacterial growth kinetic equations to predict gas generation. As the understanding of the biochemical processes in the landfill improved, it was possible to quantify the kinetic constants involved in such processes. Bryers (1985) presented a structured model of anaerobic digestion of organic particulates. Based on a similar approach, Haarstrick et al. (2001) made a structured model specifically applied to landfill conditions using Monod-type kinetic equations. Suk et al. (2000) presented a model for gas and water phase solute transport describing the change in leachate quality and gas production considering biochemical reactions. Oldenburg (2001) modeled landfills including biochemical processes coupled with transport of liquid, gas, and heat for two-dimensional geometry. The overall biochemical process was very much simplified in this model.

Lobo et al. (2002a and b) presented an integrated leachate flow and biodegradation model. The model could be calibrated for leachate flow and solid waste biodegradation and the gas generation over time could be estimated. Vavilin et al. (2003) developed a coupled leachate flow and biochemical model and showed spatial distribution of biomass species depending on the mixing conditions. El-Fadel et al. (1996b) concluded that although temperature is one of the important factors affecting gas production, moisture content, cellulose structure and lignin

The biochemical models presented by the researchers mentioned above include predefined solid waste biodegradation reactions. Some of these models allow changing of the basic composition of solid waste. In a bioreactor landfill, several processes such as anaerobic and aerobic solids biodegradation, nitrogen and sulfate related processes, precipitation and dissolution of metals, and adsorption and gasification of various anthropogenic organic compounds occur simultaneously. These processes may involve reactions of several species; the available biochemical models for solid waste biodegradation do not provide users with the flexibility to selectively simulate these processes. In contrast the models developed for simulating subsurface contaminant transport provide some flexibility to users in their choice of reactions and species. Brun and Engesgaard (2002) mentioned some of these models and their features in modeling of transport and biogeochemical processes in pollution plumes. Yeh et al. (2001) presented some of the theoretical issues that needed to be considered for proper application of reaction-based biogeochemical models. On these lines Fang et al. (2006) presented an improved methodology for reaction-based models. A majority of models used for subsurface
biogeochemical processes modeling simulate reactions primarily in aqueous phase and lack applications to processes of solid waste biodegradation, where solids undergo hydrolysis and the liquid phase species partition into the gas phase. The study of available numerical models emphasized the need of a robust numerical model to simulate chemical and microbiological processes of MSW bioreactor landfills in a three-phase system.

2.2 The biochemical model for solid waste biodegradation

The pathway of anaerobic digestion in sulfate-depleted environment for biological polymers, marshes, trees, and digesting sludge was presented by Zender et al. (1982). Figure 1-1 shows the anaerobic biodegradation reaction scheme used in this paper on afore mentioned pathway. Complex models of anaerobic biodegradation of particulate matter were compiled by Gavala et al. (2003). A more complex model for solid waste biodegradation may involve interaction of sulfur and nitrogen species depending on the characteristics of solid waste. In order to model solid waste biodegradation, four reaction processes could be considered (Figure 2-1); hydrolysis of solids, acetogenesis, acetate utilizing methanogenesis, and hydrogen utilizing methanogenesis processes which are described in following sub-sections.

2.2.1 Hydrolysis

Solids in landfills could be modeled as a homogeneous mixture of inorganic soil and composite organic solid waste. The above treatment of solids can also help in defining the contribution from the cover soil by suitably changing the proportions of soil and solid waste (Eq.
1.1). Eq. (1.2) is a simplification of the complex hydrolysis process.

\[ C_{GO} = \left( \sum_{i=1}^{n} v_i C_{Gi} \right) + S_I \]  

(1.1)

where,

\( C_{GO} \) is the composite organic solid component

\( C_{Gi} \) solid components representing carbohydrates, proteins, lipids, and inerts

\( v_i \) fraction of \( C_{GO} \) represented by \( C_{Gi} \)
Hydrolysis is the transformation of complex particulate organic matter into simple monomer or dimer forms that can pass the bacterial cell membrane. Hydrolysis during anaerobic digestion may occur primarily due to the action of extracellular enzymes and may depend on several physicochemical factors such as particle size, pH, diffusion and adsorption of enzymes to particles (Gavala et al., 2003). This makes hydrolysis the least defined among all the processes of anaerobic solid waste biodegradation. Comparison of various methodologies to model the hydrolysis kinetics during anaerobic biodegradation of particulate organic matter was presented by Vavilin et al. (1996 and 2008). In these modeling studies with data from anaerobic processes with high organic loadings, the Contois kinetics (Contois, 1959) and two-phase kinetics which considered the ratio of the characteristic sizes of bacteria and solid particles, both showed a better fit. The first-order model was described as a particular case of the above two models. The Contois model is given by Eq. (1.3).

\[
CG_i = -k_{H,j} \left( \frac{CG_i/B_C}{K_H + CG_i/B_C} \right) B_C
\]  

(1.3)

where,

- \( B_C \) is the total microorganism population affecting hydrolysis
- \( k_{H,j} \) & \( K_H \) are hydrolysis rate constant and normalized half-saturation constant respectively

\( S_i \) soluble inert fraction

\[
\text{Solid Waste} + H_2O \rightarrow \text{Soluble Compounds}
\]  

(1.2)
Since hydrolysis is a process of solubilization of complex insoluble organics by enzymes excreted by hydrolytic microorganisms, it depends on the quantity of active biomass present in the system. The inhibition terms applicable to Monod-type kinetics may be applied to hydrolysis as well. The kinetic hydrolysis step is dependent on pH, temperature, and moisture content.

Degradation of solid waste particulate matter produces sugar monomers, simple amino acids, and volatile fatty acids upon hydrolysis. Veeken et al. (2000) found no accumulation of monomeric products from hydrolysis of organic fractions of solid waste at pH 6.0 and 7.0. Therefore the hydrolysis of solid waste components can be modeled to directly produce various volatile fatty acids (VFAs), carbon dioxide, and hydrogen following the pathway in Figure 2-1. However, for the simplicity of calculations and presentation these product species are expressed in terms of intermediate monomer forms (Eqs. 1.4 through 1.6). Amino acids contribute to higher fatty acids such as valerate and butyrate (Batstone et al., 2003). Upon balancing the stoichiometry of methane production, the yield of hydrolysis products of amino acids could be determined.

\[
C_6H_{12}O_6 + 2H_2O \rightarrow 2C_2H_4O_2 + 4H_2 + 2CO_2 \tag{1.4}
\]

\[
3C_6H_{12}O_6 \rightarrow 4C_3H_6O_2 + 2C_2H_4O_2 + 2CO_2 + 2H_2O \tag{1.5}
\]

\[
C_6H_{12}O_6 \rightarrow C_4H_8O_2 + 2H_2 + 2CO_2 \tag{1.6}
\]

2.2.2 Acetogenesis

In anaerobic digestion, acetogenesis mainly refers to the formation of acetate from anaerobic oxidation of long chain fatty acids (Eqs. 1.7 through 1.9). In the present work valerate, butyrate, and propionate are the major fatty acids that undergo anaerobic oxidation to form...
acetate. In order to sustain valerate, butyrate, and propionate oxidation the energetics require that the products formed from these reactions are consumed. This results in mutual interdependency between acetogenic and methanogenic bacteria. Thermodynamically, actogenesis is severely inhibited at high hydrogen concentrations (Mosay, 1983). As such a non-competitive inhibition due to hydrogen can be adopted during the acetogenesis of valerate, butyrate, and propionate.

\[
C_5H_{10}O_2 + 2H_2O \rightarrow C_3H_6O_2 + C_2H_4O_2 + 2H_2 
\]  
\[ (1.7) \]

\[
C_4H_8O_2 + 2H_2O \rightarrow 2C_2H_4O_2 + 2H_2 
\]  
\[ (1.8) \]

\[
C_3H_6O_2 + 2H_2O \rightarrow C_2H_4O_2 + 2H_2 + CO_2 
\]  
\[ (1.9) \]

2.2.3 Methanogenesis

In anaerobic digestion about 65 to 70% methane is produced from acetate while the remaining from hydrogen and carbon dioxide. Methanogenic microorganisms are extremely sensitive to temperature, pH, organic loading rate and are inhibited by number of compounds (Gavala et al., 2003). The methanogenic reactions are represented by Eqs. (1.10) and (1.11). Monod kinetics can be used to model the acetogenic and methanogenic processes.

\[
C_2H_4O_2 \rightarrow CH_4 + CO_2 
\]  
\[ (1.10) \]

\[
4H_2 + 2CO_2 \rightarrow CH_4 + H_2O 
\]  
\[ (1.11) \]
2.2.4 Chemical equilibrium reactions

The bioreactor landfill system has large number of chemical species that take part in chemical kinetic and equilibrium reactions. Any biochemical model used to simulate bioreactor landfill processes must be capable of handling a large number of well defined reactions. The chemical equilibrium reactions that may be required to simulate the anaerobic biodegradation of solid waste are described by Eqs. (1.12) through (1.18). These reactions help in predicting the pH of the system.

\[ \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{H}^+ \quad (1.12) \\
\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}^+ \quad (1.13) \\
\text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+ \quad (1.14) \\
\text{HAc} \rightleftharpoons \text{Ac}^- + \text{H}^+ \quad (1.15) \\
\text{HPr} \rightleftharpoons \text{Pr}^- + \text{H}^+ \quad (1.16) \\
\text{HBu} \rightleftharpoons \text{Bu}^- + \text{H}^+ \quad (1.17) \\
\text{HVa} \rightleftharpoons \text{Va}^- + \text{H}^+ \quad (1.18) \\

The long chain fatty acids are not included in equilibrium reactions as the number of charged sites per mass is small and does not contribute significantly to pH predictions (Batstone et al. 2002).
2.2.5 Aqueous and gas phase partitioning reactions

The contribution from the partitioning of aqueous and gas phase reactions can be modeled using Eq. (1.19). Although the value of the overall mass transfer coefficient, $K_L$, may vary with the rate of generation of gas, a constant value can be used throughout the simulation.

$$\rho_k = K_L \left( S_{\text{liq},i} - K_H P_{\text{gas},j} \right)$$  

(1.19)

where,

- $\rho_k$ is the rate of mass transfer between the liquid and the gas phase species in the k-th reaction
- $K_L$ is the overall mass transfer coefficient
- $S_{\text{liq},i}$ is the concentration of i-th liquid phase species
- $P_{\text{gas},j}$ is the partial pressure of j-th gas species

2.2.6 Heat and temperature

The change in the temperature of the reaction system can be related to the change in free energy of a reaction. Haarstrick et al. (2001) used the change in enthalpies of the biochemical reactions in anaerobic processes to get the energy yield and ultimately the temperature change. In anaerobic processes the majority of heat is produced during the acid production phase. In order to simplify the calculations of heat generation, the rate of heat produced could be related to the rate of acid produced (El-Fadel et al. 1996(a) as per Eq. (1.20).
\[ q = \sum \omega_i \frac{dC_i}{dt} \] (1.20)

Where,

\( q \) = heat generation rate

\( \omega_i \) = net heat gain proportionality constant for \( i \)-th acids species

\( C_i \) = concentration of \( i \)-th acid species

The heat generation rate is related to temperature change as per Eq. (1.21)

\[ q = c_p \Delta T \] (1.21)

\( c_p \) = specific heat capacity of solid waste

### 2.3 Numerical model

This literature review showed that the available biochemical models to date have certain limitations in order to simulate bioreactor landfill processes. The lack of generalization, limited number of species and process reactions are a few of them. A generalized computer model BIOKEMOD was presented by Salvage and Yeh (1998) to simulate microbiological and chemical reactions essentially in one phase. The model developed in this research will be structurally similar to BIOKEMOD and will be expanded for a three-phase system.
2.4 Model Calibration

Model calibration is a process that demonstrates the capability of a model in reproducing measured data (Anderson and Woessner, 1992, in Cheng J.C., 1995). The calibration procedure helps in finding sets of parameters such that the simulation matches actual data. El-Fadel et al. (1996c) conducted sensitivity analysis of parameters affecting the biogas generation. A majority of processes in bioreactor landfills are significantly affected by the pH. The sensitivity analysis for most of the model parameters when conducted while taking the effect of pH show that they fall in a very narrow range. Therefore a visual calibration was used during the application of this model for landfill processes as employed by Vavilin et al. (2003) and Stamatelatou et al. (2003). Biochemical models like BIOKEMOD-3P simulate processes in a completely mixed system. Therefore experimental data from laboratory scale solid waste bioreactors were used as the small scale of laboratory bioreactors ensure near uniform and mixed conditions.

References


CHAPTER 3:
MODELING MICROBIOLOGICAL AND CHEMICAL PROCESSES IN MUNICIPAL SOLID WASTE BIOREACTOR, PART I: DEVELOPMENT OF A THREE-PHASE NUMERICAL MODEL BIOKEMOD-3P
Submitted for publication

Abstract

The numerical computer models that simulate municipal solid waste (MSW) bioreactor landfills have mainly two components – a biodegradation process module and a multi-phase flow module. The biodegradation model describes the chemical and microbiological processes. The models available to date include predefined solid waste biodegradation reactions and participating species. Some of these models allow changing the basic composition of solid waste. In a bioreactor landfill several processes like anaerobic and aerobic solids biodegradation, nitrogen and sulfate related processes, precipitation and dissolution of metals, and adsorption and gasification of various anthropogenic organic compounds occur simultaneously. These processes may involve reactions of several species and the available biochemical models for solid waste biodegradation do not provide users with the flexibility to simulate these processes by choice. This paper presents the development of a generalized biochemical process model BIOKEMOD-3P which can accommodate a large number of species and process reactions. This model is able to simulate bioreactor landfill operation in a completely mixed condition, when coupled with a multi-phase model it will be able to simulate a full-scale bioreactor landfill. This generalized biochemical model can simulate laboratory and pilot-scale operations in order to determine
biochemical parameters important for simulation of full-scale operations.

3.1 Introduction

Methane is a major greenhouse gas and the estimation and monitoring of methane emissions from landfill has become an important issue in solid waste management. Attempts were made over the past twenty five years to predict gas production from landfills using various models to simulate and estimate the gas generation. To date this still remains an area of active research that requires a better understanding of various landfill processes.

The earlier landfill models were leaching models ranging from empirical models and simple water balances, to complex unsaturated flow models. Lethlean (1998) presented a brief review of landfill models development. A few of those were moisture flow and leaching of organics by Straub and Lynch (1982, a & b), unsaturated flow model for moisture transport by Korfiatis and Demetracopoulos (1984), hydrological models like Hydrologic Evaluation of Landfill Performance (HELP) model by Schroeder et al. (1983), and generation and transport of solute contaminants through landfill by Demetracopoulos et al. (1986). Some were empirical based, calculating the rate of gas production for the estimated life of a landfill (Findikakis and Leckie, 1979).

With the understanding of the impact of moisture content on solid waste biodegradation process, the concept of operating the landfill as a bioreactor evolved (Pohland, 1975). Bioreactor landfills allow for increased moisture content and expedite the biodegradation processes (Reinhart and Townsend, 1997). Bioreactor landfills not only offer incentives related to
increased availability of space for solid waste placement, but also reduce the time period for long
term monitoring and gas collection. The high methane production rates facilitate turning this
greenhouse gas into a valuable energy resource (Halvadakis, 1983). Bioreactor landfill operation
involves either addition of liquids or recycling the leachate to increase the moisture content.
Various types of liquid injection and leachate collection configurations are used to achieve this
objective. The heterogeneity of solid waste landfill is a major obstruction in achieving uniform
distribution of moisture (McCreanor and Reinhart, 2000). The changes in the landfill operation
practice require appropriate modeling techniques to be employed to simulate the landfill
processes and ultimately predict the methane generation.

Halvadakis (1983) presented a simplified biochemical landfill model that considered
hydrolysis of solid waste, utilization of soluble carbon, growth and decay of acidogenic and
methanogenic biomass and finally methane and carbon dioxide production.

More models were developed with inclusion of simultaneous heat, mass and momentum transfer
in multiphase systems (Young, 1992; Swarbrick et al., 1995; El-Fadel et al., 1996(a and b),
principles of chemical thermodynamics to model the landfill degradation processes and predict
contaminant concentrations in leachate. Others (El-Fadel et al., 1996a) used Monod-type
bacterial growth kinetic equations to predict gas generation. As the understanding of the
biochemical processes in the landfill improved, it was possible to quantify the kinetic constants
involved in such processes. Bryers (1985) presented a structured model of anaerobic digestion of
organic particulates. Based on a similar approach, Haarstrick et al. (2001) made a structured
model specifically applied to landfill conditions using Monod-type kinetic equations. Suk et al.
(2000) presented a model for gas and water phase solute transport describing the change in leachate quality and gas production considering biochemical reactions. Oldenburg (2001) modeled landfills including biochemical processes coupled with transport of liquid, gas, and heat for two-dimensional geometry. The overall biochemical process was very much simplified in this model. Lobo et al. (2002a and b) presented an integrated leachate flow and biodegradation model. The model could be calibrated for leachate flow and solid waste biodegradation and the gas generation over time could be estimated. Vavilin et al. (2003) developed a coupled leachate flow and biochemical model and showed spatial distribution of biomass species depending on the mixing conditions. El-Fadel et al. (1996b) concluded that although temperature is one of the important factors affecting gas production, moisture content, cellulose structure and lignin content may exert greater influence. Mora-Naranjo et al. (2004) presented a biochemical model that included the effects of temperature and moisture content. White et al. (2004) presented a spatially distributed numerical model to simulate flow of leachate and gases with consolidation of solid waste. A biochemical sub-model was included to simulate the biochemical processes. McDougall (2007) presented a conceptual model primarily for settlement analysis of landfill with coupling of hydraulic, biodegradation, and mechanical behavior. Reichel et al. (2007) presented a mechanistic model for biological and chemical processes considering dependencies of pH, temperature, and moisture content.

In general, any model that is required to simulate bioreactor landfill processes with an aim to predict the gas generation must have at least two components, a physical component to simulate the flow of liquids and gases, and a biochemical component to accommodate various chemical and microbiological processes. Figure 3-1 shows various process in the bioreactor
landfill operation.

Figure 3-1. Biochemical and transport processes in bioreactor landfill operation.

The multi-phase flow models were primarily developed for application to hydrogeological processes in porous media and extensive research has already been done in this area. A majority of these models find application in hazardous waste site remediation projects. The biochemical processes in landfills are unique and different from the subsurface site remediation processes. A majority of biochemical models for solid waste degradation mentioned earlier do not allow the addition of user specified biochemical processes. Several simultaneous processes occur during solid waste biodegradation and they involve multiple chemical and microbiological species. For example acidogenic, methanogenic, aerobic, sulfidogenic, nitrifiers and denitrifiers organisms are some of the microbiological species that could be included while there could be very large number of chemical species involved in a complex solid waste biodegradation process. A majority of models mentioned above are unable to model simultaneous equilibrium
reactions involving chemical species.

This paper presents the development of a biochemical process model that could be coupled with a multi-phase model to simulate a full-scale bioreactor landfill. The motivation for the work comes from the fact that the models explained above are all made with a fixed biochemical structure in terms of the processes and the species. Whereas the model presented here is a generalized numerical model that can accommodate user specified chemical and microbiological processes involving a very large number of species. This model is able to simulate bioreactor landfill operation in a completely mixed condition which when coupled with a multi-phase model, will be able to simulate a full-scale bioreactor landfill. This generalized biochemical model can simulate laboratory and pilot-scale operations to determine biochemical parameters for full-scale operations.

3.2 Model development and concept

The present model BIOKEMOD-3P, is an extension of models KEMOD (Yeh and Tripathi, 1991) and BIOKEMOD (Salvage and Yeh, 1998) but for a three-phase system. The chemical and microbiological reactions for a multi-phase system are presented in this section. The governing equations describing the model are presented in the following section. This paper explains the additions and modifications over the work presented by Salvage and Yeh (1998).

3.2.1 Physical and chemical processes
In BIOKEMOD-3P, the equilibrium and kinetic chemical reactions are the same as the parent model BIOKEMOD. These include the aqueous complexation, surface-solution, and precipitation/dissolution reactions. The acid/base reactions are simulated using a specified pH or computed pH. BIOKEMOD-3P uses the excess hydrogen ion concentration to calculate the pH. This approach leads to the same results when pH is computed using a charge balance. The approach of using excess hydrogen ion is advantageous when there is little knowledge about possible ionic species other than those involved in acid-base type reactions. In such case, ionic strength can be specified in the model and pH can be easily defined by the excess of protons and there is no need for using fictitious ionic species for charge balance. The electron potential (pe) can be calculated using the reduction/oxidation processes by doing an electron balance on the aqueous and solid phase species. The ionic strength can be kept at a specified value or calculated using the Davies Equation (Stumm and Morgan, 1981). Like its predecessor models, BIOKEMOD-3P is able to simulate an unlimited number of chemical species, provided sufficient chemical reactions are included to solve for the unknown variables. The precipitation and dissolution, adsorption, and ion-exchange reactions are described in detail by Salvage and Yeh (1998), hence not included here. Chemical complexation, ‘Constant Capacitance’ and ‘Triple Layer’ models (Stumm, 1992) are included to simulate adsorption. The ion-exchange process is described by chemical equilibrium and/or kinetic reactions. The effect on these reactions due to any change in the solid phase has been considered in the present work. The disintegration of solids due to complex mechanical/physical/chemical processes is lumped and simulated as a first-order kinetic reaction. The partitioning of soluble gases in the aqueous phase is an addition made in the present model. The equilibrium constants for the mass action reactions
and rate constants for the kinetic reactions are corrected for a change in temperature using thermodynamics.

3.2.2 Microbiological processes

The microbiologically mediated reactions are essential to degradation of solid waste to gaseous products. Mathematical models may be structured to describe changes at cellular level (e.g. concentration of enzymes, ATP etc.). In environmental applications, various steps at the cellular level are lumped together to describe a process by one overall rate. Monod kinetics (Monod, 1949) for biomass growth and substrate degradation is one of the most commonly used approaches to model environmental processes. The effect of endogenous respiration, electron acceptor, nutrient availability and inhibition were incorporated into the Monod Equation in the previous model BIOKEMOD (Salvage and Yeh, 1998). In BIOKEMOD-3P, Contois Kinetics (Contois, 1959) describing the microbiologically mediated reaction has been added which describes the hydrolysis of matter in solid phase into aqueous products. A biodegradation model for subsurface application such as bioreactor landfill would not be practical without including the effect of changes in the degree of saturation, temperature and the pH on the microbiological reactions; these effects are included in the present model BIOKEMOD-3P.

3.2.3 Data Input
The input data require stating all the components and species in all three phases of the system under consideration. Input includes relevant chemical components, their total analytical concentrations, and stoichiometry of chemical product species for mass balance equation of components. The description of microbial species includes their initial concentration, endogenous decay rate and the effect of temperature and pH on the growth rate. The solid phase species are defined by their concentration in the system volume. The gas phase species are defined by their initial partial pressure in the system. The description of chemical reactions includes the reaction stoichiometry and the type of reaction. Equilibrium constants for chemical equilibrium reactions and kinetic constants for chemical kinetic reactions must be defined. The microbiological reactions data include the stoichiometry, identification of substrate among the reactants, maximum specific growth rate for microorganisms, half saturation constant, electron acceptor, nutrient, lag time, and information about inhibition if any. The information on the partitioning reaction between the aqueous and gas phase includes the stoichiometry and the kinetic rate constants. The pH, pe and ionic strength may be computed or user specified with constraint on their values. The porosity of solid phase, degree of saturation of aqueous phase, density of liquid, surface area of solid grains, and surface density of adsorbent sites on the grains are described. Any additional headspace volume can be added to the system and the total gas phase pressure can be constrained to a specified value. The temperature of the system can be set at a specified input value or allowed to vary depending on the heat generated from the microbiological reactions. The specific heat capacity of species in three phases is an input which is used for computation of temperature change in the model. The information on source/sink of species in any of the three phases is part of the input.
3.3 Governing Equations

The governing equations describing the biochemical model BIOKEMOD-3P are presented in this section. Chemical ‘components’ are defined as a set of linearly independent variables and the chemical ‘product’ species can be represented as a combination of those components. Like its predecessor models KEMOD and BIOKEMOD, BIOKEMOD-3P uses molarity (mass of chemical species/volume of solution) for total analytical concentrations of components and molality (mass of chemical species/mass of phase in which the species exists) for individual species concentrations. This however is limited to chemical and microbiological species in aqueous and solid phase. The solid phase species are represented by their mass concentration (mass of solid species/batch volume). In the derivation of the governing equations, a mass based approach has been considered for the gas phase species, but finally modified to a form where individual gas species are represented by their partial pressure in the gas phase. The mass balance equations that define the rate of change of various species are given by Eqs. (3.1) through (3.5). Eq. (3.1), (3.2) and (3.3) were described by Salvage and Yeh (1998), whereas the Eq. (3.4) and (3.5) and corresponding reactions have been added in the present work.

\[
\frac{\partial (\rho_n \theta_n c_n)}{\partial t} = \rho_n \theta_n r_n - \rho_n \theta_n \lambda_n c_n + q_n , \ n \in N
\]

\[
\frac{\partial (\rho_m \theta_m p_m)}{\partial t} = \rho_m \theta_m r_m - \rho_m \theta_m \lambda_m p_m + q_m , \ m \in M
\]
\[
\frac{\partial}{\partial t} (\rho_b \theta_b b_b) = \rho_b \theta_b r^u_b - \rho_b \theta_b r^d_b + \rho_b \theta_b r^w_b + q_b , \ b \in B 
\]  \quad (3.3)

\[
\frac{\partial}{\partial t} (\rho_b h_b) = \rho_b r_b - \rho_b \lambda_b h_b + q_b , \ h \in H 
\]  \quad (3.4)

\[
\frac{\partial}{\partial t} (\rho_s \theta_s g_s) = \rho_s \theta_s r_s - \rho_s \theta_s \lambda_s g_s + q_s , \ g \in G 
\]  \quad (3.5)

Where, \( n, m, b, h, \) and \( g \) denote the chemical component species, chemical product species, solid phase species, and gas phase species, respectively.

\( t \) \quad time (T)

\( N \) \quad number of chemical components (aqueous and adsorbent)

\( M \) \quad number of chemical product species (aqueous, adsorbed, and precipitated)

\( B \) \quad number of microbial species (aqueous and adsorbed)

\( H \) \quad number of solid phase species

\( G \) \quad number of gas phase species

\( c_n \) \quad concentration of the \( n \)th chemical component in its free form (mass/mass of phase, MM\(^{-1}\))

\( \rho_m \) \quad concentration of \( m \)th chemical product species (mass/mass of phase, MM\(^{-1}\))
$b_n$ concentration of $n$th microbial species (mass/mass of phase, MM$^{-1}$)

$h_n$ concentration of solid phase species (mass/mass of solid phase, MM$^{-1}$)

$g_g$ concentration of gas phase species (mass/mass of gas phase, MM$^{-1}$)

$\rho_n, \rho_m, \rho_b$

bulk density of phase in which the $n$th, $m$th or $b$th species exists respectively (mass of phase/phase volume, ML$^{-3}$)

$\theta_n, \theta_m, \theta_b$

volumetric content in which the $n$th, $m$th or $b$th species exists respectively (phase volume /batch volume, LL$^{-3}$)

$\rho_l, \rho_g$

bulk density of liquid and gas phase respectively (mass of phase/mass of phase, ML$^{-3}$)

$\theta_l, \theta_g$

volumetric content of liquid and gas phase respectively (phase volume /batch volume, LL$^{-3}$)

$\rho_s$ bulk density solid phase (mass of phase/batch volume, ML$^{-3}$)

$r_n, r_m$

production/consumption rate of the $n$th, $m$th chemical species, respectively (MM$^{-1}$T$^{-1}$)

$r_b^g, r_b^d$

the $b$th microbial species growth rate and decay rate respectively (MM$^{-1}$T$^{-1}$)

$r_b^{sp}$

transfer rate of the $b$th microbial species between aqueous and adsorbed phases (MM$^{-1}$T$^{-1}$)

$r_h$

the $h$th solid phase species production/consumption rate (MM$^{-1}$T$^{-1}$)
the gth gas phase species production/consumption rate (MM\(^{-1}\)T\(^{-1}\))

\(\lambda_n, \lambda_m\) decay constant of the \(n\)th and \(m\)th species respectively (T\(^{-1}\))

\(\lambda_h, \lambda_g\) decay constant of \(h\)th solid phase and \(g\)th gas phase species respectively (T\(^{-1}\))

\(q_n, q_m, q_b\)

source/sink rate of the \(n\)th, \(m\)th, and the \(b\)th species respectively (ML\(^{-3}\)T\(^{-1}\))

\(q_h, q_g\) source/sink rate of the \(h\)th solids and the \(g\)th gas phase species respectively (ML\(^{-3}\)T\(^{-1}\))

Species in each phase are subject to change due to different type of reactions. A general equation for production/consumption of chemical components/species can be written as given by Eq. (3.6).

\[
r_i = r_i^{\text{chem}} + r_i^{\text{bio}} + r_i^{\text{solid}} + r_i^{\text{gas}} \quad i \in \{N, M, B, H, G\}
\]  

where,

\(r_i^{\text{chem}}\) production/consumption rate of \(i\)th component/product species due to chemical reaction (ML\(^{-3}\)T\(^{-1}\))

\(r_i^{\text{bio}}\) production/consumption rate of \(i\)th component/product species due to microbial reaction (ML\(^{-3}\)T\(^{-1}\))

\(r_i^{\text{solid}}\) production/consumption rate of \(i\)th component/product species due to conversion into or from solid phase reaction (ML\(^{-3}\)T\(^{-1}\))
production/consumption rate of \( i \)th component/product species due to conversion into or from gas phase reaction \( \text{ML}^{-3}\text{T}^{-1} \)

Eq. (3.1) can be replaced with a mass balance equation governing the total concentration of the component species (Yeh and Tripathi, 1991; Salvage and Yeh, 1998). This approach ensures strict mass conservation with respect to the chemical components and also facilitates the coupling of a stand-alone model with a multi-phase flow model. By multiplying Eq. (3.2) with the stochiometric coefficient of the \( n \)th chemical component in the \( m \)th chemical product species and adding the results to Eq. (3.1), Eq. (3.7) is obtained.

\[
\frac{\partial T_n}{\partial t} = \rho_n \theta_n r_n \left|^{\text{bio}} \right. + \sum_{m=1}^{M} \rho_m \theta_m v_{m n} r_n \left|^{\text{bio}} \right. + \rho_n \theta_n r_n \left|^{\text{solid}} \right. + \sum_{m=1}^{M} \rho_m \theta_m v_{m n} r_n \left|^{\text{solid}} \right. \\
+ \rho_n \theta_n r_n \left|^{\text{gas}} \right. + \sum_{m=1}^{M} \rho_m \theta_m v_{m n} r_n \left|^{\text{gas}} \right. - \Lambda_n T_n + Q_n
\]

(3.7)

\[
T_n = \rho_n \theta_n c_n + \sum_{m=1}^{M} \rho_m \theta_m v_{m n} p_m , \quad n \in N
\]

(3.8)

\[
\Lambda_n T_n = \rho_n \theta_n \lambda_n c_n + \sum_{m=1}^{M} \rho_m \theta_m \lambda_m v_{m n} p_m , \quad n \in N
\]

(3.9)

\[
Q_n = q_n + \sum_{m=1}^{M} v_{m n} p_m , \quad n \in N
\]

(3.10)
where,

\( T_n \) total analytical concentration of the \( n \)th chemical component (mass/batch volume, ML\(^{-3}\))

\( \Lambda_n \) total decay constant of the \( n \)th chemical component (T\(^{-1}\))

\( Q_n \) total source/sink rate of the \( n \)th chemical component (ML\(^{-3}\)T\(^{-1}\)).

The definition of \( T_n \) as per Eq. (3.7) takes into consideration that a chemical component mass is conserved with respect to chemical reactions but not so with microbiological, solid phase hydrolysis, and gas partitioning reactions. BIOKEMOD-3P uses Eq. (3.7) to solve \( T_n \) \( s \), and then Eq. (3.8), Eqs. (3.2), (3.3), (3.4), and (3.5) to solve for \( c_n \) \( s \), \( p_n \) \( s \), \( b_h \) \( s \), \( h_h \) \( s \), and \( g_g \) respectively.

### 3.3.1 Chemical reactions

Any chemical reaction can be written as under:

\[
\sum_{j=1}^{N_{k+M}} v'_{k,j} \tilde{g}_j \rightleftharpoons \sum_{j=1}^{N_{k+M}} v^*_{k,j} \tilde{g}_j, \quad k \in NCR
\]  

(3.11)

where,

\( v'_{k,j} \) reactant stoichiometry of the \( j \)th species in the \( k \)th reaction

\( v^*_{k,j} \) product stoichiometry of the \( j \)th species in the \( k \)th reaction

\( \tilde{g}_j \) chemical formula of \( j \)th species chemical species, either component or product
The rate for this reaction can be represented by Eq. (3.12)

$$\Omega_k = k^f_k \prod_{j=1}^{N+M} (\gamma_j g_j)^{y''_j} - k^b_k \prod_{j=1}^{N+M} (\gamma_j g_j)^{y'_j} \quad (3.12)$$

where,

- $\Omega_k$: reaction rate of the $k$th reaction (T$^{-1}$)
- $g_j$: concentration of the $j$th chemical species, representative of c$_n$ or p$_m$ species (MM$^{-1}$)
- $\gamma_j$: activity coefficient of the $j$th species
- $k^f_k$: forward rate constant for the $k$th reaction (T$^{-1}$)
- $k^b_k$: backward rate constant for the $k$th reaction (T$^{-1}$)

The total production/consumption of a species due to chemical reactions is the sum of the contributions from all the reactions in which the species participates and is given by Eq. (3.13)

$$r_j^{chem} = \sum_{k=1}^{NCR_{chem}} \frac{V_{kj}^{r'} - V_{kj}^{r''}}{\gamma_j} \Omega_k, \quad j \in \mathbb{N} + M \quad (3.13)$$

When the reaction is an equilibrium reaction, the net reaction rate is zero resulting in the law of mass action (Salvage and Yeh, 1998). In a precipitation/dissolution reaction, the activity of solid species is assumed to be equal to unity. The effect of temperature on some chemical
reactions may be greater than on biological reactions. The van’t Hoff equation describes the variation of equilibria coefficients with temperature change (Eq. 3.14).

\[
\ln \frac{K_2}{K_1} = \frac{\Delta H^O}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
\]

(3.14)

where,

\(\Delta H^O\) heat of reaction at standard temperature and pressure, (joule)

\(R\) gas Law constant, (J/gmol-K)

\(K_1\) known equilibrium coefficient at reference temperature \(T_1\) (K)

\(K_2\) unknown equilibrium coefficient at any temperature \(T_2\) (K)

3.3.2 Microbiological reactions

Any microbiological reaction can be written in a general form as given by Eq. (3.15).

\[
\sum_{j \in 1}^{N+M+B} v'_{kj} \tilde{g}_j \Leftrightarrow \sum_{j \in 1}^{N+M+B} v''_{kj} \tilde{g}_j, \quad k \in NBR
\]

(3.15)

Monod kinetics is used to describe the rate of the microbial reaction as given by Salvage and Yeh (1998), Eq. (3.16).

\[
\Omega_k = (\Gamma_k I_{1k}) \left( \frac{S_k}{(K_{S-k} I_{2k}) + S_k} \right) \left( \frac{A_k}{K_{A-k} + A_k} \right) \left( \frac{N_k}{K_{N-k} + N_k} \right) I_k
\]

(3.16)
where,

\[ \Gamma_k \] growth rate for the \( k \)th microbial reaction per unit biomass activity (T\(^{-1}\))

\[ S_k \] concentration of the substrate in the \( k \)th microbial reaction (MM\(^{-1}\))

\[ A_k \] concentration of the electron acceptor in the \( k \)th microbial reaction (MM\(^{-1}\))

\[ N_k \] concentration of the nutrient in the \( k \)th microbial reaction (MM\(^{-1}\))

\[ K_{S-k} \] half saturation constant for the substrate in the \( k \)th microbial reaction (MM\(^{-1}\))

\[ K_{A-k} \] half saturation constant for the electron acceptor in the \( k \)th microbial reaction (MM\(^{-1}\))

\[ K_{N-k} \] half saturation constant for the nutrient in the \( k \)th microbial reaction (MM\(^{-1}\))

\[ L_k \] lag coefficient for the \( k \)th microbial reaction

\[ I_{1k} \] inhibition factor for growth rate in the \( k \)th microbial reaction

\[ I_{2k} \] inhibition factor for half saturation constant for substrate in the \( k \)th microbial reaction

Microbial reactions are significantly affected by temperature, pH, and water saturation. The effect of pH on growth rate of different microbial species is modeled as per the Michaelis pH function given by Angelidaki et al. (1993) and Batstone et al. (2002). Eqs. (3.17) and (3.18) give the normalized inhibition function. In BIOKEMOD-3P, the excess hydrogen ion concentration represents one of the aqueous phase components, hence no special treatment is required while calculating the pH.
\[ I(pH) = \frac{1 + 2 \cdot 10^{0.5(pH_L-pH_H)}}{1 + 10^{(pH-pH_H)} + 10^{(pH_L-pH)}} \]  \hspace{1cm} (3.17)

\[ I(pH) = \exp\left(-3.0\left(\frac{pH - pH_H}{pH_H - pH_L}\right)^2\right) \]  \hspace{1cm} (3.18)

\( pH_L \) and \( pH_H \) are the lower and upper pH inhibition values respectively. In Eq. (3.17) the upper and lower values represent the pH where the growth rates are approximately 50% of the uninhibited rates. Eq. (3.18) represent inhibition only due to the lower pH values. The model gives the user a choice to use either of the two pH inhibition functions.

The temperature correction can be applied to the microbial process rates using the Arrhenius equation. Temperature ranges from mesophilic to thermophilic conditions in a bioreactor landfill. Siegrist et al. (2002) suggested the use of mesophilic rates with corrections up to optimum thermophilic temperatures. Above the optimum temperature the growth rate decreases up to a maximum temperature limit given by Angelidaki et al. (1993). Eqs. (3.19) and (3.20) are used in the present model.

\[ \Gamma_{k,T} = \Gamma_{k,35} e^{\theta(T-35)} \]  \hspace{1cm} (3.19)

Where,

\( \Gamma_{k,T} \) growth rate of bacteria in kth microbial reaction at a temperature of T °C, (T-1)

\( \Gamma_{k,35} \) growth rate of bacteria in kth microbial reaction at mesophilic temperature, 35 °C, (T-1)
Temperature for maximum growth rate, °C

\[ T_{OPT} \]

\[ \Gamma_{k,T} = \Gamma_{MAX,OPT} \frac{(T_{MAX} - T)}{(T_{MAX} - T_{OPT})}; \text{ for } T \geq T_{opt} \]  \hspace{1cm} (3.20)

where,

\[ \Gamma_{MAX,OPT} = \Gamma_{k,35} e^{\theta(T_{opt} - 35)} \]  \hspace{1cm} (3.21)

Temperature where growth of bacteria in kth microbial reaction ceases, °C

Moisture content has a profound effect on the biodegradation rates, therefore the concept of liquids addition to increase the moisture content in landfill has evolved. Gurijala et al. (1997) in a study on samples taken out of landfill found that solid waste samples containing greater than 55% (wt/wt) moisture content produced higher amounts of methane while those with less than 33% did not produce any methane. They found a linear correlation between the rate of methane production and moisture content. These data were used by Mora-Naranjo et al. (2004) to find a function that was used for modeling the effect of moisture content on microbiological reactions. This function was linear with zero growth at moisture content of 15% (w/w). The wet moisture content of solid waste is expected to be highly variable depending on its composition. Therefore in BIOKEMOD-3P a linear effect of moisture content was considered and the degree of saturation was used as a multiplying factor for the rate of microbiological reactions. Eq. (3.16) is modified to include the effects of temperature, pH, and moisture content and represented by Eq. (3.22).
\[
\Omega_k = \left( \Gamma_{k,T} I_{1k} I_{\mu \phi} S_w \right) \left( \frac{S_k}{K_{S-k} I_{2k}} + S_k \right) \left( \frac{A_k}{K_{A-k} + A_k} \right) \left( \frac{N_k}{K_{N-k} + N_k} \right) L_k
\] (3.22)

The total production/consumption of a chemical species due to microorganism mediated processes is the sum of the contributions from each microbial reaction that involves the chemical species (Eq. 3.23).

\[
r_{j}^{\text{bio-deg}} = \sum_{k=1}^{N_{\text{B}} \text{R}} \left( \frac{v'_{k,j} - v''_{k,j}}{\gamma_j} \right) \Omega_k \{b_k\}, \ j \in N + M
\] (3.23)

where,

- \(r_{j}^{\text{bio-deg}}\) total rate of production of the \(j\)th chemical species due to microbial degradation reaction \((\text{MM}^{-1}\text{T}^{-1})\)
- \(\{b_k\}\) activity of the microbial species \(b_k\), is dimensionless and equal in magnitude to the concentration of microbial species \(b_k\).

The microorganisms undergo endogenous respiration and the rate of microbial decay can be assumed to be proportional to the biomass present (Salvage and Yeh, 1998).

\[
r_{b}^{\text{bd}} = K_{bd} b_b, \ b \in B
\] (3.24)

where,
$r_{bd}$ decay rate for the $b$th microbial species, (MM$^{-1}$T$^{-1}$)

$K_{bd}$ decay rate constant for the $b$th microbial species, (T$^{-1}$).

The endogenous respiration process may involve consumption/production of a chemical species. The production/consumption rate of such chemical species is given by Eq. (3.25) as given by Salvage and Yeh (1998).

$$r_{j}^{\text{endog}} = \sum_{b=1}^{B} \alpha_{bj} K_{db} b_{b} \left[ \frac{g_{j}}{K_{bj} + g_{j}} \right], \quad j \in N + M$$

(3.25)

where,

$r_{j}^{\text{endog}}$ rate of consumption of the $j$th chemical species due to cellular maintenance/decay, (MM$^{-1}$T$^{-1}$)

$\alpha_{bj}$ stoichiometric coefficient for the use of the $j$th chemical species in maintenance/decay of the $b$th microbial species.

The overall rate of change of chemical species due to biodegradation and endogenous respiration is given by Eq. (3.26)

$$r_{j}^{\text{bio}} = r_{j}^{\text{biodeg}} - r_{j}^{\text{endog}}, \quad j \in N + M$$

(3.26)
3.3.3 Solid phase reactions

Any reaction involving solids species can be represented by Eq. (3.27)

\[
\sum_{j=1}^{N+M+B+H} v'_{k,j} \tilde{g}_j \rightleftharpoons \sum_{j=1}^{N+M+B+H} v''_{k,j} \tilde{g}_j, \quad k \in NHR
\]

(3.27)

where, \( NHR \) represents any reaction involving any of ‘H’ solid phase species.

3.3.3.1 Solids disintegration/formation reactions

The solid phase species may disintegrate or combine due to complex physical-chemical processes; as a result there may be changes in the particle size and/or chemical characteristics. Such processes have a greater consequence on other reactions dependent on surface property like adsorption and ion-exchange processes and solids hydrolysis. The importance of the solids disintegration reaction was explained by Batstone et al. (2002). The rate of change in production/consumption of solids species is given by Eq. (3.28).

\[
r_j^{\text{solids}} = \sum_{k=1}^{NHR} \left( v''_{k,j} - v'_{k,j} \right) \frac{\Omega_k}{\gamma_j}, \quad j \in H
\]

(3.28)

A reaction rate similar to chemical kinetic reactions is considered in BIOKEMOD-3P (Eq. 3.29). Any reaction with only one reacting species and with a backward rate constant equal
to zero becomes a first-order reaction.

$$\Omega_k = k_k^b \prod_{j=1}^H (\gamma_j g_j) - k_k^b \prod_{j=1}^H (\gamma_j g_j), \quad k \in NHR$$  \hspace{1cm} (29)

3.3.3.2 Solids hydrolysis

The enzymatic hydrolysis of solids is a microorganism mediated reaction. In bioreactor landfills and subsurface environments in soil, the ratio of solids to microorganisms is very high. In such case Contois Kinetics (Contois, 1959) is well suited to describe the microorganism mediated hydrolysis reaction. Eqs. (30) and (31) describe the rate of production/consumption of any species due to solids hydrolysis.

$$r_j^{bio.h} = \sum_{k=1}^{NBHR} \left( \frac{v'_{kj} - v'_{kj}}{\gamma_j} \right) \Omega_k, \quad j \in N + M + H$$  \hspace{1cm} (30)

$$\Omega_k = \left( \Gamma_{h-k,T} I_{1k} I_{pH} S_w \right) \left( \frac{h_k/b_k}{K_{S-k} I_{2k} + h_k/b_k} \right) L_k, \quad k \in NBHR$$  \hspace{1cm} (31)

where,

$$\Gamma_{h-k,T} \quad \text{rate constant for the } k\text{th microbial hydrolysis reaction modified for temperature effect,}$$

$$h_k \quad \text{concentration of solids species undergoing the hydrolysis in the } k\text{th microbial hydrolysis}$$
reaction (ML$^{-3}$)

$\text{b}_k$ concentration of the microbial species in the $k$th microbial hydrolysis reaction (ML$^{-3}$)

$K_{S,k}$ modified half saturation constant for the $k$th microbial hydrolysis reaction, (MM$^{-1}$).

The total growth rate for any microbial species is the sum of the contributions from all the reactions in which it is involved. Eq. (3.32) gives the total growth rate for $b$th microbial species involved in NBR biodegradation reactions and NBHR hydrolysis reactions. The decay of any microbial species was already described by Eq. (3.24).

$$r^g_b = \sum_{k=1}^{NBR+NBHR} \frac{v'_{kj} - v''_{kj}}{\gamma_j} \Omega_k (\text{b}_k), \quad b \in B$$  

(3.32)

3.3.4 Gas phase reactions

Aqueous phase species often partition into gas phase. Henry’s Law best describes this partitioning effect. Eq.(3.33) represents a general form of gas phase reaction describing conversion of aqueous species to gaseous form or vice versa.

$$\sum_{j \in 1}^{N+M+G} v'_{kj} \tilde{g}_j \Leftrightarrow \sum_{i \in 1}^{N+M+G} v''_{ki} \tilde{g}_i, \quad k \in NGPR$$  

(3.33)
where, $NGPR$ represents the number of gas phase reactions. Eqs. (3.34) and (3.35) represent the rate of production/consumption of any species involved in the gas phase reaction.

$$\left. r_j \right|_{\text{gas}} = \sum_{k=1}^{NGPR} \frac{v_{k,j}^r - v_{k,j}^\prime}{\gamma_j} \Omega_k , \ j \in N + M + G$$  (3.34)

$$\Omega_j = -\Omega_i = k_L \left( \prod_{j=1}^{N+M} (\gamma_j g_j)^{v_j} - K_{H(i,j)} \prod_{i=1}^{G} (\gamma_i g_i)^{v_i} \right) , \ j \in N + M \ \text{and} \ i \in G$$  (3.35)

where,

- $K_{H(i,j)}$ Henry’s constant for partitioning of $j$th aqueous species with $i$th gas species, dimensionless
- $k_L$ over all mass transfer coefficient, (T$^{-1}$).

Partial pressure is used to indicate the gas species concentration and Eq. (3.5) was modified using the ideal gas law. The gas phase volume included gas in pore spaces and the head-space volume for gas when specified.

### 3.3.5 Heat generation

A majority of heat generation reactions in the environmental systems and bioreactor landfills are microorganism mediated, but only a few are exothermic chemical reactions.
Spontaneous combustion is an extremely fast reaction and is not included here. The free energy of reaction gives an indication of the amount of heat generated/consumed in a reaction. In the natural systems involving reactions mediated by microorganisms, the use of theoretical value of free energy of reaction may not be the ideal method for computation of temperature change. The rate of heat generation can be related to the formation of products by microorganisms (El-Fadel et al. 1996(a)). The rate of heat generation is represented by Eqn. (3.36).

\[ q = \sum_{i=1}^{NBR+NBHR} \omega_k \Omega_k (\gamma_{ik} b_i) , \ j \in B \]  

(3.36)

where,

\[ q \]  
rate of production/consumption of heat from all the biological reactions, (ML2/T3)

\[ \omega_k \]  
coefficient for production/consumption of heat, for the kth microbial reaction per unit production of microbiological species, (ML2/T3)

The change in the temperature of the system is computed by applying the heat balance for the system as under:

\[ \left( \rho, \theta_t, c_t + \rho, \theta_k, c_k + \rho, \rho, c_\beta \right) \frac{\partial (TEMP)}{\partial t} = \cdot - q_L + q_Q \]  

(3.37)

Where,

\[ c_t, c_k, c_\beta \]
are the specific heat capacities of component species in aqueous, gas and solid phase respectively.

/temp/ temperature of the system in degree Kelvin

/q_L/ rate of heat loss from the system, (ML^2/T^3)

/q_g/ addition/removal of heat due to source/sink of species in any phase, (ML^2/T^3).

The governing equations presented above are the mass balance equations for the components species in each of the three phases, mole balance equations for free component species, mass action equation for equilibrium species, and kinetic rate equations for kinetic chemical, microbial, solids, and gas phase species. Section 3.4 presents the method used to solve these equations.

3.4 Numerical Method

In BIOKEMOD-3P, the governing equations are solved iteratively in two loops. The technique is similar to that adopted by Yeh and Tripathi (1991) and Salvage and Yeh (1998). The outer loop (Figure 3-2) calculates the total concentrations of all component species in the aqueous phase, Eq. (3.7), the densities of all phases and the volumetric content of aqueous phase (theta_i) and gas phase (theta_g), and temperature (TEMP). The individual species (Eq. 3.2 through Eq. 3.5) are calculated in the inner loop (Figure 3-3) using the values of T/s, densities of various phases, degree of saturation of each phase and the temperature. The Newton-Raphson technique is adopted to solve the equations in the inner loop (Westall et al. 1976; Yeh and Tripathi, 1991;
Salvage and Yeh, 1998; Yeh et al. 1998). The model has a provision to allow the total gas pressure to change or to be maintained at a constant value, these computations are done in the outer loop. The breakdown of various computations in two loops facilitates coupling of this model with flow and transport models. The computation of precipitated species is performed as explained by Salvage and Yeh (1998). Time steps are user specified that could be constant or variable.

At the start of every time step, the changes in the concentration of species in various phases due to chemical, microbiological, solid and gas phase change reactions are determined (Eq. 3.6). The individual species concentrations are solved in the inner loop with a set of differential-algebraic equations solved by the Newton-Raphson iterative technique. This technique is explained in detail by Westall et al. (1976) and Tripathi and Yeh (1991). Full pivoting is employed in solving the matrix equations in the Newton-Raphson method. The time weighting of the solution may be either implicit or explicit. Once a convergent solution is obtained in the individual species loop, the parameters in the total concentration loop are computed using the contributions from the newly determined reaction rates. The process is repeated iteratively until convergence in the outer as well as the inner loop is achieved. Equilibrium species are solved independently of the individual concentration loop. This helps to reduce the number of equations that are required to be solved in the iterative loop and saves on computational time (Salvage and Yeh, 1998).
At the start of every time step, the changes in the concentration of species in various phases due to chemical, microbiological, solid and gas phase change reactions are determined (Eq. 3.6). The individual species concentrations are solved in the inner loop with a set of differential-algebraic equations solved by the Newton-Raphson iterative technique. This technique is explained in detail by Westall et al. (1976) and Tripathi and Yeh (1991). Full pivoting is employed in solving the matrix equations in the Newton-Raphson method. The time weighting of the solution may be either implicit or explicit. Once a convergent solution is obtained in the individual species loop, the parameters in the total concentration loop are computed using the contributions from the newly determined reaction rates. The process is repeated iteratively until convergence in the outer as well as the inner loop is achieved.
Equilibrium species are solved independently of the individual concentration loop. This helps to reduce the number of equations that are required to be solved in the iterative loop and saves on computational time (Salvage and Yeh, 1998).

Figure 3-3. Flow chart of individual species concentration loop.
3.5 Model verification

The simulation results obtained from the computer model must be compared to the analytical results to assess the model applicability to real problems. The verification of the portions of the computer code handling chemical equilibrium and chemical kinetic and microbiological reactions was presented by Yeh and Tripathi, (1991) and Salvage and Yeh, (1998). This section presents a verification example problem for the model BIOKEMOD-3P. A microorganism mediated solids hydrolysis reaction which involves conversion of the solids species into aqueous species is presented here. The analytical solution was developed for the Contois kinetic reaction of solids hydrolysis (Eq. A7, Appendix). The reaction rate in the analytical solution refers to the rate modified for the effect of temperature, pH and moisture content. Figure 3-4 shows model results compared with analytical solution for solids during the hydrolysis reaction. Figure 3-5. shows the plot of analytical solution and model results compared to a plot of 1:1 relationship. The coefficient of determination for the model results to 1:1 relationship is $r^2=0.9999995$ and $s^2=1.89E-05$. 
Figure 3-4. Model results compared with analytical solution for solids during hydrolysis reaction.

Figure 3-5. Model verification with analytical calculations for solids hydrolysis reaction.
3.6 Conclusions

The formulation of a generalized computer model to simulate biochemical processes in bioreactor landfills was presented. The model was verified for the modifications to a previous model by Salvage and Yeh (1998). This model could be used to simulate a laboratory or pilot-scale landfill bioreactor. When coupled with a multi-phase flow model, this model could be used for simulation of a full-scale bioreactor landfill. To date this is the only generalized model available to simulate solid waste biodegradation with species distributed in three phases. This model will be a useful tool to users without computation background to simulate solid waste biodegradation processes. BIOKEMOD-3P can also find extensive applications in simulation of subsurface contaminant transport modeling.

References


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CHAPTER 4: MODELING MICROBIOLOGICAL AND CHEMICAL PROCESSES IN MUNICIPAL SOLID WASTE BIOREACTOR, PART II: APPLICATION OF NUMERICAL MODEL BIOKEMOD-3P

Abstract

Biodegradation process modeling of municipal solid waste (MSW) bioreactor landfills requires the knowledge of various process reactions and corresponding kinetic parameters. Mechanistic models available to date are able to simulate biodegradation processes with the help of pre-defined species and reactions. Some of these models consider the effect of critical parameters such as moisture content, pH, and temperature. Biomass concentration is a vital parameter for any biomass growth model and often not compared with field and laboratory results. A more complex biodegradation model includes a large number of chemical and microbiological species. Increasing the number of species and user defined process reactions in the simulation requires a robust numerical tool. A generalized microbiological and chemical model, BIOKEMOD-3P, was developed to simulate biodegradation processes in three-phases (Gawande et al. 2009a). This paper presents the application of this model to simulate laboratory-scale MSW bioreactors under anaerobic conditions. BIOKEMOD-3P was able to closely simulate the experimental data. The results from this study may help in application of this model to full-scale landfill operation.
4.1 Introduction

Municipal solid waste (MSW) biodegradation modeling is primarily aimed at predicting methane generation and waste stabilization in landfill bioreactors. The developments and advancement in MSW biodegradation processes modeling were described by Gawande et al. (2009). Mechanistic models available to date are able to simulate biodegradation processes with the help of pre-defined species and reactions. Some of these models consider the effect of critical parameters like moisture content, pH, and temperature. Biomass concentration is a vital parameter for any biomass growth model and often not compared with field and laboratory results. The anaerobic microorganisms consortia which is composed of several different species having varying degree of physical and chemical sensitivities are often lumped together. Increasing the number of species and reactions for simulation requires a robust numerical tool with availability of enough field and experimental data for calibration. In order to simulate the fate of xenobiotic organic compounds and metals ions in the landfill environment, more chemical and microbiological reactions may be needed. These reactions would involve many species in all three MSW phases and additional process reactions. In order to accommodate these vast requirements a generalized numerical model (BIOKEMOD-3P) for simulation of solid waste biodegradation process was presented by Gawande et al. (2009). This paper presents the calibration of BIOKEMOD-3P using experimental data.

The biodegradation of solid waste in laboratory-scale bioreactor microcosms was investigated by Barlaz et al. (1989). To date it is one of the most comprehensive laboratory-scale studies of biodegradation of solid waste under anaerobic conditions. Data from this experimental study were used for model calibration and presented in following sections.
4.2 Composition of solid waste

Solid waste can be classified into basic material components such as paper, cardboard, yard waste, and others. A gross elemental composition of the composite waste in terms of carbon, hydrogen, oxygen, nitrogen, and sulfur can be found using appropriate coefficients for individual material components of solid waste (Tchobanoglous et al., 1993). The general composition of solid waste represented by a chemical formula can be obtained from its material composition. Lobo et al. (2002) and White et al. (2004) made use of a chemical formula derived from solid waste composition for biodegradation modeling. The ultimate use of solid waste classification for anaerobic biodegradation modeling is to know the biochemical methane potential through the anaerobic digestion pathway. The model presented in this study is a generalized-model, where the solids composition and products formation are user-defined. Therefore this model permits user defined solids composition with an unlimited number of components.

The biodegradable portion of solid waste is primarily ligno-cellulosic material; the remainder includes proteins, starch and sugar. Kelly et al. (2006) found that cellulose and volatile solids were the best parameters for characterization of landfill waste bio-stability. Therefore a similar classification given by Barlaz et al. (1990) was used in the present work (Table 4-1).
### Table 4-1. Composition of solid waste.

<table>
<thead>
<tr>
<th>Solid Waste Components</th>
<th>Percent Dry wt.(^a)</th>
<th>Methane Potential (L CH(_4)/g component(^b))</th>
<th>Methane Potential (L CH(_4)/g dry SW)</th>
<th>Percent Methane Potential</th>
<th>Moles of soluble product/ g component</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hemi Cellulose</td>
<td>11.90</td>
<td>0.4633(^c)</td>
<td>0.0551</td>
<td>17.58</td>
<td>6.223E-03</td>
</tr>
<tr>
<td>Cellulose</td>
<td>51.20</td>
<td>0.4530(^c)</td>
<td>0.2319</td>
<td>73.95</td>
<td>6.085E-03</td>
</tr>
<tr>
<td>Protein</td>
<td>4.20</td>
<td>0.5791</td>
<td>0.0243</td>
<td>7.76</td>
<td>1.545E-02</td>
</tr>
<tr>
<td>Starch</td>
<td>0.50</td>
<td>0.1600</td>
<td>0.0008</td>
<td>0.26</td>
<td>(d)</td>
</tr>
<tr>
<td>Soluble Sugar</td>
<td>0.35</td>
<td>0.4073</td>
<td>0.0014</td>
<td>0.45</td>
<td>(d)</td>
</tr>
<tr>
<td>Inert</td>
<td>31.85</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100.00</strong></td>
<td><strong>0.3136</strong></td>
<td><strong>100.00</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(a\) as per Barlaz et al. (1990)

\(b\) gross value without the allowance for microorganism growth

\(c\) adopted from Barlaz (2006)

\(d\) contribution from components excluded in modeling

### 4.3 Anaerobic biodegradation reaction scheme

The pathway of anaerobic digestion in a sulfate-depleted environment for biological polymers, marshes, trees, and digesting sludge was presented by Zender et al. (1982). Figure 4-1 shows the anaerobic biodegradation reaction scheme used in this paper. Complex models of anaerobic biodegradation of particulate matter were compiled by Gavalta et al. (2003). A more complex model for solid waste biodegradation may involve interaction of sulfur and nitrogen species depending on the characteristics of solid waste. The numerical model BIOKEMOD-3P is equipped to handle such complex reactions pathway by including additional microbiological and chemical reactions. In order to model solid waste biodegradation described in this work, four reaction processes were considered (Figure 4-1), hydrolysis of solids, acetogenesis, acetate utilizing methanogenesis, and hydrogen utilizing methanogenesis processes, described in
following sections.

Figure 4-1. Anaerobic biodegradation scheme used in this study (modified from Zender et al., 1982).

4.3.1 Hydrolysis

Hydrolysis is the transformation of complex particulate organic matter into simple monomer or dimmer forms that can pass the bacterial cell membrane. Hydrolysis during anaerobic digestion may occur primarily due to the action of extracellular enzymes and may depend on several physicochemical factors includes particle size, pH, diffusion and adsorption of enzymes to particles (Gavala et al., 2003). These factors make hydrolysis the least defined among all the processes of anaerobic solid waste biodegradation. A first-order kinetics is more suited to describe hydrolysis of complex and heterogeneous substrates (Eastman and Ferguson,
1981). However, Miron et al. (2000) in a study with sludge digestion found that individually hydrolysis of carbohydrates, proteins and lipids did not follow first-order kinetics. The first-order kinetics may not always be applicable and an in-depth understanding of various processes is needed to accurately describe it (Vavilin et al., 2008). Comparison of various methodologies to model the hydrolysis kinetics during anaerobic biodegradation of particulate organic matter was presented by Vavilin et al. (1996 and 2008). In these modeling studies using data from high organic loadings, Contois kinetics (Contois, 1959) and two-phase kinetics considering surface colonization showed a better fit. The first-order model was described as a particular case of the above two models.

In the present work of modeling solid waste bioreactors, hydrolysis was modeled using Contois kinetics (Eq. 1). Hydrolysis is a result of several factors, as explained by Gavala et al. (2003). Moisture content of solid waste is one of the important parameters that stimulates hydrolysis. A linear/non-linear function is multiplied by any rate constant to consider the effect of moisture content on that process (Young, 1989; Reichel et al., 2007). Klink and Ham (1982) found that moisture flow increased methane production relative to controls at the same moisture content with no moisture flow. The liquid injection/recirculation through solid waste bioreactor may also promote the physicochemical factors such as adsorption of hydrolytic bacteria and enzyme on solid substrate, diffusion, and pH neutralization. Therefore the rate constant ‘k’ described in Eq. (4.1), was considered to be a product of maximum growth rate for hydrolytic bacteria, $\mu_{\text{max},T}$ and a hydrolysis rate multiplying factor, ‘r’, to consider various physical-chemical processes (Eq. 4.2). The maximum growth rate of bacteria could be adjusted by multiplying by the inhibition function, $I_I$; pH inhibition function, $I_{pH}$, and liquid saturation, $s_w$. 
As such the terms in the bracket in Eq. (4.2) may remain unchanged for any given case, but the factor ‘\( r \)’ may need to be calibrated depending on the degree of recirculation or the liquid flux through the solid waste reactor.

\[
\frac{\partial h}{\partial t} = k \left( \frac{h/b}{K_s I_2 + h/b} \right) b \quad (4.1)
\]

\[
k = r \cdot \left( \mu_{\text{max}, r} I_1 l_p H s_w \right) \quad (4.2)
\]

\[
I_1 = \left( 1 + \frac{[I]}{K_{I_1}} \right)^p, \quad I_2 = \left( 1 + \frac{[I]}{K_{I_2}} \right)^q \quad (4.3)
\]

Solid waste particulate matter produces sugar monomers, simple amino acids, and volatile fatty acids upon hydrolysis. Veeken et al. (2000) found no accumulation of monomeric products from hydrolysis of organic fractions of solid waste at pH 6.0 and 7.0. Therefore the hydrolysis of solid waste components from Table 4-1 was modeled to directly produce various volatile fatty acids (VFA), carbon dioxide, and hydrogen following the pathway in Figure 4-1. However, for simplicity of calculations and presentation these product species are expressed in terms of intermediate monomer forms (Eq. 4-4 through 4-7). Amino acids contribute to higher fatty acids such as valerate and butyrate (Batstone et al., 2003). Upon balancing the stoichiometry of methane potential, valerate and propionate were considered as the sole products of protein hydrolysis along with acetate and hydrogen. Stoichiometry of various hydrolysis
products formation is presented in Table 4-2.

\[ C_6H_{12}O_6 + 2H_2O \rightarrow 2C_2H_4O_2 + 4H_2 + 2CO_2 \]  
(4.4)

\[ 3C_6H_{12}O_6 \rightarrow 4C_3H_6O_2 + 2C_2H_4O_2 + 2CO_2 + 2H_2O \]  
(4.5)

\[ C_6H_{12}O_6 \rightarrow C_4H_8O_2 + 2H_2 + 2CO_2 \]  
(4.6)

\[ C_{3.2}H_{4.14}ON_{0.86} + 1.876H_2O \rightarrow 0.25C_3H_{10}O_2 + 0.256C_3H_6O_2 + 0.25C_2H_4O_2 + 0.86NH_3 + 0.682CO_2 \]  
(4.7)

4.3.2 Acetogenesis

In anaerobic digestion, acetogenesis mainly refers to the formation of acetate from anaerobic oxidation of long chain fatty acids (Eq. 4.8 through 4.10). In the present work valerate, butyrate, and propionate are the major fatty acids that undergo anaerobic oxidation to form acetate. In order to sustain valerate, butyrate, and propionate oxidation, the energetics require that the products formed from these reactions are consumed. This results in mutual interdependency between acetogenic and methanogenic bacteria. Thermodynamically, acetogenesis is severely inhibited at high hydrogen concentrations (Mosey, 1983). As such a non-competitive inhibition due to hydrogen was considered during the acetogenesis of valerate, butyrate and propionate.
Table 4-2. Matrix of stoichiometric coefficients for species taking part in process reactions.

<table>
<thead>
<tr>
<th>Phase Species</th>
<th>Global Species Number</th>
<th>Complexed Chemical Equilibrium Reactions</th>
<th>Microbiological Hydrolysis Reactions</th>
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<tr>
<td></td>
<td></td>
<td>Reactions Number →</td>
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<td>Product/Substrate Species →</td>
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<td>H₂</td>
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A negative sign indicate consumption and positive sign indicate production of species
\[ C_5H_{10}O_2 + 2H_2O \rightarrow C_4H_6O_2 + C_2H_4O_2 + 2H_2 \quad (4.8) \]

\[ C_4H_8O_2 + 2H_2O \rightarrow 2C_2H_4O_2 + 2H_2 \quad (4.9) \]

\[ C_3H_6O_2 + 2H_2O \rightarrow C_2H_4O_2 + 2H_2 + CO_2 \quad (4.10) \]

### 4.3.3 Methanogenesis

In anaerobic digestion, about 65 to 70% methane is produced from acetate with the remaining from hydrogen and carbon dioxide. Methanogenic microorganisms are extremely sensitive to temperature, pH, organic loading rate and they are inhibited by number of compounds (Gavala et al., 2003). The methanogenic reactions are represented by Eq. (4.11) and (4.12).

Monod kinetics (Eq. 4.13) was used to model the acetogenic and methanogenic processes. The stoichiometric coefficients for species taking part in acetogenic and methanogenic reactions are presented in Table 4-2.

\[ C_2H_4O_2 \rightarrow CH_4 + CO_2 \quad (4.11) \]

\[ 4H_2 + 2CO_2 \rightarrow CH_4 + H_2O \quad (4.12) \]

\[
\frac{\partial S}{\partial t} = \Omega \left( \frac{S}{K_S I_2 + S} \right) b
\]

\[
\Omega = \mu_{max,T} \frac{I_{ph}}{I_{ph}^w} \cdot S_w
\]

\[ (4.13) \]

\[ (4.14) \]
4.3.4 Aqueous and gas phase partitioning reactions

The contribution from the partitioning of aqueous and gas phase reactions was modeled using Eq. (4.15). Although the value of overall mass transfer coefficient, $K_L$, may vary with the rate of generation of gas, a constant value was used throughout the simulation.

$$r_j^{\text{gas}} = K_L \left( S_{\text{liq},j} - K_H P_{\text{gas},j} \right)$$  \hspace{1cm} (4.15)

4.4 Model Calibration

The laboratory-scale bioreactors operated by Barlaz et al. (1989) were adjusted to a water content of 73% (w/w). The wetting process generated leachate which was neutralized and recycled into the reactors on a daily basis. The present model is designed to simulate a single cell solid waste bioreactor and in order to simulate the leachate recirculation, the water content of the cell was increased. A water content corresponding to 2.75 g of liquid for every gram of initial dry solid waste was considered. This allowed the water content during simulation to be maintained at a constant value of about 73% (w/w). Leachate neutralization was achieved by the addition of sodium and bicarbonate ions during model calibration. Time profiles of bicarbonate addition were part of model input in order to simulate the experimental pH values. The initial pH during the startup of reactors was reported at 7.5. BIOKEMOD-3P uses excess hydrogen ion concentration for calculation of pH, therefore a minimal hydrogen ion deficit that allowed pH calibration throughout the model run was considered as the initial hydrogen ion concentration.
The bioreactors were maintained at a constant temperature of 41°C, therefore the temperature effect on microbiological and chemical reactions was deactivated by a control parameter. The kinetic parameters presented in this paper correspond to this temperature condition.

The primary aqueous species were considered as aqueous components, while the ones formed by chemical equilibrium reactions following the law of mass action were complexed equilibrium species (Table 4-2). All microbial species were considered to be aqueous phase species, however the model allows the use of microbial species attached to solid phase which might represent more appropriate conditions for a solid waste bioreactor. However, it may involve the use of kinetic constants for mass transfer between aqueous and solid phase which to date are not available from any experimental study of anaerobic solid waste biodegradation. The solids species as defined in Table 4-1 were included in the reaction matrix presented in Table 4-2. Upon examination of experimental data, about 70% of hemicellulose and cellulose and 80% of proteins were considered biodegradable and accessible to microorganisms while the remaining portions were very slowly hydrolysable and excluded from participation in reactions. Butyrate and acetate were considered as the products of hemicellulose and cellulose hydrolysis along with carbon dioxide and hydrogen; whereas Valerate and propionate were main products of protein hydrolysis. The stoichiometric coefficients for Eq. (4-4) through (4-6) used in Table 4-2 were derived from the initial volatile acids production when the methane production was insignificant. In all, five gas phase species were included but only carbon dioxide, methane, and hydrogen were considered to partition between aqueous and gas phases. The initial guiding values of mass transfer coefficients for methane and hydrogen were adopted from Pauss et al. (1990).
4.5 Results and Discussion

In the model run, pH was simulated as shown in Figure 4-2. The adjustments to bicarbonate input profiles were part of the calibration process. The major requirement of bicarbonate for pH neutralization ceased after the day 47 due to depletion of acids. Thereafter only minor adjustments to bicarbonate and hydrogen ions profiles were required to maintain the experimental pH conditions.

![Figure 4-2. Profile of pH during model run.](image)

The profile of solids reduction is presented in Figure 4-3. The experimental data showed almost identical reduction for hemicellulose and cellulose, therefore the overall hydrolysis rate, $k$ was kept identical for both components. Figure 4-4 presents the hydrolytic microorganisms population. The initial xylanolytic population was used derived from the experimental data,
whereas the initial condition for cellulolytic population was found from model calibration. Contrary to the experimental results, the modeled cellulolytic population was one order of magnitude higher than the xylanolytic population. Cellulose occurs in the form of fibrils embedded within a matrix consisting of other polymers like xylan, other hemicellulose components, and lignin. This polymer matrix must be hydrolyzed at least partially for efficient cellulose biodegradation. The matrix and cellulose degradation processes occur concurrently as microorganisms develop multienzyme systems that function in hydrolysis of different polymers in the plant cell wall (Pohlschröder et al., 1994). Leschine (1995) reported that the soluble products of cellulose hydrolysis are available as growth substrates for noncellulolytic commensal microorganisms, whose activities may affect cellulose degradation in many different ways. Due to the complex interactions among various hydrolytic microorganisms, the near identical populations of both xylanolytic and cellulolytic microorganisms from modeling results is possible.

Only the low pH inhibition function by Batstone et al. (2001) for inhibition was used for hydrolysis. Veeken et al. (2000) reported that hydrolysis of organic solid waste was pH dependent but was not related to undissociated or total volatile fatty acids (VFAs) for a specified range of VFA concentration. As the concentration of VFAs in this work was only marginally above this specified range, use of pH inhibition only was found to be appropriate. Upon including the non-competitive type VFA inhibition function for hydrolysis, the soluble by-products were found to be lower than the experimental data for up to day 40, after which methane production picked up substantially. However, the use of VFA inhibition may be required in case of very high VFAs concentrations.
Figure 4-3. Solids degradation during modeling compared with data.

Figure 4-4. Plot of hydrolytic microorganisms population.
The overall kinetic rate constant, \( k \) for hydrolysis was found to be 10.5 d\(^{-1}\) (Table 4-3), this value is significantly higher than a value of 1.50 d\(^{-1}\) reported by Vavilin et al. (2008). Unlike the use of specific hydrolytic microbial population in the present work, total biomass concentration expressed as volatile solids was used in Contois kinetics by Vavilin et al. (2008). The total biomass concentration was one order of magnitude higher than the hydrolytic population during this experimental study. Therefore a correspondingly high value for the kinetic rate constant may be expected. Other factors such as leachate recirculation coupled with pH neutralization also have a role in enhancing solids degradation. Leachate recirculation may also promote the physical process of hydrolytic enzymes adsorption on the solid waste matrix. Therefore dependency of such kinetic parameters on moisture flux through the solid waste matrix rather than only on moisture content may need further study. The high value of the modified half saturation constant for Contois kinetics is also a result of using only the hydrolytic microorganisms population instead of total biomass concentration.

Cellulose, hemicellulose, and proteins in solid phase are hydrolyzed to corresponding soluble sugars or amino acids. The experimental data showed no accumulation of soluble monomer by-products. Therefore direct production of VFAs as a result of solids hydrolysis was appropriate for modeling. Figure 4-5 shows the buildup of all the fractions of VFAs up to day 45. The increase in the acetate concentration was limited mainly by the slow growth of the aceticlastic methanogens. Figure 4-6 shows a gradual increase in the population of aceticlastic methanogens up to day 50, after which the biomass concentration remains high enough to outpace the acetate production. The acetogenic microorganisms have a relatively higher growth rate.
Table 4-3. Kinetic parameters from model calibration.

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Figure 4-5. Concentration of various fractions of volatile acids.

Figure 4-6. Population development of methanogenic microorganisms.
than the acetate utilizing methanogens, still there was buildup of valerate, butyrate, and propionate up to day 45. The simulation of the build up of these higher forms of VFAs was only possible by including a non-competitive inhibition for growth of acetogenic biomass due to hydrogen. Figure 4-7 shows stagnant acetogenic population up to day 30, when the hydrogen partial pressure was also high, shown in Figure 4-8. High values for hydrogen partial pressure generated from the model were not detected during the experimental study because there are possible sinks for hydrogen through interspecies hydrogen transfer. Reduction of sulfate is one such example and decrease in sulfates along with production of sulfides was observed during the experimental study. Sufficient data were not available to include these processes in the present work.

Figure 4-7. Population development of acetogenic microorganisms.
A modeling example of solid waste biodegradation while including sulfate reduction was presented by Reichel et al. (2007), however no inhibition from hydrogen was included. In a more comprehensive model, sulfur-containing chemical species and corresponding microbial species could be included. This addition is possible with BIOKEMOD-3P as it allows the use of almost unlimited number of species and reactions. In order to compensate for the high hydrogen pressure in modeling, the values for inhibition constant ($K_I$) were increased (Table 4-3). As such these values are significantly higher than 6.25 to 18.75 x $10^{-8}$ H$_2$ moles/L as reported by Seigrist et al. (2002) for mesophilic sewage sludge digestion. The additional hydrogen partial pressure up to day 30 as simulated in modeling led to marginal increase in the biomass concentration of hydrogenotrophic methanogens in comparison to experimental data (Figure 4-6). After the H$_2$/CO$_2$ methanogens were able to consume the excess hydrogen, the acetogenic biomass showed
significant growth comparable with the experimental data (Figure 4-7). In addition to hydrogen inhibition on acetogenesis, the inhibition function for low pH was used for acetogenesis and methanogenesis (Table 4-3). The growth rate for acetotrophic methanogens was less than the hydrogen consuming species, but higher than values compiled by Batstone et al. (2002). A possible explanation for this is that the acetotrophic methanogens in this model as well as reported in the experimental work, include all the possible acetate consuming microbial species. Therefore the process of acetate conversion to hydrogen and subsequently to methane may be indirectly included in the acetotrophic methanogenic process.

After around day 50, when the methanogenic population growth outpaced the acetate production rate, the modeled acetate concentration dropped significantly. This drop was more sudden than the experimental results. The experimental data reported by Barlaz et al. (1989) also reported variable decline in VFA concentrations for different reactors during the experimental study. However, a very steep drop in VFA concentrations in the model run is a result of the use of microbial growth kinetics used in a completely-mixed reactor condition. As the biomass grows and achieves a certain high value, the depletion of substrate is rapid. After this peaking of biomass concentration, the mass transfer processes may be controlling the reduction of VFAs. In addition, leachate recirculation may play an important role in enhancing the mass transfer processes. Inhibition of methanogenesis by VFA may also cause gradual decline in acids concentrations. The use of non-competitive inhibition due to undissociated VFA on growth rate for methanogenic microorganisms did not yield results consistent with the experimental values for biomass concentrations. This allowed accumulation of VFAs which were two-fold greater than the values from the experimental data. As mentioned previously inhibition due to
undissociated VFA on methanogenesis was not included in this simulation, however its use may be necessary at high VFA concentrations.

Methane concentrations from model results, shown in Figure 4-8, follow the experimental data. The model results deviate only during the period between days 45 to 55 when there was rapid depletion of VFAs. The methane generation rates were calculated manually form model results of quantity of various gas species produced over time (Figure 4-9). The model results follow the experimental results closely from one of the reactors. The model values peaked five fold over experimental results for a very short time near day 48 which was coupled with the steep drop in acetate concentration.

Figure 4-9. Methane generation rates from model run and experimental data.
4.6 Conclusions

A generalized microbiological and chemical model BIOKEMOD-3P was able to simulate solid waste biodegradation in laboratory scale bioreactors. Contois kinetics was able predict the reduction in solids concentrations. The development of various anaerobic microorganisms species were in accordance with the experimental data. The pH was found to have significant effect on all the microbiological processes. Hydrogen could be inhibitory to acetogenic biomass and may limit the conversion of higher fatty acids to acetate. In order to quantify the effect of hydrogen more precisely, sulfur-reducing processes may need to be included in conjunction with methanogenesis. The populations of methanogenic biomass were able to reach concentrations to outcompete the acetate and hydrogen production rates. However mass transfer limitations may cause slow decline of VFAs. This slow decline could be modeled by including additional mass transfer processes or alternatively introducing some type of heterogeneity in solid waste when coupled with multiphase flow models. The model BIOKEMOD-3P which simulates conditions in a mixed reactor is equipped to include additional kinetic mass transfer processes and it could also be coupled with a suitable multiphase flow model in order to simulate a full-scale operation.

Abbreviations

\( b \), hydrolytic bacteria concentration, \((\text{ML}^{-3})\)

\( h \), solids substrate concentration, \((\text{ML}^{-3})\)

\( I \), concentration of inhibitory substance \((\text{ML}^{-3})\)
$I_1$, inhibition factor for growth rate in microbial reaction (dimensionless)

$I_2$, Inhibition factor for half saturation constant in microbial reaction (dimensionless)

$I_{\text{pH}}$, pH inhibition factor for growth (dimensionless)

$k$, overall rate constant for hydrolysis (T$^{-1}$)

$K_{f1}$, inhibition coefficient for growth rate (ML$^{-3}$)

$K_{f2}$, inhibition coefficient for the half saturation constant (ML$^{-3}$)

$K_H$, Henry constant (ML$^{-3}$ Atm$^{-1}$)

$K_L$, overall mass transfer coefficient between liquid and gas phase (T$^{-1}$)

$K_S$, modified half saturation constant for hydrolysis (MM$^{-1}$)

$P_{\text{gas},j}$, partial pressure of $j$th species in gas phase, Atmosphere (ML$^{-1}$T$^{-2}$)

$p$, fitting parameter

$q$, fitting parameter

$r$, multiplying factor for hydrolysis rate (dimensionless)

$r_j|_{\text{gas}}$, contribution from gas partitioning reaction for the $j$th aqueous species (ML$^{-3}$ T$^{-1}$)

$S$, substrate concentration in Monod equation (ML$^{-3}$)

$S_{\text{liq},j}$, concentration of $j$th species in aqueous phase (ML$^{-3}$)

$s_w$, factor for effect of liquid saturation on growth rate (dimensionless)

$t$, time (T)

$\mu_{\text{max},T}$, maximum growth rate for bacteria at given temperature, (T$^{-1}$)
\( \Omega \), rate of microbiological process in Monod equation (T\(^{-1}\))

References


processes in municipal solid waste bioreactor, part I: development of a three-phase numerical model BIOKEMOD-3P, (submitted to ******).


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CHAPTER 5:
MODELING SIMULTANEOUS NITRIFICATION AND DENITRIFICATION PROCESSES IN SOLID WASTE BIOREACTOR

Abstract

In recent years research has shown that significant ammonia removal may be possible in municipal solid waste (MSW) bioreactor landfills. Research studies confirmed the occurrence of simultaneous nitrification and denitrification in the landfill environment. Modeling could be an effective tool to quantify such processes. Modeling nitrification and denitrification for wastewater treatment processes has been in practice for a number of years. However, the processes in MSW bioreactor landfills differ and are similar to processes in the subsurface environment. Gawande et al. (2009) presented a generalized model BIOKEMOD-3P to simulate microbiological and chemical processes in a three-phase system. This model was used to simulate simultaneous nitrification and denitrification in experimental MSW bioreactors. The results of this study showed that ammonia nitrogen removal in solid waste bioreactor can occur due to simultaneous nitrification and denitrification. pH was found to have a significant effect on nitrification process. It affected denitrification to a lesser extent in the range of pH values reported in the experimental study. Temperature influenced ammonia and nitrite oxidation, and denitrification as well. In order to achieve high nitrogen removal rates, buffering of pH may be required to compensate for the acidity generated during nitrification and excess carbon dioxide produced as a result of biodegradation of solid waste.
5.1 Introduction

A strategy for complete removal of nitrogen in bioreactor landfills was presented by Berge et al. (2007a). Bioreactor landfills when operated aerobically can provide an environment suitable for the growth of both nitrifying and denitrifying microorganisms (Onay and Pohland, 1998; Berge et al., 2006; Mertoglu et al., 2006; He and Shen, 2006). These studies confirmed the occurrence of simultaneous nitrification and denitrification in the landfill environment. Berge et al. (2006) reported that nitrate formed during nitrification was also removed via denitrification and appeared in the gas phase as dinitrogen (N₂) and nitrous oxide (N₂O). The study mentioned possible autotrophic denitrification of about 30% of nitrate based on the stoichiometry of sulfate appearance and about 70% through heterotrophic denitrification. However, in the batch microcosm experiments of the same study, sulfate concentration remained nearly constant, suggesting heterotrophic denitrification as the major pathway for nitrate denitrification. Modeling can be an effective tools to quantify nitrogen removal occurring in a system with complex reactions.

Modeling autotrophic nitrification and heterotrophic denitrification for wastewater treatment processes has been practiced for a number of years (Gujer et al., 1995). Solid waste bioreactor landfills differ in their environment, having relatively low liquid contents and allowing aerobic and anaerobic regions to exist simultaneously when air is added. dos Santos et al. (1996) modeled integrated nitrogen removal by considering two separate layers of nitrifying and denitrifying microorganisms on gel beads. The model described diffusion of various components, substrate consumption, and growth, all occurring simultaneously in the beads. Quantification of such models may require measurements of various chemical and
microbiological species in a thin film. Cao et al. (2002) modeled single-step nitrification and simultaneous denitrification without considering internal diffusion. Berge et al. (2007b) described a model for ammonia removal in laboratory municipal solid waste (MSW) microcosms. This model described an overall ammonia removal rate using Monod kinetics. The model considered impacts of temperature and gas-phase oxygen on kinetics of ammonia removal. The effect of pH was accounted for in the model by considering an average system value. However, the use of dynamic values of pH may be more appropriate for such pH-dependent microbiological systems.

This paper presents numerical modeling of the experimental data of nitrogen removal in laboratory microcosms (Berge et al., 2006; Berge et al., 2007a and b). Nitrification and denitrification processes were modeled to occur simultaneously in a MSW bioreactor system. The computer model BIOKEMOD-3P (Gawande et al., 2009) was used to simulate experimental data. This numerical computer model was developed for a three-phase system expanding a one-phase model presented by Salvage and Yeh (1998). BIOKEMOD-3P is a robust computer tool which can be used to simulate microbiological and chemical kinetic-and-equilibrium reactions in a completely mixed, three-phase batch system.
5.2 Background information

5.2.1 Nitrification

Nitrification of ammonia is carried out by aerobic autotrophic microorganisms in two steps. Nitrification in a bioreactor landfill may be affected by oxygen limitation, inhibition due to ammonia, temperature, and pH. Stoichiometry of the two-step process of ammonia oxidation to nitrate can be represented by Eqs. (5.1) and (5.2) (Grady et al., 1999).

\[
\begin{align*}
55NH_4^+ + 76O_2 + 109HCO_3^- &\rightarrow C_5H_7O_2N + 54NO_2^- + 57H_2O + 104H_2CO_3^{-} \\
409NO_2^- + NH_4^+ + 4H_2CO_3 + 199.5O_2 + HCO_3^- &\rightarrow C_5H_7O_2N + 409NO_3^- + 3H_2O
\end{align*}
\] (5.1) (5.2)

*Nitrosomonas* bacteria are examples of microorganisms that carry out the oxidation of ammonia to nitrite. The oxidation of nitrite to nitrate is carried out by bacteria such as *Nitrobacter* and *Nitrospira*. Kim et al. (2006) reported *Nitrosomonas* as the main ammonia oxidizing bacteria during landfill leachate nitrification whereas *Nitrobacter* and *Nitrospira* are the main nitrite oxidizing bacteria. Mertoglu et al. (2006) also reported the presence of *Nitrosomonas* like ammonia oxidizers and *Nitrospira*-related nitrite oxidizers in an aerated landfill bioreactor. During autotrophic nitrification, oxygen acts as an electron acceptor and inorganic carbon is the source of carbon for bacterial growth. This process causes reduction of pH due to production of excess hydrogen ions. Alkalinity may also be consumed due to the
formation of nitrous acid.

5.2.2 Denitrification

Nitrate and nitrite formed during nitrification can be converted to nitrous oxide and dinitrogen by the action of heterotrophic denitrifying microorganisms. The overall process of sequential reduction of nitrate to dinitrogen can be described by Eqs. (5.3) through (5.6).

\[
\begin{align*}
NO_3^- + 2e^- + 2H^+ & \rightarrow NO_2^- + H_2O \quad (5.3) \\
NO_2^- + e^- + 2H^+ & \rightarrow NO + H_2O \quad (5.4) \\
2NO + 2e^- + 2H^+ & \rightarrow N_2O + H_2O \quad (5.5) \\
N_2O + 2e^- + 2H^+ & \rightarrow N_2 + H_2O \quad (5.6)
\end{align*}
\]

Heterotrophic denitrifying microorganisms under anoxic conditions use nitrate as an electron acceptor and convert it to dinitrogen in sequential reactions. When this reduction is incomplete, intermediate species of nitrogen may be detected. This process uses an organic carbon source for microorganism growth and also increases alkalinity due to consumption of hydrogen ions. Heterotrophic microorganisms use ammonia as the nitrogen source for growth. Berge (2006) reported the possibility of autotrophic denitrification due to the appearance of sulfate with simultaneous nitrate reduction. However based on a mass balance of sulfate concentrations, heterotrophic denitrification was concluded to be the major pathway for nitrate reduction.
5.2.3 Simultaneous nitrification and denitrification

Berge et al. (2006) reported simultaneous nitrification and denitrification which was attributed to the presence of aerobic and anaerobic regions in a solid waste landfill bioreactor. Quantification of nitrification and denitrification processes is difficult because one nitrogen species may be involved in two or more different reactions. The change in hydrogen ion concentration could serve as the control parameter to quantify these processes. Bogaert et al. (1997) implemented control of the denitrification process in wastewater treatment based on pH monitoring. Such a monitoring and control system includes modeling the acidobasic balance of the heterotrophic denitrification process, discussed comprehensively by Drtil et al. (1995). They described the influence of organic substrate composition on production of various inorganic carbon species during heterotrophic denitrification and the resulting effect on pH change. In a solid waste bioreactor with relatively older waste that has a low ratio of organic carbon to nitrogen, the pH stabilizes near or above a neutral value due to reduction in the concentrations of organic acids. The nitrification process which lowers the pH and the heterotrophic denitrification process which tends to increase the pH could be modeled simultaneously for such stabilized solid waste.

5.3 Experimental study

Data from the microcosm experiments as described by Berge et al. (2006) and Berge et
al. (2007 b) were used in this modeling exercise. In the experimental study, digested MSW from an aerobic MSW compost facility was used. The stabilized MSW was acclimated for ammonia removal in two continuously operated aerobic reactors by addition of nitrifying mixed liquor from a wastewater treatment facility and periodic addition of ammonium bicarbonate. Acclimated MSW from these reactors was used in the batch microcosm experiments to study nitrogen removal. The acclimation reactors were operated at 22, 35, and 45 °C, corresponding to the temperatures of microcosm experiments. The microcosm experiments were conducted at 5, 17, and 100%, by volume, oxygen concentration in the gas phase. Berge (2006) reported high ammonia removal rates with increasing oxygen content in the gas phase and also marginally reduced rates at 100% oxygen content. However a statistically significant effect of oxygen on ammonia removal could not be conclusively described. Therefore one set of data at uniform 100% oxygen concentrations for all three temperature conditions was used in this modeling work. In order to see the effect of oxygen, two additional data sets with oxygen concentrations of 5 and 20% at 35 °C were modeled. The microcosms were subjected to initial ammonia concentrations of 500 mg/L and 1000 mg/L in two groups of experiments. Berge et al. (2007b) reported near identical ammonia removal rate for experiments at 500 mg/L and 1000 mg/L. In the absence of data from a broad range of initial ammonia concentrations, studies with 500 mg/L were modeled in this work. During these experiments the sulfate concentrations remained nearly constant. Each microcosm unit contained 200 g of digested municipal solid waste acclimated to ammonia in a laboratory aerobic reactor mixed with 20 g of wood chips. Ammonium bicarbonate was used as the source of ammonia to achieve target concentrations, which also contributed to alkalinity. The experiments were conducted at near 63% moisture content (M/M) on a wet basis.
5.4 Model description

The numerical computer model BIOKEMOD-3P (Gawande et al., 2009) was used to simulate the experiments of the microcosm study described by Berge et al. (2006) and Berge (2007a and b). BIOKEMOD-3P is a generalized computer program that simulates microbiological and chemical kinetic-and-equilibrium reactions in a solid, liquid, and gas phase system. BIOKEMOD-3P provides the flexibility of using any number of user defined species and reactions. Chemical components in aqueous and adsorbed phase are the primary chemical species and species formed from the chemical components due to chemical equilibrium and kinetic reactions are also considered. Microbiological species can be defined as either aqueous or adsorbed type. The solid phase may be comprised of one or more components with varying densities. The gas phase species are defined by the partial pressures of these components. Temperature, pressure, porosity of solids, and degree of liquid and gas saturation of pore spaces are parameters required to define the given system. A headspace volume for gas phase can be defined to simulate batch experiments. The governing equations for mass balance of species in each phase are described by Gawande et al. (2009).

BIOKEMOD-3P allows the use of several different types of reactions. These reactions are – the solids disintegration reaction defined by first-order kinetics; the microorganisms mediated solids hydrolysis reaction defined by Contois kinetics; the microorganisms reactions for species in aqueous and adsorbed phases defined by Monod kinetics; equilibrium reactions for chemical species defined by the law of mass action; kinetic reactions for chemical transformation
of chemical species with rate law defined by collision theory; adsorption of chemical and microbiological species defined by constant capacitance and triple layer model; and liquid-gas phase partitioning reactions for liquid and gas phase species defined by a kinetic reaction considering Henry’s constant and a mass transfer kinetic constant. The model uses the excess hydrogen ion concentration to compute the pH and similarly free electrons to compute the pe. The simulations can be performed for steady state as well as dynamic conditions.

The present modeling exercise involved the use of chemical equilibrium reactions, Monod type microbiological reactions and liquid-gas phase partitioning mass transfer reactions. The computation of equilibrium reactions has been described by Yeh and Tripathi (1991). The Monod type reaction for microbiological processes was described by Salvage and Yeh (1998). Gawande et. al. (2009) modified the microbiological reactions to include the effect of temperature, pH, and the degree of saturation of liquid phase. The Monod type reactions and the gas phase partitioning reactions are described here.

The total production/consumption of any j-th chemical species due to microorganism mediated processes is the sum of the contributions from each microbial reaction that involves the chemical species (Eq. 5.7). The rate of this equation is defined by Monod kinetics (Eq. 5.8).

\[
    r_{j}^{\text{biodeg}} = \sum_{k=1}^{\text{NBR}} \frac{V''_{k,j} - V'_{k,j}}{\gamma_{j}} \Omega_{k} \{b_{k}\}
\]  

(5.7)

\[
    \Omega_{k} = \left( \frac{S_{k}}{K_{S,k}I_{1k}^{I_{2k}} S_{w}} + \frac{A_{k}}{A_{k} + A_{k}} + \frac{N_{k}}{N_{k} + N_{k}} \right) L_{k}
\]  

(5.8)

\[
    I_{1k} = 1 + \frac{[I]}{K_{11}}, \quad I_{2k} = 1 + \frac{[I]}{K_{12}}
\]

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similarly the rate of production/consumption of \( j \)-th chemical or \( i \)-th gaseous species due to liquid-gas phase partitioning reaction is described by Eq. (5.9).

\[
\Omega_j = -\Omega_i = k_L \left( \gamma_j g_j - K_{H_{i,j}} \gamma_i g_i \right)
\] (5.9)

The model computes the change in concentrations for various species due to kinetic reactions during a time step, whereas the computations for equilibrium reactions are done at the end of every time step. Input to the model includes defined species and their initial concentrations in solid, liquid, and gas phases, stoichiometry of reactants and products, and equilibrium and kinetic constants for the reactions. The output from the numerical model includes the concentrations of all the species in various phases and change in liquid and gas content values.

### 5.5 Data modeling

In order to model the experimental data presented by Berge (2006), also described above in brief, appropriate reactions were identified. Nitrification of ammonia to nitrate was modeled using two separate reactions (Eqs. 5.1 and 5.2). The stoichiometry of various chemical and microbiological species in these reactions is well defined. A suitable pathway for denitrification process was required to be identified. Denitrification of nitrate follows sequential reactions as per Eqs. (5.3) through (5.6). Nitrite is formed as an intermediate during both nitrification and
denitrification processes. Therefore for the experimental results the processes contributing to the appearance of nitrite needed to be identified. In the microcosm experiments with no external addition of ammonia, Berge (2006) found some reduction in nitrate concentration although at a slower rate as compared to when ammonia was added. The production of dinitrogen was observed even at oxygen concentration of 100% in the gas phase. In these control experiments nitrite and nitrous oxide were not detected in the liquid and gas phases respectively. This suggested that nitrate was reduced directly to dinitrogen and denitrification was not inhibited by the presence of oxygen in the gas phase.

In the two-step nitrification process, the resulting pH is mainly affected by the conversion of ammonia to nitrite, while Bogaert et al. (1997) showed that the pH effect of denitrification is mainly associated with the intermediate conversion of nitrite to N₂O. Berge (2006) reported less than 10, 18, and 1 percent N₂O production compared to initial nitrogen mass at 22, 35, and 45 °C respectively. Due to the low levels of N₂O as compared to dinitrogen in the gas phase, the denitrification reaction was modeled by a single reaction in this modeling problem, i.e. reduction of nitrate was modeled to produce dinitrogen in one step. By considering two nitrification reactions and a single denitrification reaction it was also possible to predict their effect on pH.

The composition of the carbon source used in heterotrophic denitrification has an influence on the resulting pH. Drtil et al. (1995) discussed the acidobasic balance reactions for varying carbon source during heterotrophic denitrification. They described the rules for determination of pH change according to the substrate composition. The application of these rules makes use of average oxidation number of carbon (AONC) in an organic carbon source. The technique described by Drtil et al.(1995) was adopted to model the resulting pH. Glucose,
acetate, and carbon from direct endogenous decay were modeled as a carbon sources for denitrification of nitrate to dinitrogen. Acetate showed a better fit when nitrification and denitrification were modeled simultaneously. The stoichiometry of denitrification using acetate as the carbon source is given by Eq. (5.10).

$$C_2H_3O_2^- + 0.64NO_3^- + 0.24NH_4^+ \rightarrow 0.24C_2H_2O_2N + 0.8CO_2 + 0.32N_2 + 1.64OH^- + 0.2H_2O \quad (5.10)$$

Table 5-1 shows all the species and the reactions considered in the simulation of microcosm experiments. There are eight aqueous component species, whereas five aqueous complex species are formed as a result of chemical equilibrium reactions. The values for equilibrium constants were adopted from Dean (1999). The two nitrification and one denitrification reactions were modeled using Monod kinetics (Eqs. 5.7 and 5.8). Liquid-gas phase partitioning was modeled using kinetic mass transfer reaction (Eq. 5.9). The measurements on the liquid phase concentrations of oxygen and nitrogen species that partitioned with gas phase were not performed in the experimental study. As the experiments were conducted in a closed system, an equilibrium between the liquid and gas phase concentrations of any partitioning species was expected. Therefore high values for mass transfer rates were adopted in phase partitioning reactions. The initial ammonia concentration in the microcosm experiments was near 500 mg/L. A high ammonia concentration may lead to its partitioning into gas phase. As the experiments were conducted in a closed microcosm system and final ammonia concentrations reduced to very
Table 5-1. Matrix of species and reactions used in modeling.

<table>
<thead>
<tr>
<th>Phase Species</th>
<th>Global Species Number</th>
<th>Species</th>
<th>Aqueous Complexed Chemical Equilibrium Reactions</th>
<th>Microbiological Reactions</th>
<th>Liquid-Gas Phase Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>OH</td>
<td>CO$_3^-$</td>
<td>H$_2$CO$_3^*$</td>
</tr>
<tr>
<td>Aqueous component</td>
<td></td>
<td></td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>Aqueous Species</td>
<td>1</td>
<td>H$_3^+$</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>HCO$_3^-$</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>NH$_4^+$</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>NO$_2^-$</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>NO$_3^-$</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>Acetate</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>O$_2^+$</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>N$_2^+$</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>Aqueous Microbiological Species</td>
<td>1</td>
<td>Nitrosomonas</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>Nitrobactor</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>Denitrifiers</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>Solid Phase Species</td>
<td>1</td>
<td>Solids</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>Gas Phase Species</td>
<td>1</td>
<td>O$_2$</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>N$_2$</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>CO$_2$</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
</tbody>
</table>

A negative sign indicate consumption and positive sign indicate production of species.
low values, ammonia partitioning into gas phase was not considered in the model. Only oxygen, nitrogen, and carbon dioxide were modeled to partition between liquid and gas phases.

The mass and volume of each phase and concentrations of species therein were part of the input to the numerical computer model. In the experimental study, the concentration of oxygen was not measured in the liquid phase. Therefore it was not possible to use an oxygen limiting factor for nitrification and an oxygen inhibition factor for the denitrification process. Biomass decay was modeled to produce acetate and ammonia nitrogen with a reduction factor to account for inert material. The effect of change in pH and temperature on the activity of nitrifying microorganisms was studied by Grunditz and Dalhammar (2001). A pH inhibition function for low pH described by Batstone et al. (2002) was used (Eq. 5.11). The effect of temperature on growth rate of microorganisms was removed by using a control parameter in the model input. Instead, kinetic constants were found separately for the experiments at three different temperatures and different oxygen concentrations in gas phase.

\[
I(pH) = \exp \left( -3.0 \left( \frac{pH - pH_{II}}{pH_{II} - pH_{I}} \right)^2 \right) \quad (5.11)
\]

Simulations were run by providing model-input information as described above. Figure 5-1 shows a plot of pH from a microcosm experiment at 35 °C compared with model results of pH at varying growth rates of ammonia oxidizers. During the three simulations in Figure 5-1, all other kinetic parameters were kept unchanged. The pH lowering effect of nitrification could be compensated by the hydrogen ion consumption during denitrification. Therefore during data
fitting the rates of nitrification and denitrification were adjusted to balance the pH such that it matched the experimental values. As such, given the constraints of concentrations of ammonia, nitrite, and nitrate along with alkalinity and the pH profile, there exists a unique combination for the nitrification and denitrification rates for any set of experiments. Fitting of experimental data was performed using a visual calibration method.

Figure 5-1. Effect of growth rate of ammonia oxidizers on model pH at 35 °C

5.6 Results and discussion

Figure 5-2 shows the plots of different nitrogen species concentrations and pH for microcosm experiments at 22, 35, and 45 °C with 100% oxygen concentration in the gas phase. It can be seen that ammonia concentration declined rapidly at all temperatures, but most rapidly at 35 °C. Nitrite initially increased and gradually decreased at 22 and 35 °C and it was not detected at 45 °C. Figure 5-3 shows plots for microcosm experiments at 35 °C for varying oxygen
Figure 5-2. Behavior of nitrogen species and pH at 100% oxygen in gas phase at different temperatures.
Figure 5-3. Behavior of nitrogen species and pH for varying oxygen concentrations at 35 °C.
contents in the gas phase. Table 5-2 shows the model results of maximum velocity of nitrogen removal in Monod kinetics during nitrification and denitrification at varying temperatures and oxygen concentrations. Maximum velocities for the three microbiological processes were calculated by multiplying the maximum growth rate by the biomass concentration per unit nitrogen removed. Denitrification was least affected by oxygen content, while nitrite nitrification rates decreased at 5 and 20% oxygen contents. The low variation in denitrification rates indicates that anoxic regions may exist even at high oxygen concentrations in the gas phase.

Table 5-2. Model results of maximum velocity of nitrogen removal rate.

<table>
<thead>
<tr>
<th>Gas phase oxygen concentration (percent) →</th>
<th>100</th>
<th>100</th>
<th>100</th>
<th>20</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (ºC) →</td>
<td>22</td>
<td>35</td>
<td>45</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>Ammonia oxidation</td>
<td>0.84</td>
<td>2.45</td>
<td>1.38</td>
<td>2.04</td>
<td>2.13</td>
</tr>
<tr>
<td>Nitrite Oxidation</td>
<td>0.74</td>
<td>1.88</td>
<td>1.81</td>
<td>1.13</td>
<td>1.50</td>
</tr>
<tr>
<td>Nitrate Denitrification</td>
<td>0.81</td>
<td>2.21</td>
<td>1.36</td>
<td>2.08</td>
<td>2.10</td>
</tr>
</tbody>
</table>

The values of kinetic parameters for microorganisms growth are presented in Table 5-3. Apart from temperature, the growth rates could be affected by the availability of oxygen in the microcosms which may have similarly affected the decay rates. The values for growth rates and decay rates in Table 5-3 are comparable to the values for nitrifying and denitrifying microorganisms reported by Siegrist et al. (1999). They reported reduced growth and decay rates under oxygen limiting conditions. Nowak et al. (1994) in a study with nitrifying sludge reported
significant reduction in decay rates under anoxic conditions, similar results were reported by Leenen et al. (1997). Therefore the growth and decay rates presented in Table 5-3 may be an indicator of oxygen transfer limitations in the experimental bioreactors and may need further investigation.

Table 5-3. Model results of kinetic parameters for different microorganisms at 100% oxygen concentration in gas phase.

<table>
<thead>
<tr>
<th>Temperature (ºC)</th>
<th>Ammonia oxidizers</th>
<th>Nitrite oxidizers</th>
<th>Denitrification</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>0.23/0.035</td>
<td>0.18/0.035</td>
<td>1.60/0.26</td>
</tr>
<tr>
<td>35</td>
<td>0.42/0.083</td>
<td>0.33/0.083</td>
<td>2.50/0.32</td>
</tr>
<tr>
<td>45</td>
<td>0.34/0.13</td>
<td>0.31/0.13</td>
<td>2.32/0.35</td>
</tr>
</tbody>
</table>

In Figure 5-2 and 5-3 it can be observed that the nitrate concentrations increase after ammonia levels reduce significantly. Ammonia is required for the growth of heterotrophic denitrifying microorganisms, which becomes limiting as ammonia is removed therefore a nutrient limitation term was included in the Monod kinetics for denitrification (Eq. 5.8). The values of half saturation constants for substrate ($K_S$) and for nutrient ($K_N$) for denitrification are presented in Table 5-4.

Denitrification was modeled for varying concentrations of acetate as substrate. In the model runs acetate concentrations were allowed to increase or decrease using a chemical species input or species out profiles respectively. Acetate concentration was also maintained at a constant value and its effect on denitrification was observed. A constant value of acetate showed
a better fit for the model, suggesting that availability of substrate may have limited the denitrification process. This is expected of an already aerobically stabilized solid waste which was used in the experimental study. A constant value of 1.80 mg acetate/L was adopted as the substrate concentration for denitrification. Berge (2006) reported the COD of leachate during waste acclimation process between 500 mg/L to 1000 mg/L while the BOD was near 1 mg/L. The value of acetate concentration used in modeling corresponds well with the BOD value of 1 mg/L in the leachate from the solid waste acclimation bioreactor. The low concentration of biodegradable organics in liquid phase suggests a slowly biodegradable portion of solid waste as the possible organic carbon source for denitrification. Further experimental investigation may be required to verify the carbon source and its concentration during nitrogen removal processes.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Half saturation constant, $K_S$ for ammonia oxidation, mg N/L</td>
<td>11.20</td>
</tr>
<tr>
<td>Half saturation constant, $K_S$ for nitrite oxidation, mg N/L</td>
<td>7.0</td>
</tr>
<tr>
<td>Half saturation constant, $K_S$ for denitrification, mg acetate/L</td>
<td>3.0</td>
</tr>
<tr>
<td>Half saturation constant for ammonia as nutrient, $K_N$ for denitrification, mg N/L</td>
<td>14.0</td>
</tr>
<tr>
<td>Lower value of pH for complete inhibition of nitrification</td>
<td>5.5</td>
</tr>
<tr>
<td>Optimum value of pH for nitrification</td>
<td>8.0</td>
</tr>
<tr>
<td>Lower value of pH for complete inhibition of denitrification</td>
<td>5.0</td>
</tr>
<tr>
<td>Optimum value of pH for denitrification</td>
<td>8.0</td>
</tr>
</tbody>
</table>

The results of maximum velocity of nitrogen removal from Table 5-2 show that the highest ammonia oxidation was achieved at 35 °C. Grunditz and Dalhammar (2001) in an
experimental study reported 35 ºC as the optimum temperature for *Nitrosomonas* activity. Nitrite oxidation was nearly identical at 35 and 45 ºC, suggesting an optimum value between these temperatures. Grunditz and Dalhammar (2001) reported an optimum temperature value for *Nitrobacter* activity at 38 ºC. Denitrification was highest at 35 ºC, suggesting mesophilic conditions as optimum for the growth of heterotrophic denitrifying organisms. Dosta and Mata-Alvarez (2007) also found optimum temperature for nitrogen removal in a SBR process at 37 ºC. Kim et al. (2006) studied MSW landfill leachate nitrification and reported an increase in nitrification activity with increase in temperature up to 33 ºC.

Table 5-4 gives the model values of pH adopted for optimum growth and for complete inhibition of nitrification and denitrification processes. Berge et al. (2007b) presented a model for ammonia removal where an average value of pH during the entire experiment was used. Adopting a dynamic value of pH in the model may be more practical. The maximum nitrogen removal rate for denitrification when calculated using the Monod equation further reduced by a factor of 0.38 corresponding to the numerical value of S/(K_S+S) in Eq.(5.8). A low value for denitrification rates in comparison to nitrification could be due to the inhibition of denitrification at the experimental pH values between 6.50 and 7.50. Glass and Silverstein (1998) in an experimental study with high nitrate concentration wastewaters found that the denitrification of nitrate was significantly inhibited at pH 6.50 and 7.0 compared to higher pH values. With an increase in the pH there was an increase in nitrate reduction rate. Glass and Silverstein (1998) also showed the change in pH as an indicator of occurrence of denitrification, including the ability to distinguish between the negligible pH effects of nitrate reduction to nitrite and the pH increase associated with conversion of nitrite to non-ionic nitrogen species. Based on the values
adopted in the pH inhibition function, nitrification was affected to a greater extent than
denitrification in the range of experimental pH values.

The model results of nitrifying and denitrifying biomass concentrations at 35°C are
shown in Figure 5-4. He and Shen (2006) in an experimental study on nitrogen removal in
bioreactor landfill system also reported nitrifying bacteria population between $10^6$ and $10^8$
cells/dry g waste.

![Graph showing variation of biomass concentrations at 35 °C.](image)

Figure 5-4. Model results of variation of biomass concentrations at 35 °C.

5.7 Conclusions

Ammonia nitrogen removal in a solid waste bioreactor can occur due to simultaneous
nitrification and denitrification. One nitrogen species may be involved in more than one of these
processes. As such a dynamic model which can accommodate several species in three different
phases of a bioreactor system is required for simulation. The numerical model BIOKEMOD-3P was able to simulate these simultaneous processes. It was possible to quantify the nitrogen removal/turnover rates of these processes. pH was found to have a significant effect on nitrification process. It affected denitrification to a lesser extent in the range of pH values reported in the experimental study. Maximum velocities of ammonia oxidation and denitrification rates were found to be 2.45 and 2.21 gN(kg dry SW)⁻¹d⁻¹ respectively at 35 ºC. Temperature influenced ammonia and nitrite oxidation and denitrification. Based on model results of experimental study, the optimum temperature for ammonia oxidation was near 35 ºC and that for nitrite oxidation, between 35 and 45 ºC. Therefore temperature may also play an important role in nitrogen removal during nitrification and denitrification processes. Although nitrification was highest at 100 % oxygen in the gas phase the effect of reduction in oxygen concentrations could not be quantified. Denitrification was affected to a lesser extent by oxygen concentration in gas phase. Heterotrophic denitrification was affected due to availability of ammonia nitrogen which is required for biomass growth. The model was able to simulate this phenomenon by including a nutrient limitation term for denitrifier growth rate.

It may be possible to achieve high nitrogen removals in full-scale solid waste bioreactors with relatively stabilized waste that has low COD/N ratio. In order to achieve high nitrogen removal rates, buffering of pH may be required to compensate for the acidity generated during nitrification and excess carbon dioxide produced as a result of biodegradation of solid waste from other regions of landfill.
**Abbreviations**

\[ A_k \] concentration of the electron acceptor in the \( k \)th microbial reaction (MM\(^{-1}\))

\[ b_k \] concentration of microbial species in the \( k \)th microbial reaction (MM\(^{-1}\))

\[ g_j \] concentration of \( j \)th aqueous species due to liquid-gas phase partitioning (MM\(^{-1}\))

\[ g_i \] concentration of \( i \)th gas species due to liquid-gas phase partitioning (MM\(^{-1}\))

\[ I \] concentration of inhibitory compound in the \( k \)th microbial reaction (MM\(^{-1}\))

\[ I_{ik} \] inhibition factor for growth rate in the \( k \)th microbial reaction

\[ I_2 \] inhibition factor for half saturation constant for substrate in the \( k \)th microbial reaction

\[ K_{A-k} \] half saturation constant for the electron acceptor in the \( k \)th microbial reaction (MM\(^{-1}\))

\[ K_{I_1} \] constant for inhibition factor for growth rate in the \( k \)th microbial reaction (MM\(^{-1}\))

\[ K_{I_2} \] constant for inhibition factor for substrate half saturation constant in the \( k \)th microbial

\[ K_{N-k} \] half saturation constant for the nutrient in the \( k \)th microbial reaction (MM\(^{-1}\))

\[ K_{S-k} \] half saturation constant for the substrate in the \( k \)th microbial reaction (MM\(^{-1}\))

\[ K_{H(i,j)} \] Henry’s constant for partitioning of \( j \)th aqueous species with \( i \)th gas species,

dimensionless

\[ k_L \] over all mass transfer coefficient, (T\(^{-1}\))

\[ L_k \] lag coefficient for the \( k \)th microbial reaction (MM\(^{-1}\))

\[ N_k \] concentration of the nutrient in the \( k \)th microbial reaction (MM\(^{-1}\))

\[ pH_H \] and \( pH_L \)

the upper and lower pH inhibition values at which the microorganisms were not inhibited, and at which inhibition is complete respectively.

\[ S_k \] concentration of the substrate in the \( k \)th microbial reaction (MM\(^{-1}\))

\[ v''_{j/k} \] reactant stoichiometry of the \( j \)th species in the \( k \)-th reaction

\[ v'_{j/k} \] product stoichiometry of the \( j \)th species in the \( k \)-th reaction
\[ \Omega_k \] rate of the \( k \)th reaction per unit biomass activity (T\(^{-1}\))

\[ \Gamma_{k,T} \] growth rate for the \( k \)th microbial reaction per unit biomass activity at temperature ‘\( T \)’ (T\(^{-1}\))

\[ \Omega_j \] rate of change of \( j \)th aqueous species due to liquid-gas phase partitioning (MM\(^{-1}\)T\(^{-1}\))

\[ \Omega_i \] rate of change of \( i \)th gas species due to liquid-gas phase partitioning (MM\(^{-1}\)T\(^{-1}\))

\[ \gamma_j \] activity coefficient of the \( j \)th aqueous species

\[ \gamma_i \] the activity coefficient of the \( i \)th gas species

References


CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

This research work demonstrated the development of numerical computer model BIOKEMOD-3P to simulate microbiological and chemical reactions in a three-phase system. The computer model BIOKEMOD-3P was able to simulate processes of anaerobic biodegradation of municipal solid waste in experimental bioreactors. The pH was well simulated showing the capability to use a large number of equilibrium reactions along with various kinetic reactions. The concentration of species such as hydrogen that partition between liquid and gas phase and that may have very low concentrations in the liquid phase requires the use of small time steps, which increases the computer simulation time. Therefore a trade off may be evaluated between the desired accuracy of results and the time to run simulations. The structure of BIOKEMOD-3P allows it to be easily coupled with a multi-phase flow model to simulate operations at full-scale.

The application of a robust computer model BIOKEMOD-3P to simulate nitrification and denitrification processes demonstrated its use to identify several simultaneous processes that occur in a solid waste bioreactor system. In these processes where one nitrogen species may be involved in more than one reaction, it was possible to quantify the rates of individual processes at varying temperatures. This modeling exercise showed that like wastewater applications, pH can serve as a control parameter to determine the extent of nitrification and denitrification
occurring in solid waste bioreactor.

The structure of model BIOKEMOD-3P makes it easy to be coupled with a suitable multi-phase flow module. The model is presented with a users manual which may permit users without computer programming knowledge to simulate experimental and pilot-plant operations in a batch system.

6.2 Recommendations

The use of numerical computer model, BIOKEMOD-3P, requires the user to identify necessary equilibrium and kinetic reactions to simulate bioreactor processes in a three-phase system. Two model applications are presented in this work, additional microbiological and chemical species and corresponding reactions need to be identified for other processes that occur in a solid waste bioreactor. pH has influence on the dissociation of weak acids and bases, where it can affect the concentration of dissociated or undissociated species even when the total component concentration does not change. When one of the dissociated or undissociated species is involved in additional kinetic reactions, its availability in these reactions may become limiting. This problem can be solved by either reducing the time step during simulation or modifying the reaction scheme to make the predominant species of a chemical component available for kinetic reactions. In the model applications presented in this work, a majority of kinetic reactions were microbiological reactions, which do not require modification of the reaction scheme. This is because the microbiological systems operate in a narrow pH range. However, for application of this model to geochemical kinetic reactions that are faster than microbiological reactions and
operate at extreme pH conditions, a modification to this model may be required. A provision is required to automatically select a chemical species with high concentration than its dissociated or undissociated form.
APPENDIX A:
ANALYTICAL SOLUTION FOR BIODEGRADATION WITH CONTOIS KINETICS
The Contois Kinetics for substrate biodegradation is given by Eq. (A1) and Eq. (A2)

\[
\frac{\partial S}{\partial t} = -k \left[ \frac{S}{K_S X + S} \right] X
\]

(A1)

\[
\frac{\partial X}{\partial t} = -Y_s k \left[ \frac{S}{K_S X + S} \right] X
\]

(A2)

Combining Eq. (A1) and Eq. (A2) gives:

\[
\frac{\partial X}{\partial S} = -Y_s
\]

(A3)

Integrating Eq. (A3)

\[
X = -Y_s S + Y_s S_o + X_o
\]

(A4)

Substituting Eq. (A4) into Eq (A1)

\[
\frac{\partial S}{\partial t} = -k \left[ \frac{S}{K_S (-Y_s S + Y_s S_o + X_o) + S} \right] (-Y_s S + Y_s S_o + X_o)
\]

(A5)

\[
\int_0^t \frac{1}{k} \left[ \frac{K_S}{S} + \frac{1}{(-Y_s S + Y_s S_o + X_o)} \right] \partial S
\]

(A6)

The solution is given by:

\[
t = \frac{K_S}{k} \ln \left[ \frac{S_o}{S} \right] + \frac{1}{k Y_s} \ln \left[ \frac{X_o + Y_s S_o - Y_s S}{X_o} \right]
\]

(A7)
APPENDIX B:
USERS MANUAL FOR BIOKEMOD-3P
1. Introduction

Any computer model that is required to simulate bioreactor landfill processes with an aim to predict the gas generation must have at least two components, a physical component to simulate the flow of liquids and gases, and a biochemical component to accommodate various chemical and microbiological processes.

The multi-phase flow models were primarily developed for application to hydro-geological processes in porous media and extensive research already done in this area. A majority of these models find application in hazardous waste site remediation projects. The biochemical processes in landfill are unique and different from the subsurface site remediation processes. A majority of biochemical models for solid waste degradation and mentioned earlier may not allow the addition of user specified biochemical processes. Often such additions require minor modifications in the computer code. Several simultaneous processes occur during solid waste biodegradation and they involve several chemical and microbiological species. Acidogenic, methanogenic, aerobic, sulfidogenic, nitrifiers, denitrifiers are some of the microbiological species while there could be very large number of chemical species involved in a complex solid waste biodegradation process. A majority of models mentioned above are unable to model simultaneous equilibrium reactions involving chemical species. Laboratory experiments could be performed for one or more of the above processes but often it is difficult to find a computer model that could efficiently simulate these processes.

This research work presents the development of a biochemical process model that could be coupled with a multi-phase model to simulate a full scale bioreactor landfill. The motivation
to the work comes from the fact that the models explained above are all made with a fixed biochemical structure in terms of the processes and the species. Whereas the model presented here is a generalized numerical model that can accommodate user specified chemical and microbiological processes involving a very large number of species. This model is able to simulate bioreactor landfill operation in a completely mixed condition, when coupled with a multi-phase model will be able to simulate a full-scale bioreactor landfill. This generalized biochemical model would help simulation of laboratory and pilot scale operation to determine biochemical parameters.

The present model BIOKEMOD-3P, is an extension of models KEMOD (Yeh and Tripathi, 1991) and BIOKEMOD (Salvage and Yeh, 1998) but for a three phase system. The chemical and microbiological reactions for a multi phase system are presented in this section. The governing equations describing the model are presented in the following section. This paper explains the additions and modifications over the work presented by Salvage and Yeh (1998).
2. Identification of Process Reactions and Governing Equations

The most frequently mentioned nomenclatures in chemical speciation modeling are components and species as used by Salvage and yeh (1998). Definition of these terms loosely follow those of Westall et al. (1976). Components are a set of linearly independent “basis” chemical entities such that every species can be uniquely represented as a combination of those components and no component can be represented by other components than itself. In addition, we require that the global mass of a component be a reaction invariant (Rubin, 1983). A species is the product of a chemical reaction involving the components as reactants (Westall et al., 1976).

Let us consider a system of $N$ chemical components, $M_a$ microbial species, $M_h$ solid phase species, and $M_g$ gas phase species. The $N$ chemical components consist of $N_a$ aqueous phase components (mobile components) and $N_s$ adsorbent components (immobile adsorbing sites) and NSITE immobile ion exchange sites. The $N_a$ aqueous component will react with each other to form $M_x$ complexed species and $M_p$ precipitated species. In addition, any aqueous component that is not bound with other components is termed as aqueous component species. The total number of aqueous chemical species, $M_{aq}$, is the sum of $N_a$ aqueous aqueous component species and $M_x$ complexed species. The $N_a$ aqueous components and $N_s$ adsorbents will react to form $M_y$ adsorbed species for the case of sorption via surface complexation (adsorption). An adsorbent component that is not bound with other components is termed as the adsorbent component species. Some or all of the $N_a$ aqueous component species and $M_x$ aqueous complexed species may compete with each other for ion exchange sites, resulting in $M_z$ ion exchanged species on the surface. The total number of sorbent species, $M_z$, is the sum of $N_s$.
adsorbent component species, $M_y$ adsorbed species, and $M_z$ ion-exchanged species. The total number of chemical species, $M$, is therefore equal to the sum of $M_{aq}$, $M_s$, and $M_p$.

Microorganisms can exist in both the aqueous and adsorbed phases. The $M_b$ microbial species consist of $M_b$ mobile aqueous phase species and $M_a$ adsorbed phase species. Similar to that is described in BIOKEMOD, the term “microbial species” may refer to either an individual type of organism or a consortia or organism.

The solid phase species, $M_s$, are composed of immobile solids component species $M_{s}^i$, and the mobile solids species, $M_{s}^b$ suspended in liquid phase. The mobile solid phase species could be transported along with the addition and removal of the bulk liquid. The solid phase species are different from the precipitated species in a way that they could be inert solids or undergo microbe mediated hydrolysis to form aqueous phase species.

The gas phase species, $M_g$ form the basic component species of the gas phase. The gas phase species undergo reversible kinetic reaction to dissolve in the bulk aqueous phase to form aqueous chemical species.

2.1 Mass Balance Equations

The governing equations for BIOKEMOD-SW are based on the principles of mass balance, mass action, and kinetic laws. These are based on the similar lines as given by Salvage and yeh (1998) and the detailed derivations by Yeh and Tripathi (1989). The balance equations for all species are written as under:
\[
\frac{\partial}{\partial t} \rho \phi s_w c_i = \rho \phi s_w r_j - \rho \phi s_w \lambda^j c_j - \left( \rho_i \phi s_u c_j \right) \alpha \frac{\partial p}{\partial t} + m^i, \quad j \in N_a 
\] (2.1.1)

\[
\frac{\partial}{\partial t} \rho_b s_j = \rho_b r_j - \rho_b \lambda^j s_j - \left( \rho_b s_j \right) \alpha \frac{\partial p}{\partial t} + m^j, \quad j \in N_b
\] (2.1.2)

\[
\frac{\partial}{\partial t} \rho_s s_w x_i = \rho_s s_w r_i - \rho_s s_w \lambda^i x_i - \left( \rho_s s_w x_i \right) \alpha \frac{\partial p}{\partial t} + m^i, \quad i \in M_x
\] (2.1.3)

\[
\frac{\partial}{\partial t} \rho_s y_i = \rho_s r_i - \rho_s \lambda^i y_i - \left( \rho_s y_i \right) \alpha \frac{\partial p}{\partial t} + m^i, \quad i \in M_y
\] (2.1.4)

\[
\frac{\partial}{\partial t} \rho_s z_i = \rho_s r_i - \rho_s \lambda^i z_i - \left( \rho_s z_i \right) \alpha \frac{\partial p}{\partial t} + m^i, \quad i \in M_z
\] (2.1.5)

\[
\frac{\partial}{\partial t} \rho_s p_i = \rho_s r_i - \rho_s \lambda^i p_i - \left( \rho_s p_i \right) \alpha \frac{\partial p}{\partial t} + m^i, \quad i \in M_p
\] (2.1.6)

\[
\frac{\partial}{\partial t} \rho_b s_w b_i = \rho_i \phi s_u r_i - \rho_i \phi s_u r_i^b - \left( \rho_i \phi s_u b_i \right) \alpha \frac{\partial p}{\partial t} + m^i + \rho_i \phi s_u r_i^{sp}, \quad i \in M_b
\] (2.1.7)

\[
\frac{\partial}{\partial t} \rho_b a_i = \rho_i r_i - \rho_i r_i^{ad} - \left( \rho_i a_i \right) \alpha \frac{\partial p}{\partial t} + m^i + \rho_i r_i^{sp}, \quad i \in M_a
\] (2.1.8)

\[
\frac{\partial}{\partial t} \rho_b h_i = \rho_i r_i^b - \rho_i \lambda^i h_i - \left( \rho_b h_i \right) \alpha \frac{\partial p}{\partial t} + m^i, \quad i \in M_h
\] (2.1.9)
\[
\frac{\partial}{\partial t} \rho_g (1 - \phi s_w) g_i = \rho_g (1 - \phi s_w) r^g_i - \rho_g (1 - \phi s_w) \alpha \frac{\partial p}{\partial t} + m^g_i, \quad i \in M_g
\]  

(2.1.10)

where,

\[\rho_i = \text{density of liquid or mass of liquid per volume of liquid, } \left( M/L^3 \right)\]

\[\phi = \text{porosity of solids grain, volume/unit batch volume, } \left( L^3/L^1 \right) \text{, (batch volume } = \text{volume of solids + volume of liquid + volume of gas + headspace if any)}\]

\[s_w = \text{degree of saturation of water phase, volume of liquid per volume of pores, } \left( L^3/L^3 \right)\]

\[t = \text{time, } \left( T \right)\]

\[p = \text{pressure, } \left( M/LT^2 \right)\]

\[\rho_b = \text{bulk density, mass of solid phase per batch volume, } \left( M/L^3 \right)\]

\[\alpha = \text{compressibility of the media, } \left( LT^2/M \right)\]

\[c_j = \text{concentration of the j-th aqueous component species, mass/liquid mass, } \left( M/M \right)\]

\[r^c_j = \text{production/consumption of the j-th aqueous component species, (mass/liquid mass)/time, } \left( (M/M)/T \right)\]

\[\lambda^c_j = \text{decay constant of the j-th aqueous component species, } \left( 1/T \right)\]

\[m^c_j = \text{source/sink rate of the j-th aqueous component species, (mass/batch volume)/time, } \left( M/L^3 \right)\]
\[
\left(\frac{M}{L^1}\right)/T
\]

\[N_a = \text{number of aqueous component species} = \text{number of aqueous components}\]

\[s_j = \text{concentration of the } j\text{-th adsorbant component species, mass/solid mass, } \left(\frac{M}{M}\right)\]

\[r_j = \text{production/consumption of the } j\text{-th aqueous component species, } (\text{mass/liquid mass})/\text{time},\ 
\left(\frac{M}{M}\right)/T\]

\[\lambda_j = \text{decay constant of the } j\text{-th adsorbent component species, } (1/T)\]

\[m_j = \text{source/sink rate of the } j\text{-th adsorbent component species, } (\text{mass/batch volume})/\text{time},\ 
\left(\frac{M}{L^1}\right)/T\]

\[N_s = \text{number of adsorbent component species} = \text{number of adsorbt components}\]

\[x_i = \text{concentration of the } i\text{-th complexed species, mass/liquid mass, } (M/M)\]

\[r_i = \text{production/consumption of the } i\text{-th complexed species, } (\text{mass/liquid mass})/\text{time},\ 
\left(\frac{M}{M}\right)/T\]

\[\lambda_i = \text{decay constant of the } i\text{-th complexed species, } (1/T)\]

\[m_i = \text{source/sink rate of the } i\text{-th complexed species, } (\text{mass/batch volume})/\text{time},\ 
\left(\frac{M}{L^1}\right)/T\]

\[M_s = \text{number of complexed species}\]

\[y_i = \text{concentration of the } i\text{-th adsorbed species, mass/solid mass, } (M/M)\]
\( r_i^y = \) production/consumption of the i-th adsorbed species, (mass/solid mass)/time,
\[ ((M/M)/T) \]

\( \lambda_i^y = \) decay constant of the i-th adsorbed species, (1/T)

\( m_i^y = \) source/sink rate of the i-th adsorbed species, (mass/batch volume)/time,
\[ ((M/L^3)/T) \]

\( M_y = \) number of adsorbed species

\( z_i = \) concentration of the i-th ion-exchanged species, mass/solid mass, (\( M/M \))

\( r_i^z = \) production/consumption of the i-th ion-exchanged species, (mass/solid mass)/time,
\[ ((M/M)/T) \]

\( \lambda_i^z = \) decay constant of the i-th ion-exchanged species, (1/T)

\( m_i^z = \) source/sink rate of the i-th ion-exchanged species, (mass/batch volume)/time,
\[ ((M/L^3)/T) \]

\( M_z = \) number of ion-exchanged species

\( p_i = \) concentration of the i-th precipitated species, mass/solid mass, (\( M/M \))

\( r_i^p = \) production/consumption of the i-th precipitated species, (mass/solid mass)/time,
\[ ((M/M)/T) \]

\( \lambda_i^p = \) decay constant of the i-th precipitated species, (1/T)

\( m_i^p = \) source/sink rate of the i-th precipitated species, (mass/batch volume)/time,
\( \left( \frac{M}{L^1} \right)/T \)

\( M_p \) = number of precipitated species

\( b_i \) = concentration of the \( i \)-th aqueous phase microbial species, mass/liquid mass, \( \left( \frac{M}{M} \right) \)

\( r_i^{bg} \) = growth rate of the \( i \)-th aqueous phase microbial species, (mass/liquid mass)/time,

\( \left( \frac{(M/M)}{T} \right) \)

\( r_i^{bd} \) = death/decay rate of the \( i \)-th aqueous phase microbial species, (mass/liquid mass)/time,

\( \left( \frac{(M/M)}{T} \right) \)

\( r_i^{sp} \) = death/decay rate of the \( i \)-th aqueous phase microbial species, (mass/liquid mass)/time,

\( \left( \frac{(M/M)}{T} \right) \)

\( m_i^b \) = source/sink rate of the \( i \)-th aqueous phase microbial species, (mass/batch volume)/time,

\( \left( \frac{(M/L^1)}{T} \right) \)

\( M_b \) = number of aqueous phase microbial species

\( a_i \) = concentration of the \( i \)-th adsorbed microbial species, mass/solid mass, \( \left( \frac{M}{M} \right) \)

\( r_i^{ag} \) = growth rate of the \( i \)-th adsorbed microbial species, (mass/solid mass)/time,

\( \left( \frac{(M/M)}{T} \right) \)

\( r_i^{ad} \) = death/decay rate of the \( i \)-th adsorbed microbial species, (mass/solid mass)/time,

\( \left( \frac{(M/M)}{T} \right) \)

\( m_i^a \) = source/sink rate of the \( i \)-th adsorbed microbial species, (mass/batch volume)/time,

\( \left( \frac{(M/L^1)}{T} \right) \)
\( M_a \) = number of aqueous phase microbial species

\( h_i \) = concentration of the i-th solids phase species, mass/solid mass, \((M/M)\)

\( r_i^h \) = production/consumption rate of the i-th solid phase species, \((mass/solid mass)/time\)

\( \lambda_i^h \) = decay constant of the i-th solid phase species, \((1/T)\)

\( m_i^h \) = source/sink rate of the i-th solid phase species, \((mass/batch volume)/time,\)

\( M_s \) = number of solid phase species = number of solid phase components

\( g_i \) = concentration of the i-th gas phase species, mass/gas mass, \((M/M)\)

\( r_i^g \) = production/consumption rate of the i-th gas phase species, \((mass/gas mass)/time\)

\( \lambda_i^g \) = decay constant of the i-th gas phase species, \((1/T)\)

\( m_i^g \) = source/sink rate of the i-th gas phase species, \((mass/batch volume)/time,\)

\( M_g \) = number of gas phase species = number of gas phase components

Equation (2.1.1.) through (2.1.6) state mass balance of chemical species. Each equation mentions that the rate of accumulation of an element is equal to the sum of its production/consumption rate, decay rate, and artificial source/sink rate. The term on the left hand side of each equation
represents the accumulation rate. The first term on the right hand side of each equation represents the rate of production/consumption in chemical and microbiological reactions. The second term on the right hand side of each equation represents the decay rate. The third term on the right hand side of each equation represents the artificial source/sink rate.

Similarly, Equations (2.1.7) and (2.1.8) are a statement of mass balance for microbial species. The rate of accumulation of a microbial species is equal to the rate of its growth, less the rate of its death/decay, plus the rate of any artificial source/sink and transfer of the species to the other system phase (aqueous or adsorbed). The left hand side of each equation represents the accumulation rate. The first term on the right hand side of each equation represents the rate of microbial growth. The second term on the right hand side of each equation represents the effect of media compression. The fourth term on the right hand side of each equation represents the artificial source/sink rate. The last term on the right hand side of each equation represents the rate of transfer of the microbial species between the aqueous and adsorbed phases.

Equations (2.1.9) represent the mass balance for solid phase species. The rate of accumulation of solids species is equal to the sum of its production/consumption rate, decay rate, and artificial source/sink rate. The term on the left hand side represents the accumulation rate. The first term on the right hand side represents the rate of production/consumption in solids disintegration and microbe mediated hydrolysis reactions. The second term on the right hand side represents the decay rate. The third term on the right hand side of each equation represents the effect of media compression. The fourth term on the right hand side represents the artificial source/sink rate.

The rate of production / consumption for each chemical species includes the combined effects of
chemical and microbiological reactions:

\[ r_j^c = r_j^{chem} + r_j^{bio} + r_j^{solid p} + r_j^{gas p} \quad (2.1.11) \]

\[ r_j^s = r_j^{chem} + r_j^{bio} + r_j^{solid p} \quad (2.1.12) \]

\[ r_i^x = r_i^{chem} + r_i^{bio} + r_i^{solid p} + r_i^{gas p} \quad (2.1.13) \]

\[ r_i^y = r_i^{chem} + r_i^{bio} + r_i^{solid p} \quad (2.1.14) \]

\[ r_i^z = r_i^{chem} + r_i^{bio} + r_i^{solid p} \quad (2.1.15) \]

\[ r_i^p = r_i^{chem} + r_i^{bio} \quad (2.1.16) \]

\[ r_i^h = r_i^{chem} + r_i^{solid p} \quad (2.1.17) \]

\[ r_i^g = r_i^{gas p} \quad (2.1.18) \]

\( r_j^c \) is the total production/consumption of the j-th aqueous component species,
total production/consumption of the $j$-th aqueous component species due to chemical reactions, (mass/liquid mass)/time, $(M/M)$

$\dot{r}_c^{che}$

total production/consumption of the $j$-th aqueous component species due to microbial processes, (mass/liquid mass)/time, $(M/M)$

$\dot{r}_c^{bio}$

$\dot{r}_c^{bioc}$

total production/consumption of the $j$-th aqueous component species due to inter-conversion to solid phase, (mass/liquid mass)/time, $(M/M)$

$\dot{r}_c^{sol}$

$\dot{r}_c^{p}$

$\dot{r}_c^{pg}$

total production/consumption of the $j$-th aqueous component species due to inter-conversion to gas phase, (mass/liquid mass)/time, $(M/M)$

$\dot{r}_c^{gas}$

$\dot{r}_c^{p}$

total production/consumption of the $j$-th adsorbent component species, (mass/liquid mass)/time, $(M/M)$

$\dot{r}_s^{che}$

$\dot{r}_s^{chems}$

$\dot{r}_s^{bios}$

$\dot{r}_s^{bioc}$

total production/consumption of the $j$-th adsorbent component species due to chemical reactions, (mass/liquid mass)/time, $(M/M)$

$\dot{r}_s^{che}$

$\dot{r}_s^{chems}$

$\dot{r}_s^{bios}$

$\dot{r}_s^{bioc}$

$\dot{r}_s^{p}$

$\dot{r}_s^{sol}$

$\dot{r}_s^{p}$

$\dot{r}_s^{pg}$

$\dot{r}_s^{p}$

$\dot{r}_s^{sol}$

$\dot{r}_s^{p}$

$\dot{r}_s^{pg}$

$\dot{r}_s^{p}$

$\dot{r}_s^{sol}$

$\dot{r}_s^{p}$

$\dot{r}_s^{pg}$
\( r_j^{\text{solid} \, p} \) total production/consumption of the j-th adsorbent component species due to inter-conversion to solid phase, \((\text{mass/liquid mass})/\text{time}, \left( \frac{M}{M} \right)/T\)

\( r_i^{x} \) total production/consumption of the i-th aqueous complexed species,
\((\text{mass/liquid mass})/\text{time}, \left( \frac{M}{M} \right)/T\)

\( r_i^{x \, \text{chem}} \) total production/consumption of the i-th aqueous complexed species due to chemical reactions, \((\text{mass/liquid mass})/\text{time}, \left( \frac{M}{M} \right)/T\)

\( r_i^{x \, \text{bio}} \) total production/consumption of the i-th aqueous complexed species due to microbial processes, \((\text{mass/liquid mass})/\text{time}, \left( \frac{M}{M} \right)/T\)

\( r_i^{\text{solid} \, p} \) total production/consumption of the i-th aqueous complexed species due to inter-conversion to solid phase, \((\text{mass/liquid mass})/\text{time}, \left( \frac{M}{M} \right)/T\)

\( r_i^{x \, \text{gas} \, p} \) total production/consumption of the i-th aqueous complexed species due to inter-conversion to gas phase, \((\text{mass/liquid mass})/\text{time}, \left( \frac{M}{M} \right)/T\)

\( r_i^{y} \) total production/consumption of the i-th adsorbed species,
\((\text{mass/liquid mass})/\text{time}, \left( \frac{M}{M} \right)/T\)

\( r_i^{y \, \text{chem}} \) total production/consumption of the i-th adsorbed species due to chemical reactions, \((\text{mass/liquid mass})/\text{time}, \left( \frac{M}{M} \right)/T\)

\( r_i^{y \, \text{bio}} \) total production/consumption of the i-th adsorbed species due to microbial
processes, \((\text{mass/liquid mass})/\text{time}\), \((M / M) / T\)

\(r_i^{\text{solid \,p}}\) total production/ consumption of the i-th adsorbed species due to inter-
conversion to solid phase, \((\text{mass/liquid mass})/\text{time}\), \((M / M) / T\)

\(r_i^{z}\) total production/ consumption of the i-th ion-exchanged species,
\((\text{mass/liquid mass})/\text{time}\), \((M / M) / T\)

\(r_i^{\text{chem \,z}}\) total production/ consumption of the i-th ion-exchanged species due to
chemical reactions, \((\text{mass/liquid mass})/\text{time}\), \((M / M) / T\)

\(r_i^{\text{bio \,z}}\) total production/ consumption of the i-th ion-exchanged species due to microbial
processes, \((\text{mass/liquid mass})/\text{time}\), \((M / M) / T\)

\(r_i^{p}\) total production/ consumption of the i-th precipitated species,
\((\text{mass/liquid mass})/\text{time}\), \((M / M) / T\)

\(r_i^{\text{chem \,p}}\) total production/ consumption of the i-th precipitated species due to
chemical reactions, \((\text{mass/liquid mass})/\text{time}\), \((M / M) / T\)

\(r_i^{\text{bio \,p}}\) total production/ consumption of the i-th precipitated species due to microbial
processes, \((\text{mass/liquid mass})/\text{time}\), \((M / M) / T\)

\(r_i^{h}\) total production/ consumption of the i-th solids component species,
\((\text{mass/liquid mass})/\text{time}\), \((M / M) / T\)
\[ r_i^{h,\text{chem}} \] total production/consumption of the i-th solids component species due to chemical reactions, \((\text{mass/liquid mass})/\text{time}, \left((M/M)/T\right)\)

\[ r_i^{h,\text{solids}} \] total production/consumption of the i-th solids component species due to conversion to or from solid phase, \((\text{mass/liquid mass})/\text{time}, \left((M/M)/T\right)\)

\[ r_i^{g,\text{gas}} \] total production/consumption of the i-th gaseous component species, \((\text{mass/gas mass})/\text{time}, \left((M/M)/T\right)\)

\[ r_i^{g,\text{gas,\text{gas}}\text{gas,\text{gas}}} \] total production/consumption of the i-th gaseous component species due to inter-conversion from gas phase, \((\text{mass/gas volume})/\text{time}, \left((M/L^3)/T\right)\)
Equations (2.1.1) and (2.1.2) can be replaced with balance equations governing the total concentration of the components rather than the concentration of the component species. This approach enforces mass conservation with respect to the chemical reactions for all components and provides the basic framework for the model that could be linked with a hydrologic transport model. This approach is the same adopted by Yeh and Salvage (1998). To derive the governing equation for aqueous components for the alternative approach, we multiply Eqs. (2.1.3) through (2.1.6) with corresponding stiochiometric coefficient and add the results to Eq. (2.1.1) to obtain

\[
\frac{\partial T_j^c}{\partial t} = -\Lambda_j T_j^c - (T_j^c)\alpha \frac{\partial p}{\partial t} + M_j^c
\]

\[
+ \rho_s \phi s_w \left( r_j^{\text{bio}} + \sum_{i=1}^{M_s} a_j^{\text{bio}} r_i^{\text{bio}} + r_j^{\text{gas}} + \sum_{i=1}^{M_s} a_j^{\text{gas}} r_i^{\text{gas}} + \sum_{i=1}^{M_s} a_j^p r_i^p \right), \quad j \in N_a
\]

\[
T_j^c = \rho_s \phi s_w \left( c_j + \sum_{i=1}^{M_s} a_j^{\text{bio}} x_i + \sum_{i=1}^{M_s} a_j^{\text{gas}} y_i + \sum_{i=1}^{M_s} a_j^p z_i + \sum_{i=1}^{M_s} a_j^p p_i \right), \quad j \in N_a
\]

\[
\Lambda_j T_j^c = \rho_s \phi s_w \left( \lambda_j c_j + \sum_{i=1}^{M_s} a_j^{\text{bio}} \lambda_i x_i + \sum_{i=1}^{M_s} a_j^{\text{gas}} \lambda_i y_i + \sum_{i=1}^{M_s} a_j^p \lambda_i z_i + \sum_{i=1}^{M_s} a_j^p \lambda_i^p p_i \right), \quad j \in N_a
\]
\[ M_j^c = m_j^c + \sum_{i=1}^{M_s} a_{ij}^c m_i^c + \sum_{i=1}^{M_r} a_{ij}^r m_i^r + \sum_{i=1}^{M_m} a_{ij}^m m_i^m + \sum_{i=1}^{M_p} a_{ij}^p m_i^p, \quad j \in N_a \]  

(2.1.22)

where,

\[ T_j^c \quad \text{total concentration of the j-th aqueous component, mass/batch volume} \quad (M/L^3) \]

\[ \Lambda_j^c \quad \text{bulk decay constant of the j-th aqueous component, } (1/T) \]

\[ M_j^c \quad \text{source/sink rate of the j-th aqueous component, } (\text{mass/batch vol})/\text{time} \quad (M/L^3/T) \]

\[ a_{ij}^c \quad \text{stoichiometry of the j-th aqueous component in the i-th complexed species,} \]

\[ a_{ij}^r \quad \text{stoichiometry of the j-th aqueous component in the i-th adsorbed species,} \]

\[ a_{ij}^m \quad \text{stoichiometry of the j-th aqueous component in the i-th ion-exchanged species,} \]

\[ a_{ij}^p \quad \text{stoichiometry of the j-th aqueous component in the i-th precipitated species,} \]

In derivation of Eqn. (2.1.19), it was assumed that for a component, mass is conserved only with respect to chemical reactions in same phase. Mass is not conserved with respect to chemical decay, microbiological reactions, and inter-phase mass transfer between solid, aqueous, and gas phases.
Eqn. (2.1.23) states that the rate at which a component is consumed in chemical reactions is balanced by the rate at which the product species containing that component are formed.

The governing equations for adsorbent components can be written as under:

$$\frac{\partial W^j}{\partial t} = - \Lambda^j W^c - (W^j) \frac{\partial p}{\partial t} + M^j + \rho_b \left( r^{\text{bio}}_j + r^{\text{solid}}_j + \sum_{i=1}^{M_s} a^{y}_j r^{\text{chem}}_i \lambda^{z}_i \right), \quad j \in N_s$$

(2.1.24)

in which

$$W^j = \rho_b s_j + \sum_{i=1}^{M_s} a^{y}_j y_i, \quad j \in N_s$$

(2.1.25)

$$\Lambda^j W^c = \rho_b \lambda^j s_j + \sum_{i=1}^{M_s} a^{y}_j \lambda^z_j y_i, \quad j \in N_s$$

(2.1.26)

$$M^j = m^j + \sum_{i=1}^{M_s} a^{y}_j m_i, \quad j \in N_s$$

(2.1.27)
where,

\( W_j \)  \( \) total concentration of the j-th adsorbent component, mass/batch volume \( (M/L^3) \),

and is calculated by a summation over \( M_k \) solid phase species which contributed to the adsorption sites.

\( \Lambda_j \)  \( \) bulk decay constant of the j-th adsorbent component, \( (1/T) \)

\( M'_j \)  \( \) source/sink rate of the j-th adsorbent component, (mass/batch vol)/time \( (M/L^3)/T) \)

the derivation of Eqn. (2.1.24) is based on the consideration that:

\[
\rho_b \left( r_j^{chem} \right) + \sum_{i=1}^{M} a_{ij} r_i^{chem} = 0, \quad j \in N_x
\]  \( (2.1.28) \)

The governing equation for ion-exchange sites is written as under:

\[
\frac{\partial (N_{eq,j})}{\partial t} = -N_{eq,j} (N_{eq,j}) \alpha \frac{\partial p}{\partial t} + M_j^{eq} \\
+ \rho_b \left( \sum_{i=NOMZJ(j)+1}^{NOMZJ(j)+NOMZI(j)} v_i r_i^{bio} + \sum_{i=NOMZJ(j)+1}^{NOMZI(j)+NOMZI(j)} v_i r_i^{solid} \right), \quad j \in NSITE  \( (2.1.29) \)
\]

where,
\[ N_{eqj} = \rho_b \sum_{i=NOMZI(j)+1}^{NOMZI(j)} v_i z_i, \quad j \in NSITE \]  \hspace{1cm} (2.1.30)

\[ \Lambda_j N_{eqj} = \rho_b \sum_{i=NOMZI(j)+1}^{NOMZI(j)} v_i \lambda_i^2 z_i, \quad j \in NSITE \]  \hspace{1cm} (2.1.31)

\[ M_{eqj} = \sum_{i=NOMZI(j)+1}^{NOMZI(j)+NOMZI(j)} v_i m_i^* , \quad j \in NSITE \]  \hspace{1cm} (2.1.32)

and

\[ M_S = \sum_{j=1}^{NSITE} NOMZI(j) \]  \hspace{1cm} (2.1.33)

where,

-  \( N_{eqj} \)  ion exchange capacity for the \( j \)-th ion-exchange site, or number of equivalents/batch volume, \( (M/L^3) \) and is calculated by a summation over \( M_s \) solid phase species which contributed to the ion-exchange sites.
-  \( \Lambda_j \)  bulk decay constant of the \( j \)-th ion-exchange site, \( (1/T) \)
-  \( M_{eqj} \)  source/sink rate of the \( j \)-th ion-exchange site, (equivalents/batch vol)/time \( ((M/L^3)/T) \)
-  \( NOMZI(j) \)  number of ion-exchanged species participating in reactions at the \( j \)-th ion-
exchange site.

\[ NOMZJ(j) \] number of ion-exchanged species in the 1-st through the \((j-1)\)th ion-exchange sites.

\[ \nu_n \] valence of the \(n\)-th ion exchanged species.

The following relationship holds true in derivation of Eqn. (2.1.29).

\[
\rho_b \sum_{i=NOMZJ(j)+1}^{NOMZJ(j)+NOMZJ(j)} \nu_i r_i^{chem} = 0, \quad j \in NSITE
\]  

(2.1.34)

Solids are proposed to be entirely defined by independent components unlike the aqueous phase species. Biodegradation process of solids is mostly irreversible processes, it results in formation of products of simple forms either in solid or aqueous phase. As such, using components and species for solid phase offers little advantage. Solid species are composed of contribution of very fine solids dispersed in aqueous phase denoted by \( \left( h^b \right) \) and occupying the pore volume and the solids in solid matrix denoted by \( \left( h^s \right) \).

The governing equation for solids species can be written as:

\[
\frac{\partial}{\partial t} \rho_i \phi_s w_i h_i^b = -\lambda_j \rho_i \phi_s w_i h_i^b - (\rho_i \phi_s w_i h_i^b) \frac{\partial p}{\partial t} + m_i^{h^b} + \rho_i \phi_s w_i \left( r_i^{chem} + r_i^{solid \rho} \right), \quad i \in N_b
\]

(2.1.35)
For solids species forming the solid matrix, the following relations can be derived:

\[
\frac{\partial h_i^b}{\partial t} = -\lambda_i^b h_i^b - \left(h_i^b\right) \alpha \frac{\partial p}{\partial t} + \frac{1}{\rho_s \phi_S} m_i^{chem} + r_i^{chem} + r_i^{solid} \left| \frac{1}{\rho_s \phi_S} \frac{\partial \phi_S}{\partial t} h_i^b, \quad i \in N_{h^b}
\]

(2.1.36)

or

\[
\frac{\partial \rho_b h_i^s}{\partial t} = -\lambda_i^b \rho_b h_i^s - \left(\rho_b h_i^s\right) \alpha \frac{\partial p}{\partial t} + m_i^{chem} + \rho_b \left( r_i^{chem} + r_i^{solid} \right), \quad i \in N_{h^b}
\]

(2.1.37)

or

\[
\frac{\partial h_i^s}{\partial t} = -\lambda_i^s h_i^s - \left(h_i^s\right) \alpha \frac{\partial p}{\partial t} + \frac{1}{\rho_b} m_i^{chem} + r_i^{chem} + r_i^{solid} \left| \frac{1}{\rho_b} \frac{\partial \rho_b}{\partial t} h_i^s, \quad j \in N_{h^s}
\]

(2.1.38)

where,

- \( h^b \) concentration of the i-th solid species in aqueous phase, (mass/liquid mass) \((M/M)\)
- \( h^s \) concentration of the i-th solid species in solid phase, (mass/solid mass) \((M/M)\)
- \( \lambda_i^b \) decay constant of the i-th solids component species, \((1/T)\)
- \( m_i^b \) source/sink rate of the i-th solid component species, (mass/liquid mass)/time \( ((M/M)/T) \)

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source/sink rate of the i-th solid component species, \((\text{mass/solid mass)/time} \ (M/M)/T)\)

An equation governing the degree of saturation for the aqueous phase can be obtained on the mass balance equation for water. Water is considered as an aqueous chemical component.

\[
\frac{\partial \rho \phi s_w C_w}{\partial t} + \sum_{i=M_w} a_{i}^{x} \frac{\partial \rho \phi x_i}{\partial t} + \sum_{i=M_z} a_{i}^{x} \frac{\partial \rho z_i}{\partial t} + \sum_{i=M_p} a_{i}^{x} \frac{\partial \rho p_i}{\partial t} = -\Lambda_w T_w - \frac{\partial \rho}{\partial t} T_w + M_w
\]

\[
+ \rho \phi s_w \left( r_w^{\text{bio}} + \sum_{i=1}^{M_w} a_{i}^{x} r_i^{\text{bio}} + r_w^{\text{solid}} + \sum_{i=1}^{M_z} a_{i}^{x} r_i^{\text{solid p}} + r_w^{\text{gas p}} + \sum_{i=1}^{M_p} a_{i}^{x} r_i^{\text{gas p}} \right)
\]

\[
+ \rho_b \left( \sum_{i=1}^{M_w} a_{i}^{x} r_i^{\text{bio}} + \sum_{i=1}^{M_z} a_{i}^{x} r_i^{\text{bio}} + \sum_{i=1}^{M_p} a_{i}^{x} r_i^{\text{bio}} \right)
\]

(2.1.39)

\[
T_w = \rho_1 \phi s_w \left( c_w + \sum_{i=1}^{M_w} a_{i}^{x} x_i \right) + \rho_b \left( \sum_{i=1}^{M_w} a_{i}^{x} y_i + \sum_{i=1}^{M_z} a_{i}^{x} z_i + \sum_{i=1}^{M_p} a_{i}^{x} p_i \right)
\]

(2.1.40)

\[
\Lambda_w T_w = \rho_1 \phi s_w \left( \lambda_c c_w + \sum_{i=1}^{M_w} a_{i}^{x} \lambda_{i}^{x} x_i \right) + \rho_b \left( \sum_{i=1}^{M_w} a_{i}^{x} \lambda_{i}^{x} y_i + \sum_{i=1}^{M_z} a_{i}^{x} \lambda_{i}^{x} z_i + \sum_{i=1}^{M_p} a_{i}^{x} \lambda_{i}^{x} p_i \right)
\]

(2.1.41)

rewriting above equation in
\[
\frac{\partial \rho_s \phi_s}{\partial t} = -\Lambda w T_w - \alpha \frac{\partial p}{\partial t} T_w + M_w - B - \left( \rho_s \phi_s \right) \frac{\partial A}{\partial t}
\]
\[= \rho_s \phi_s \left( r_w^{\text{bio}} + \sum_{i=1}^{M_w} a_{i,w}^{x} r_i^{\text{bio}} \right) + r_w^{\text{solid}} + \sum_{i=1}^{M_w} a_{i,w}^{x} r_i^{\text{solid}} + r_w^{\text{gass}} + \sum_{i=1}^{M_w} a_{i,w}^{x} r_i^{\text{gass}} \]
\[+ \rho_b \left( \sum_{i=1}^{M_i} a_{i,b}^{x} r_i^{\text{bio}} + \sum_{i=1}^{M_i} a_{i,b}^{x} r_i^{\text{bio}} + \sum_{i=1}^{M_i} a_{i,b}^{p} r_i^{\text{bio}} \right) \]
(2.1.42)

\[
A = \left( c_w + \sum_{i \in M_s} a_{i,w}^{x} x_i \right) \]  
(2.1.43)

\[
B = \left( \sum_{i \in M_s} a_{i,w}^{y} \frac{\partial \rho_s}{\partial t} + \sum_{i \in M_s} a_{i,w}^{z} \frac{\partial \rho_b}{\partial t} + \sum_{i \in M_p} a_{i,p}^{y} \frac{\partial \rho_p}{\partial t} \right) \]  
(2.1.44)

The gaseous phase saturation can be related to the aqueous phase as per Eqn. (2.1.45)

\[
s_g = 1 - s_w \]
(2.1.45)

The governing equation for the aqueous phase density can be written as:

\[
\rho_s \phi_s = \rho_s \phi_s \left( c_w M_w + \sum_{j=1}^{N_j} c_j M_j + \sum_{i=1}^{M_i} x_i M_i + \sum_{i=1}^{M_j} h_i M_j + \sum_{i=1}^{M_i} a_i M_i \right) \]
(2.1.46)
\[ \rho_i = \frac{1}{c_i M_w + \sum_{j=1}^{N_i} c_j M_j + \sum_{i=1}^{M_i} x_i M_i + \sum_{i=1}^{h_i} x_i M_i + \sum_{i=1}^{q_i} M_i} \] (2.1.47)

Similarly, the equation governing the density of the solid phase can be written as

\[ \rho_b = \frac{1}{\sum_{i=1}^{M_i} h_i^s M_i + \sum_{i=1}^{z_i} M_i + \sum_{i=1}^{p_i} M_i} \] (2.1.48)

The governing equation for gaseous phase components can be written as under:

\[
\frac{\partial (\rho g \phi (1 - s_w) g_i^g)}{\partial t} = -\lambda_i^{\text{gas}} \rho g \phi (1 - s_w) g_i^g + r_i^{\text{inout}} - \rho s \phi (1 - s_w) g_i^s \left( \alpha \frac{\partial p}{\partial t} \right) + m_i^g, \quad g_i^g \in M_g \tag{2.1.49}
\]

\[ g_i^g = \frac{\omega_i p_i^g}{\sum_{k=1}^{M_i} \omega_k p_k^g} \] (2.1.50)

\[ \omega_i = \frac{p_i}{P_g} \] (2.1.51)
\[ P_g = \sum_{i=1}^{M_g} P_i ; \quad \sum_{i=1}^{M_g} \omega_i = 1 \]  

(2.1.52)

\[ \rho_i^g = \frac{1}{RT} (MW)_i P_g \]  

(2.1.53)

\[ \rho_g = \sum_{i=1}^{M_g} \omega_i \rho_i^g \]  

(2.1.54)

\( g_i^g \) concentration of the i-th gaseous component species, mass/gas mass \( (M / M) \)

\( \lambda_i^g \) bulk decay constant of the i-th gaseous component species, \( (1 / T) \)

\( m_i^g \) source/sink rate of the i-th gaseous component species, \( (\text{gas mass/batch vol})/\text{time} \)

\( \omega_i \) partial pressure of the i-th gaseous component species, volume fraction \( (V / V) \)

\( P_i \) partial pressure exerted by i-th gaseous component, pressure volume fraction \( (M / LT^2) \)

\( P_g \) total gas pressure, pressure volume fraction \( (M / LT^2) \)

\( (MW)_i \) molecular weight of the i-th gaseous component species

\( \rho_i^g \) density of the i-th gaseous component species at pressure \( P_g \), \( (M / L^3) \)

\( \rho_g \) average density of the gas phase at pressure \( P_g \), \( (M / L^3) \)
As gas pressure is better indicator of gas concentration, Eqn. (2.1.49) can be transformed to (2.1.55) using Eqns. (2.1.50) to (2.1.54)

\[
\frac{\partial}{\partial t} \left[ \varphi (1 - s_w) \frac{(MW_i) P_i}{RT} \right] = -\lambda^g_i \varphi (1 - s_w) P_i (MW_i) + r_i^{gas,p} \\
- \frac{\varphi (1 - s_w) P_i (MW_i)}{RT} \left( \alpha \frac{\partial p}{\partial t} \right) + m_i^g
\]  

(2.1.55)

The calculation of temperature of the reaction system can be computed by applying the heat balance over the system.

\[
\frac{\partial Q}{\partial t} = q + M_q + M_{qb}
\]  

(2.1.56)

where,

\[
Q = \text{the heat energy of the system, (Joule/batch vol), } \left( ML^2 / T^2 \right)
\]

\[
q = \text{the rate of production of heat in chemical and microbiological reactions, (Joule/batch vol)/time } \left( ML^2 / T^3 \right)
\]

\[
M_q = \text{source/sink of heat in the system, (Joule/batch vol)/time } \left( ML^2 / T^3 \right)
\]

\[
M_{qb} = \text{source/sink of heat due to boundary conditions, (Joule/batch vol)/time } \left( ML^2 / T^3 \right)
\]

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Equations (2.1.3) through (2.1.8), (2.1.19) and (2.1.20), (2.1.24) and (2.1.25), (2.1.29) and (2.1.30), (2.1.36) and (2.1.38), (2.1.42), (2.1.45), (2.1.47), (2.1.48), (2.1.54), (2.1.55) and (2.1.56) constitute
\[ s_w + s_g + \rho_l + \rho_b + \rho_g + \text{TEMP} \] equations which constrain chemical and bacterial species by the law of conservation of mass and ion-exchange sites. These equations involve the unknowns:
\[ M_x, M_y, M_z, M_p, P_i, M_a, a', M_b, b', N_a, T_j, s, N_s W_j, \]
\[ N_s s_j, N_h h_j, NSITE N e_{eqj}, s, M_x r_x^j, s, M_y r_y^j, s, M_z r_z^j, s, M_p r_p^j, s, M_g r_g^{phase}, s, \]
\[ M_h r_h^{phase}, s, M_a r_a^{ag}, s, M_a r_a^{ad}, s, M_h r_h^{bg}, s, M_h r_h^{bd}, s, M_a + M_h + 2M_a + 2M_b - NSITE. \] The formulation will be complete as the unknowns are more than above equations. A
\[ (M_x + M_y + M_z + M_p + M_g + M_h + 2M_a + 2M_b - NSITE) \] equations are still required.

2.2 Mass balance equation for hydrogen and electrons

The mass balance equations for hydrogen and operational electrons are the ones as explained by Salvage and Yeh (1998). As explained by them, in a system involving acid-base reactions, an additional parameter describing the acidity of the system is needed. This additional parameter is the activity of proton (or the pH value). The pH value may be simulated by using either the electroneutrality or proton condition. These two approaches can be shown to be mathematically but not computationally equivalent. The use of proton condition eliminates the use of any fictitious species that may be needed for maintaining the electroneutrality condition.

The treatment of redox reactions is similar to that given by Salvage and Yeh (1998), and it is
assumed that the phase change between liquid and gaseous phase will not involve transfer of “operational” electrons. Multiplying Eqs. (2.1.1) through (2.1.6) and (2.1.9) with corresponding stiochiometric coefficient for operational electrons in all species and sum the results to give

\[
\frac{\partial T_e}{\partial t} = -\Lambda_e T_e - T_e \alpha \frac{\partial p}{\partial t} + M_e + \rho_b \phi s_w \left( \sum_{j=1}^{N_e} a_{je} r_j^{\text{bio and solid} p} + \sum_{i=1}^{M} a_{ie}^{x} r_i^{x} \right) \\
+ \rho_b \left( \sum_{j=1}^{N_e} a_{je}^{r} r_i^{r} + \sum_{i=1}^{M} a_{ie}^{y} r_i^{y} + \sum_{i=1}^{M} a_{ie}^{z} r_i^{z} + \sum_{i=1}^{M} a_{ie}^{p} r_i^{p} \right)
\]

(2.2.1)

\[
T_e = \rho_b \phi s_w \left( \sum_{j=1}^{N_e} a_{je}^{x} c_j + \sum_{i=1}^{M} a_{ie}^{x} x_i \right) + \rho_b \left( \sum_{j=1}^{N_e} a_{je} s_j + \sum_{i=1}^{M} a_{ie} y_i + \sum_{i=1}^{M} a_{ie} z_i + \sum_{i=1}^{M} a_{ie}^{p} P_i + \sum_{j=1}^{M} a_{je}^{h} h_j \right)
\]

(2.2.2)

\[
M_e = \sum_{j=1}^{N_e} a_{je}^{c} m_j^{c} + \sum_{i=1}^{M} a_{ie}^{x} m_i^{x} + \sum_{j=1}^{N_e} a_{je}^{r} m_j^{r} + \sum_{i=1}^{M} a_{ie}^{y} m_i^{y} + \sum_{i=1}^{M} a_{ie}^{z} m_i^{z} + \sum_{i=1}^{M} a_{ie}^{p} m_i^{p} + \sum_{i=1}^{M} a_{ie}^{h} m_i^{h}
\]

(2.2.3)

where,

\[T_e\] = total concentration of “operational” electrons, mass/batch volume \(\left(\frac{M}{L^3}\right)\),

\[\Lambda_e\] = bulk decay constant of the “operational” electron, \((1/T)\),

\[M_e\] = source/sink of the “operational” electron, (mass/batch volume)/time \(\left(\frac{(M/L^3)}{T}\right)\),

\[a_{je}^{c}\] = stiochiometric coefficient of the electron in the j-th aqueous component species,
The above stoichiometric coefficients are given by Walsh et al. (1984) and explained by Salvage and Yeh (1998). The simulation of pH and or pe uses mole balance equations, that the expressions are identical to Eq. (2.1.20), the proton and/or electron can be treated as aqueous components and no special consideration is needed to distinguish the proton and/or electron from other regular aqueous components. The only things we must keep in mind are that (1) the stiochiometric coefficient of the proton (or electron) in a species may be negative resulting in the possibility of a negative total analytical concentration of protons (or electrons) and (2) when a chemical element is present at several oxidation states, only one of these can be considered a component and the others must be treated as species.

2.3 Artificial sources/sinks

The definition for artificial source/sink used by Salvage and Yeh (1998) was extended to involve species in all the three phases in here. However the removal is limited to aqueous component and complex species and gaseous phase species. Any solids species can be forced to sink by using
opposite mathematical sign for the source term. The source and sink terms are defined as under:

\[ m_i^x = Q_{\text{inp}} x_{\text{inp}}, \quad i \in M_x \quad (2.3.1) \]

\[ m_i^y = Q_{\text{inp}} y_{\text{inp}}, \quad i \in M_y \quad (2.3.2) \]

\[ m_i^z = Q_{\text{inp}} z_{\text{inp}}, \quad i \in M_z \quad (2.3.3) \]

\[ m_i^p = Q_{\text{inp}} p_{\text{inp}}, \quad i \in M_p \quad (2.3.4) \]

\[ m_i^b = Q_{\text{inp}} b_{\text{inp}}, \quad i \in M_b \quad (2.3.5) \]

\[ m_i^a = Q_{\text{inp}} a_{\text{inp}}, \quad i \in M_a \quad (2.3.6) \]

\[ M_j^c = Q_{\text{inp}} T_{\text{inp}}, \quad j \in N_a \quad (2.3.7) \]

\[ M_j^s = Q_{\text{inp}} W_{\text{inp}}, \quad j \in N_s \quad (2.3.8) \]

\[ M_j^{eq} = Q_{\text{inp}} N_{\text{eq}j}, \quad j \in \text{NSITE} \quad (2.3.9) \]
\[ M_w = Q_w^{\text{inp}} \left( t_w^{\text{inp}} + \sum_{i=1}^{M_x} a_{i,w}^x z_i^{\text{inp}} + \sum_{i=1}^{M_y} a_{i,w}^y y_i^{\text{inp}} + \sum_{i=1}^{M_z} a_{i,w}^z z_i^{\text{inp}} + \sum_{i=1}^{M_p} a_{i,w}^p p_i^{\text{inp}} \right) \] (2.3.10)

\[ m_i^{h'} = Q_w^{\text{inp}} \left( h_i^{\text{inp}} \right)^{\text{inp}} \] (2.3.11)

\[ m_i^{b'} = Q_w^{\text{inp}} \left( h_i^{\text{inp}} \right)^{\text{inp}} \] (2.3.12)

\[ m_i^{c'} = Q_w^{\text{inp}} \left( g_i^{\text{inp}} \right)^{\text{inp}} \] (2.3.13)

For Artificial Sink:

\[ m_i^x = Q_w^{\text{out}} \rho_i x_i, \quad i \in M_x \] (2.3.14)

\[ m_i^b = Q_w^{\text{out}} \rho_i b_i, \quad i \in M_x \] (2.3.15)

\[ M_j^c = Q_w^{\text{out}} \rho_j T_j^c \]

which becomes
\[ M_j^c = \frac{Q_{w}^{\text{out}}}{\phi s_w} \left[ \rho_j \phi_s w \left( c_j + \sum_{i=1}^{M} a_{w}^{\text{out}} x_i \right) \right], \quad j \in M_s \]  

(2.3.16)

\[ M_w = Q_{w}^{\text{out}} \rho_w \left( c_w + \sum_{i=1}^{M} a_{w}^{\text{out}} x_i \right) \]  

(2.3.17)

\[ M_i^h = Q_{w}^{\text{out}} \rho_i h_i^h, \quad i \in M_h \]  

(2.3.18)

\[ M_i^g = Q_{w}^{\text{out}} \rho_g g_i, \quad i \in M_g \]  

(2.3.19)

where,

\[ Q_{w}^{\text{in}} = \text{inflow source rate normalized over the batch system volume, (volume of liquid/time)/(batch volume), } \left( \frac{L^3}{T} \right)/L^3 \]

\[ Q_{w}^{\text{out}} = \text{outflow rate, normalized over the batch system volume, (volume of liquid/time)/(batch volume), } \left( \frac{L^3}{T} \right)/L^3 \]

2.4 Geochemical reactions
The approach adopted in formulation of chemical equilibrium, and chemical kinetic reactions is as explained by Salvage and Yeh (1998). A general chemical reaction can be represented by

\[
\sum_{j \in M} V'_{kj} \hat{e}_j \iff \sum_{j \in M} V''_{kj} \hat{e}_j, \quad k \in NRXN
\]  

(2.4.1)

The rate of reaction for equilibrium reaction is given by:

\[
\Omega_k = k^f_i \prod_{j \in M} (y_j e_j)^{v_j} - k^h_i \prod_{j \in M} (y_j e_j)^{v_j}
\]  

(2.4.2)

For equilibrium reactions forming \(i^{th}\) aqueous complexed product species, Eqn 2.4.2 becomes

\[
0 = k^f_i \prod_{j \in N_a}(y_j e_j)^{v_j} - (y_i x_i)^{v_i}
\]  

(2.4.3)

Similarly, for equilibrium reactions producing \(i^{th}\) adsorbed product species, Eqn. 2.4.2 becomes

\[
0 = k^f_i \prod_{j \in (N_a + N_A)}(y_j e_j)^{v_j} - (y_i x_i)^{v_i}
\]  

(2.4.4)

For equilibrium reactions forming \(i^{th}\) precipitated complexed product species, Eqn 2.4.2 becomes

\[
0 = k^f_i \prod_{j \in N_p}(y_j e_j)^{v_j} - (y_i p_i)^{v_i}
\]  

(2.4.5)
For kinetic reactions with its rate law prescribed by the users, the reaction rate can be described by Eqn. 2.4.2.

The total production or consumption of $i^{th}$ species due to chemical reactions is the sum of the contributions from each of the reactions in which the species participates:

$$
\frac{r^x_i}{\gamma_i} = \sum_{k=1}^{NRXNK} \frac{v'_{kj} - v_{kj}}{\gamma_i} \Omega_k
$$

$$
\frac{r^x_i}{\gamma_i} = \text{total production or consumption rate of the } i^{th} \text{ species due to chemical reactions (mass/liquid mass)/time, } \left(\frac{M}{M_i}/T\right)
$$

The kinetic reaction rates specified by the users cannot be arbitrary. They must satisfy the following constraints

$$
\sum_{i=1}^{M} a_{ij} \sum_{k=1}^{NRXNK} \frac{v'_{kj} - v_{kj}}{\gamma_i} \Omega_k = 0, \quad j \in N
$$

$$
\sum_{k=1}^{NRXNK(j)+NOMZI(j)} v_i \sum_{k=1}^{NRXNK} \frac{v'_{kj} - v_{kj}}{\gamma_i} \Omega_k = 0, \quad j \in NSITE
$$
\[ a_{ij} = \text{stoichiometry of the } j^{\text{th}} \text{ component in the } i^{\text{th}} \text{ species.} \]

2.5 Ion Exchange

The ion exchange reactions are treated in the similar manner as explained by Salvage and Yeh (1998). For each ion-exchange site it is necessary to specify one of the ion-exchanged species as a “reference species”. All the ion-exchange reactions at a site must be written in terms of exchange of this reference species.

2.6 Adsorption

The simple surface complexation model and capacitance model explained by Salvage and Yeh (1998) are included. In the simple surface complexation model, the effect of electrostatic forces is not included. The capacitance model will enable to model any adsorption reactions occurring between soil and/or solid waste matrix and the aqueous components.

In BIOKEMOD, the total analytical concentration of the \( i^{\text{th}} \) adsorbent component is calculated from the analytically measured surface site density and specific surface area using:

\[
W_j = \frac{\rho_{b} S_A N_{S_j}}{N_A} \tag{2.6.1}
\]

\[ S_A = \text{specific surface area of the solid, (area/solid mass), } \left( \frac{L^2}{M} \right) \]
\[ N_{s_j} = \text{surface site density for the } j^{\text{th}} \text{ surface site, (number of sites/area), } \left( \text{sites/} L^2 \right) \]
\[ N_d = \text{Avogadro’s number} \]

In a constant capacitance model, one additional unknown is introduced defined under:

\[ c_o = \exp \left( -\frac{e\Psi_o}{kT} \right) \] \hspace{1cm} (2.6.2)

where \( k \) is the Boltzman constant, \( T \) is the absolute temperature, \( e \) is the electric charge, \( \Psi_o \) is the electric potential at the surface. The additional unknown can be known by setting up an additional equation such that the total charge calculated by summing over the charges on the ‘o’ plane is equal to the total charge calculated by electro-static theory as under:

\[ BC\Psi_o = \sum_{i=1}^{M_o} a_i^\gamma y_i \] \hspace{1cm} (2.6.3)

where \( C \) is the capacitance of the region, \( B \) is a conversion factor from charge per unit area to moles per mass of solid, and \( a_i^\gamma \) is the stoichiometric coefficient of \( c_o \) in the \( i^{\text{th}} \) adsorbed species \( y_i \).

2.7 Precipitation and dissolution
A check is made on the solubility of the potentially precipitated species and whether conditions permit the precipitated species to exist. A check is made that a phase rule violation does not occur if a species is allowed to precipitate. The absence of the precipitated species activities from the chemical action expressions characterizes the chemical reaction of precipitation-dissolution and distinguishes it from other heterogeneous classes of chemical reactions such as adsorption and ion exchange, and from homogeneous reactions such as soluble complexation.

2.8 Activity coefficients and thermodynamic equilibrium constants

The ionic strength value should be known in order to calculate the value of the activity coefficient. The ionic strength $I$, is given by the following formula:

$$ I = \sum_{i=1}^{M_{aq}} a_i v_i^2, \quad (2.8.1) $$

where,

- $v_i =$ charge of the $i$-th aqueous species
- $a_i =$ the molality of the $i$-th aqueous species
- $M_{aq} =$ the number of aqueous chemical species which is equal to the number of aqueous component species plus the number of aqueous complexed species

The activity coefficients of aqueous species are calculated using the semi-empirical formulae
based on the Debye-Huckel theory of ion clustering. The formulae have been generalized from (Kincaid et. al., 1984):

$$\log(\gamma_i) = -A \nu_i^2 \left( \frac{\sqrt{I}}{1 + a_i B \sqrt{I}} + B'i \right) + b_i I + B_i I^2,$$  \hspace{1cm} (2.8.2)

On similar approach as the BIOKEMOD, the Davis formula will be used to determine aqueous activity coefficients, with \( A = 0.5, \ a_i B = 1, \ B' = -0.3, \ b_i = 0 \) and \( B_i = 0 \). The activity coefficients of all adsorbed species are assumed to be 1. The activity coefficients of the ion-exchanged species are assumed to be the inverse of the total molal concentration at the exchange site. Following equations are used to compute the activity coefficients for all species:

\[ \gamma_j^x \] or \( \gamma_i^x = \text{given by Eqn. (1.8.2), } j \in N_o \text{ or } i \in M_s \)

\[ \gamma_j^y \] or \( \gamma_i^y = 1.0, \ j \in N_s \text{ or } i \in M_y \)

\[ \gamma_i^z = \frac{1}{\text{NOMZI}(j)} \sum_{k=\text{NOMZI}(j)+1}^{\text{NOMZI}(j)+\text{NOMZI}(j)+1} z_k, \ i \in \text{NOMZI}(j), \ j \in \text{NSITE} \]  \hspace{1cm} (2.8.3)

\[ \gamma_i^p p_i = 1.0, \ \gamma_i^p = 1.0, \ i \in M_p \]
where,

\[ \gamma_j^c = \text{activity coefficient of the } j\text{-th aqueous component species}, \]
\[ \gamma_i^x = \text{activity coefficient of the } i\text{-th aqueous complexed species}, \]
\[ \gamma_j^r = \text{activity coefficient of the } j\text{-th adsorbent component species}, \]
\[ \gamma_i^y = \text{activity coefficient of the } i\text{-th adsorbed species}, \]
\[ \gamma_i^z = \text{activity coefficient of the } i\text{-th ion-exchange species}, \]
\[ \gamma_i^p = \text{activity coefficient of the } i\text{-th precipitated species}, \]

The thermodynamic equilibrium constants or chemical kinetic forward and backward rate constants are normally given for conditions of 25°C and 1 atm. The variation of temperature in landfill is much more than that of the pressure. As such it is proposed to apply only the temperature corrections to these equilibrium constants, the van’t Hoff equation describes the variation of equilibria coefficients with temperature change given by Eqn. (2.8.4)

\[
\ln \frac{K_2}{K_1} = \frac{\Delta H^o}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \tag{2.8.4}
\]

2.9 Microbiological reactions

Microbiological reactions are defined in BIOKEMOD using the same general approach as that for chemical reactions, but one of the species involved is a microbial species:
Typically, reactant species will include a substrate, an electron acceptor, and other necessary nutrients. Product species will include the byproducts of the biodegradation reaction and new biomass. Using the modified Monod kinetics to describe the rate of the k-th microbiological reaction,

\[
\Omega_k = \Gamma_k \frac{S_k}{K_{S-k} + S_k} \frac{A_k}{K_{A-k} + A_k} \frac{N_k}{K_{N-k} + N_k} \]

where

\( \Omega_k \) = rate of the k-th reaction per unit biomass activity, \((1/T)\)

\( \Gamma_k \) = growth rate constant for the k-th reaction per unit biomass activity T, \((1/T)\)

\( S_k \) = concentration of substrate in the k-th microbial reaction, (mass/mass of phase) \((M/M)\)

\( A_k \) = concentration of the electron acceptor in the k-th microbial reaction, (mass/mass of phase) \((M/M)\)

\( N_k \) = concentration of nutrient the k-th microbial reaction, (mass/mass of phase) \((M/M)\)

\( K_{S-k} \) = half saturation constant for the substrate in the k-th microbial reaction,
\( K_{A-k} \) = half saturation constant for the electron acceptor in the k-th microbial reaction, (mass/mass of phase) \( (M / M) \)

\( K_{N-k} \) = half saturation constant for the nutrient in the k-th microbial reaction, (mass/mass of phase) \( (M / M) \)

\( NBRXNK \) = number of kinetic microbiological reactions

In BIOKEMOD, the substrate, electron acceptor, and nutrients may be any chemical species in any phase, i.e. \( (S_k, A_k, N_k) \in (N_a + N_s + M_x + M_y + M_z + M_p) \).

Metabolic lag coefficient (Kono, 1968; Wood et. al., 1994) is used as per BIOKEMOD for an acclimation period, if any, of microorganisms to new substrates:

\[
L_k = \begin{cases} 
0 & \text{if } t \leq \tau_{L-k} \\
\frac{\tau_k - \tau_{L-k}}{\tau_{E-k} - \tau_{L-k}} & \text{if } \tau_{L-k} < t \leq \tau_{E-k} \\
1 & \text{if } t > \tau_{E-k} 
\end{cases} \quad (2.9.3)
\]

where

\( L_k \) = lag coefficient for the k-th reaction

\( \tau_k \) = time microorganisms in the k-th reaction have been exposed to the substrate, \( (T) \)

\( \tau_{L-k} \) = lag time for the k-th reaction, \( (T) \)
\( \tau_{E-k} \) = time for microorganisms in the k-th reaction to reach exponential growth, \( (T) \)

The inhibition effects such as competitive, noncompetitive, uncompetitive, and mixed inhibition are adopted as per the BIOKEMOD given in table 2.9.1.

<table>
<thead>
<tr>
<th>Competitive Inhibition</th>
<th>( \Gamma_{k(\text{apparent})} = \Gamma_{k(\text{no inhibitor})} )</th>
<th>( K_{S(\text{apparent})} &gt; K_{S(\text{no inhibitor})} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Noncompetitive Inhibition</td>
<td>( \Gamma_{k(\text{apparent})} &lt; \Gamma_{k(\text{no inhibitor})} )</td>
<td>( K_{S(\text{apparent})} = K_{S(\text{no inhibitor})} )</td>
</tr>
<tr>
<td>Uncompetitive Inhibition</td>
<td>( \Gamma_{k(\text{apparent})} &lt; \Gamma_{k(\text{no inhibitor})} )</td>
<td>( K_{S(\text{apparent})} &lt; K_{S(\text{no inhibitor})} )</td>
</tr>
<tr>
<td>Mixed Inhibition</td>
<td>( \Gamma_{k(\text{apparent})} &lt; \Gamma_{k(\text{no inhibitor})} )</td>
<td>( K_{S(\text{apparent})} &gt; K_{S(\text{no inhibitor})} )</td>
</tr>
</tbody>
</table>

Two inhibition coefficients are used to incorporate the effects of inhibition in as explained by Salvage and Yeh (1998), those are included here.

\[
I_{1k} = \left( 1 + \frac{[I]}{K_{I1}} \right)^p, \quad I_{2k} = \left( 1 + \frac{[I]}{K_{I2}} \right)^q
\]  \hspace{1cm} (2.9.4)

where,

\( I_{1k} = \) inhibition factor for the growth rate for the k-th reaction

\( I_{2k} = \) inhibition factor for the half saturation constant for the k-th reaction

\([I] = \) concentration of the inhibitory substance, \( (M/M) \)

\( K_{I1} = \) inhibition coefficient for the growth rate for the k-th reaction, \( (M/M) \)

\( K_{I2} = \) inhibition coefficient for the half saturation constant for the substrate in the k-th reaction, \( (M/M) \)

\( p = \) fitting parameter, generally 0 (no inhibition, 1 or -1 (inhibition))

\( q = \) fitting parameter, generally 0 (no inhibition, 1 or -1 (inhibition))

2.9.1 The effect of pH

Inhibition due to free acid and base pH is found to be important, particularly for microbes with low energy yield and utilize proton motive force for ATP synthesis (Henderson, 1971). Aceticlastic methanogens, hydrogenotrophic methanogens and acetogenic organisms are the most affected by free organic acids, which can be implicitly included by defining the dependency of growth rate on pH. The effect of pH on growth rate of different microbial species is modeled.
as per the Michaelis pH function given by Angelidaki et al. (1993). Equation 2.9.5 gives the normalized inhibition function plotted in Fig. 2.9.1.

\[
I_{\text{pH}} = \frac{1 + 2 \cdot 10^{0.5(pH_l - pH_h)}}{1 + 10^{1(pH_l - pH_h)} + 10^{15}(pH_l - pH_h)}
\]  

(2.9.5)

\(pH_l\) and \(pH_h\) are the lower and upper pH drop off values, where the growth rates are approximately 50% of the uninhibited rates.

![Figure 2.9.1 Normalized Michaelis pH function for \(pH_l = 6.50\) and \(pH_h = 7.50\) (adopted from Angelidaki et al., 1993.)](image)

2.9.2 The effect of temperature

The temperature correction can be applied to the microbial process rates using the Arrhenius equation. Temperature ranges from mesophilic to thermophilic conditions in a bioreactor landfill. Siegrist et al. (2002) suggested the use of mesophilic rates with corrections up to optimum thermophilic temperatures. Above the optimum temperature the growth rate decreases up to a
maximum temperature limit given by Angelidaki et al. (1993). Eqns. 2.9.6 and 2.9.7 are used in the present model. Figure 2.9.2 shows the variation of temperature inhibition factor for an optimum temperature of 55 °C and maximum 70 °C.

\[ \Gamma_{k,T} = \Gamma_{k,35} e^{\theta(t-35)} ; \text{ for } T < T_{opt} \]  

(2.9.6)

Where,
\( \Gamma_{k,T} = \) growth rate at temperature, T °C
\( \Gamma_{k,35} = \) growth rate at mesophilic temperature, 35 °C
\( T_{opt} = \) Temperature for maximum growth rate.

\[ \Gamma_{k,T} = \Gamma_{k,OPT}^{MAX} \left( \frac{T_{MAX} - T}{T_{MAX} - T_{OPT}} \right) ; \text{ for } T > T_{opt} \]  

(2.9.7)

where,
\( \Gamma_{k,OPT}^{MAX} = \Gamma_{k,35} e^{\theta(T_{opt}-35)} \)

\( T_{MAX} = \) temperature where growth ceases

Figure 2.9.2 Variation of temperature inhibition factor
2.9.3 The effect of Moisture Content

Moisture content has a profound effect on the biodegradation rates, and therefore the concept of leachate re-circulation to increase the moisture content in landfill has evolved. There is less experimental data available correlating biodegradation rates with moisture contents. Wreford et al. (2000) collected data for full-scale landfill and studied the effect of moisture addition from infiltration on methane production. They suggested a straight line relationship between moisture added and methane production rate. The data as presented in this study are normalized and shown in Fig. 1.9.3. In the normalization procedure, the landfill was initially assumed to be at field capacity. Young (1992) showed a logistic relationship with less effect at high moisture contents. The low biodegradation rates for low moisture contents could be justified, but the effect at high moisture contents is contrary to the observation made by Fujishima et al. (2000) on anaerobic digestion of dewatered sludge. Although the study was conducted at high moisture contents in the range of 89 to 97 %, even this reduction showed two folds reduction in the methane production.
Figure 2.9.3 Effect of degree of saturation on normalized methane production rate

In the present modeling work, a straight line relationship is proposed between degree of saturation and microbial reaction rates. As saturations lower than 20% are rarely expected in a bioreactor landfill with leachate recirculation, the straight line relation at lower moisture contents will not be applicable. The effect of moisture content can be incorporated by multiplying the growth rate constant, $\Gamma_{k,T}$ with the aqueous phase saturation, $s_w$.

Incorporating all the dependencies for growth of microorganisms, Eqn 2.9.2 becomes

$$
\Omega_k = \left( \Gamma_{k,T} I_{1k} I_{pH} s_w \right) \left( \frac{S_k}{(K_{S-k} I_{2k}) + S_k} \right) \left( \frac{A_k}{K_{A-k} + A_k} \right) \left( \frac{N_k}{K_{N-k} + N_k} \right) L_k \tag{2.9.8}
$$

The production/consumption rate of the j-th chemical species due to the k-th microbial biodegradation reaction is:

$$
r_j^{k \text{bio\-deg}} = \frac{v_j^e - v_j^r}{\gamma_j} \Omega_k \left( \gamma_{Bk} B_k \right), \quad j \in M \tag{2.9.9}
$$
where,

\[ r_{j|k}^{\text{bio-deg}} = \text{the contribution of the } k\text{-the microbial biodegradation reaction to the rate of} \]

production or consumption of the \( j \)-th chemical species, \( \text{(mass/mass of phase)/time,} \)

\( ((M / M) / T) \)

\[ B_k = \text{concentration of the } k\text{-th microbial species, either aqueous } (b_k) \text{ or adsorbed } (a_k), \]

\( \text{(mass/mass of phase), } (M / M) \)

\[ \gamma_{Bk} = \text{activity coefficient for the microbial species, } (B_k), (M / M) \]

The activity coefficients for microbial species are assumed to be unity. The total production / consumption rate of the \( j \)-th chemical species due to microbiological degradation reactions is the sum of the contributions from all the reactions in which the \( j \)-th species participate:

\[
\left. r_j^{\text{bio-deg}} \right|_i = \sum_{k=1}^{\text{NBRXNK}} r_{j|k}^{\text{bio-deg}} = \sum_{k=1}^{\text{NBRXNK}} \left( \frac{v_{ki}^j - v_{kji}^j}{\gamma_i^j} \right) \Omega_k (\gamma_{Bk} B_k), \quad j \in M \]

(2.9.10)

The production rate of biomass due to the \( k \)-th microbial reaction is given by:

\[
\left. r_{i|k}^{BG} \right| = \left( \frac{v_{ki}^j - v_{kji}^j}{\gamma_i} \right) \Omega_k (\gamma_{Bk} B_k), \quad i \in M_B \]

(2.9.11)

\[ r_{i|k}^{BG} = \text{growth rate of the } i\text{-th microbial species, either aqueous } (b_k) \text{ or adsorbed } (a_k), \text{ due to the} \]

\( k \)-th microbial reaction, \( \text{(mass/mass of phase)/time,} \)

\( ((M / M) / T) \)

The total growth of each microbial species is the sum of the contributions from each biodegradation reaction in which the microbial species participates:

\[
\left. r_{i}^{BG} \right|_k = \sum_{k=1}^{\text{NBRXNK}} \left( \frac{v_{ki}^j - v_{kji}^j}{\gamma_i} \right) \Omega_k (\gamma_{Bk} B_k), \quad i \in M_B \]

(2.9.12)

where,

\[
r_{i}^{BG} = \text{total growth rate of the } i\text{-th microbial species, either aqueous or adsorbed,} \text{(mass/mass of} \]

phase)/time, \( ((M / M) / T) \)

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The commonly used Monod kinetic parameters are incorporated in the above equations using the following relationships:

\[
\mu_{\text{max}_i} = \left( v_{ki} - v'_{ki} \right) \Gamma_k, \quad i \in M_B \tag{2.9.13}
\]

\[
Y_{j-k} = \left( \frac{v_{ki} - v'_{ki}}{v_{kj} - v'_{kj}} \right), \quad i \in M_B, \quad j \in M \tag{2.9.14}
\]

where

\[
\mu_{\text{max}_i} = \text{maximum specific growth rate for the k-th microbial reaction, (1/T)}
\]

\[
Y_{j-k} = \text{growth yield coefficient for the j-th species in the k-th microbial reaction, mass of microorganisms produced/mass of the j-th chemical species utilized, (M/M)}
\]

The value of \( \Gamma_k \) is calculated from the user input value of \( \mu_{\text{max}_i} \). Also the above formulation allows for a growth yield coefficient for each chemical species participating in the reaction.

The rate of microbial decay will be proportional to the concentration of biomass present:

\[
r_i^{bd} = K_i^d B_i, \quad i \in M_B \tag{2.9.15}
\]

where

\[
r_i^{bd} = \text{death/decay rate of the i-th microbial species, either aqueous or adsorbed, (mass/mass of phase)/time, ((M/M)/T)}
\]

\[
K_i^d = \text{rate constant for death/decay of the i-th microbial species (1/T)}
\]

Cellular decay processes and endogenous respiration processes utilizes chemical species, most commonly oxygen as an electron acceptor. Endogenous respiration’s effect on electron acceptor concentration has been observed to follow Monod type kinetics (Kappeler and Gujer, 1992). Unlike consumption of electron acceptor species, the cellular decay process may cause production of some other species. The program offers the flexibility of specifying any chemical species consumption/production through this process:
\[ r_j^{\text{bioresp}} = \sum_{i=1}^{M} \alpha_{ij} K_{ij}^d B_i \left( \frac{g_i}{\kappa_{ij} + g_j} \right), \quad j \in M \]  

(2.9.16)

where

- \( r_j^{\text{bioresp}} \) is the rate of consumption of the j-th chemical species due to cellular maintenance /decay processes.
- \( \alpha_{ij} \) is the stoichiometric coefficient for the j-th chemical species due to maintenance /decay of the i-th microbial species.
- \( \kappa_{ij} \) is the half saturation constant for the j-th chemical species in the maintenance /decay processes of the i-th microbial species.

Incorporating the consumption of chemical species due to microbiological decay, the total rate of production /consumption due to microbiological reactions combines Eqn. 1.1.8 and Eqn 1.8.16 and becomes:

\[ r_j^{\text{bio}} = r_j^{\text{bio-deg}} - r_j^{\text{bioresp}}, \quad j \in M \]  

(2.9.17)

### 2.10 Adsorption of Microbial Species

As proposed by Salvage and Yeh (1998), microorganisms may be either aqueous phase or adsorbed phase species, and may be transferred from one phase to the other. The transfer of microbial species between phases is modeled by a simple kinetic transfer reaction:

\[ v_{ki} b_i \leftrightarrow v_{ki}^* a_j, \quad i \in M_b, \quad j \in M_a \]  

(2.10.1)

The reaction rate is described using forward and backward rate constants, as for kinetic chemical reactions, but microbial species activities are used instead of chemical species activities:

\[ \Omega_k = k_k^f \left( v_{ki} b_i \right)^{v_{ki}^*} - k_k^b \left( v_{ki}^* a_j \right)^{v_{ki}}, \quad i \in M_b, \quad j \in M_a \]  

(2.10.2)
where
\[ \Omega_k = \text{reaction rate of the } k\text{-th reaction, } (1/T) \]
\[ k^f_k = \text{forward rate constant for the } k\text{-th reaction, } (1/T) \]
\[ k^b_k = \text{backward rate constant for the } k\text{-th reaction, } (1/T) \]

Therefore the rate of change of the \( i\)-th microbiological species between phases is given by:
\[
\frac{d\gamma_i^r}{dt} = \frac{(v_{ki} - v_{ki}^*)}{\gamma_i} \Omega_k, \quad i \in M_B \tag{2.10.3}
\]

2.11 Phase change reactions

The phase change reactions between solid, aqueous, and gaseous phases could be modeled as a chemical kinetic or an equilibrium or a microbiologically mediated reactions. This does not need special treatment except knowing the reaction constants or rates put together with appropriate mass balance units (dimensions).

2.11.1 Aqueous and gas phase reaction

Any chemical phase change reaction between aqueous and gaseous phase can be written as per Eqn. 2.11.1.
\[
v'_{ki} x_i \leftrightarrow v^*_{kj} P_j, \quad i \in N_a, M_x, \quad j \in M_g \tag{2.11.1}
\]

For equilibrium conditions, the partial pressure of \( j\)-th gaseous component can be related to the concentration of corresponding \( i\)-th aqueous species by Henry’s law given in Eqn. 2.11.2.
\[
x_i = K_{H(i,j)} P_j, \quad i \in N_a, M_x, \quad j \in M_g \tag{2.11.2}
\]

The model formulation provides the flexibility to either keep the gas pressure at a constant value or change after every time step. The transfer of gas from the liquid to gas phase can be treated as
a temperature dependent kinetic chemical reaction, where phase change can be accommodated.

Often the Stationary liquid-film theory is applied for transfer of gas from the liquid to gas phase (Metcalf & Eddy, 1991). Applying the kinetic mass transfer rate is the obvious choice for such conditions. Mass rate of transfer from liquid to gas can be given by the Eqn. 2.11.3 A simplified assumption is made for kinetic gas phase reactions that there exists only one aqueous species for corresponding gas phase component.

\[
\left. r_j \right|^{\text{gas}} = - \left. r_i \right|^{\text{gas}} = k_L a (x_i - K_{H(i,j)} P_j) \quad \text{(2.11.3)}
\]

where,

\( k_L a \) = overall gas transfer coefficient.

\( K_{H(i,j)} \) = Henry constant for gas, j

Seigrist et. al. (2002) provided numerical calculations for \( k_L a \) as a function of temperature.

Water vapour pressure

Liquid water is assumed to be in equilibrium with water vapor in gas phase. Water vapor in gas phase is a function of saturated vapor pressure and the capillary pressure. The saturated vapor pressure is a function of temperature. The equation proposed by White and Oostrom (1996) (STOMP) will be used. Eqn. 2.11.4 gives the saturated vapor pressure as a function of temperature.

\[
P_{\text{sat}} = P_w^c \exp \left( \frac{T_w}{T} \left( \frac{\sum_{j=1}^{s} k_j X^j}{1 + k_s X + k_\gamma X^2} \right) - \left( \frac{X}{k_s X^2 + k_\gamma} \right) \right) \quad \text{(2.11.4)}
\]
2.11.2 Phase change from solids to liquid

Hydrolysis involves the phase change of biodegradable solids (solid components) to soluble fractions (aqueous species). Hydrolysis follows disintegration and is a non-biological step of breaking complex solid organics into simpler forms without the change of phase. Literature shows first order models for disintegration process, whereas hydrolysis being modeled in different ways. Vavilin et. al. (1996) showed that the Contois kinetics is applicable in systems with low biomass to substrate ratios and therefore biomass becomes rate limiting. Since biomass concentrations are low in bioreactor landfills, this model becomes a natural choice. The rate of change of i-th species as per applying the Contoi’s model is given by Eqn. 2.11.6.

\[
\frac{d}{dt} \rho_i^{solid} = \sum_{k=1}^{NBHRXNK} \frac{(v''_{ki} - v'_{ki})}{\gamma_i} \Omega_k
\]

\[
\Omega_k = \left( k_{a,t} T_{pH} s_w \left( \frac{h_k / B_k}{K_{S,a,k} + h_k / B_k} \right) L_i \left( \gamma_{h_k B_k} \right), \quad h \in M_{a,b}, M_{a,c} \right)
\]

\[
NBHRXNK = \text{number of microbiologically mediated hydrolysis reactions}
\]

2.11.3 Solids disintegration
A physical or non-enzymatic breakdown of the solids may precede the hydrolysis process of conversion of solids components into aqueous species. The rate of this reaction involving solids can be defined by the user.

\[
\sum_{j=1}^{M_h} v'_j \dot{h}_j \iff \sum_{j=1}^{M_h} v'_j \dot{h}_j, \quad k \in \text{NSDRXNK}
\]  

(2.11.8)

2.12 Heat generation reactions

A majority of heat generation reactions in the environmental systems and bioreactor landfills are microorganisms mediated, only a few are chemical kinetic reactions. Spontaneous combustion is extremely fast reaction and not included here. The free energy of reaction gives is an indication of the amount of heat generated/consumed in a reaction. In the natural systems involving reactions mediated by microorganisms, therefore the use of theoretical value of free energy of reaction may not be ideal method for computation of temperature change. The rate of heat generation could be related to the formation of products by microorganisms (El-Fadel et. al 1996(a)).

\[
\dot{q} = \sum_{k=1}^{N\text{REXNK}} \omega_k r_{i_k} = \sum_{i=1}^{N\text{REXNK}} \omega_k \frac{v'_{i_k} - v'_{i_l}}{\gamma_i} \Omega_k \left( \gamma_{\text{mL}} B_i \right), \quad i \in M_B
\]  

(2.12.1)

where,

\[\omega_k = \text{coefficient for production/consumption of heat, for the k-th reaction cal/mole,} \]
\[\left(\frac{ML^2}{T^2}\right) / \text{mole}\]

2.12 Summary of Governing Equation

The governing equations are mole balance and equivalents balance equations, mass action
equations for the equilibrium chemical species and reaction rate expressions for the kinetic chemical, microbial species, solids species and gas phase species. Each chemical component species is represented by a mole balance equation. Each ion-exchange site is represented by an equivalents balance equation. Each chemical product species is represented by one equation: either mass action equation for an equilibrium species or the sum of the rate expressions for all the kinetic reactions in which the species participates. The summary of equations is given as under:

The mass balance equation for total analytical concentrations of the aqueous chemical components (from Eqns. 2.1.19, 2.3.7, and 2.3.16)

\[
\frac{\partial T_{c}^j}{\partial t} = -N_j T_{c}^j - (T_{c}^j) \frac{\partial P}{\partial t} + Q^{inp} T_{c}^{inp} - \frac{Q^{out}}{\phi S_w} [T_{c}^j - (S_j + P_j)]
\]

\[
+ \rho_{s} \phi_{s} \left( r_{j}^{\text{bio}} + \sum_{i=1}^{M_{p}} a_{ij}^{p} r_{i}^{\text{bio}} + r_{j}^{\text{solid}} + \sum_{i=1}^{M_{p}} a_{ij}^{p} r_{i}^{\text{solid}} + \sum_{i=1}^{M_{p}} a_{ij}^{p} r_{i}^{\text{bio}} \right)
\]

(2.13.1)

\[
+ \rho_{b} \left( \sum_{i=1}^{M_{p}} a_{ij}^{p} r_{i}^{\text{bio}} + \sum_{i=1}^{M_{p}} a_{ij}^{p} r_{i}^{\text{bio}} + \sum_{i=1}^{M_{p}} a_{ij}^{p} r_{i}^{\text{bio}} \right), \quad j \in N_a
\]

The mass balance equation for total analytical concentrations of the adsorbent chemical components (from Eqn. 2.1.24)
\[
\frac{\partial W^c_j}{\partial t} = -N^c_j W^c_j - \left(W^c_j \right) x \frac{\partial p}{\partial t} + Q^{imp} W^{imp}_j + \rho_b \left( r^b_j \left| r^bio_j \right| \sum_{i=1}^{M_x} a^z_{ij} r^z_{ij} \right), \quad j \in N_s
\]

(2.13.2)

The equivalents balance equations for NSITE ion-exchange sites (from Eqn. 2.1.29)
\[
\frac{\partial N_{eq,j}}{\partial t} = -N^eq_{eq,j} N_{eq,j} - \left(N^eq_{eq,j} \right) x \frac{\partial p}{\partial t} + Q^{imp} N^{imp}_{eq,j}
\]
\[
+ \rho_b \left( \sum_{i=NOMZI(j) + 1}^{NOMZI(j) + NOMZJ} v^i_j r^bio_j \right), \quad j \in NSITE
\]

(2.13.3)

For the aqueous component species concentrations (from 2.1.20)
\[
T^c_j = \rho \phi s_w \left( c_j + \sum_{i=1}^{M_x} a^{x}_{ij} x_i \right) + \rho_b \left( \sum_{i=1}^{M_x} a^{x}_{ij} y_i + \sum_{i=1}^{M_x} a^{z}_{ij} z_i + \sum_{i=1}^{M_x} a^{p}_{ij} p_i \right), \quad j \in N_a
\]

(2.13.4)

For the adsorbent component species concentrations (from Eqn. 2.1.25)
\[
W^c_j = \rho_b s_j + \sum_{i=1}^{M_x} a^c_{ij} y_i, \quad j \in N_s
\]

(2.13.5)

For the NSITE "reference" ion-exchange species (from Eqn. 2.1.30)
\[
N^eq_{eq,j} = \rho_b \sum_{i=NOMZI(j) + 1}^{NOMZI(j) + NOMZJ} v^i_j z_i, \quad j \in NSITE
\]

(2.13.6)

For equilibrium complexed species (from Eqn. 2.4.3)
\[
x_i = \left[ \frac{K^{eq}_k \prod_{j \in N_x} (y^i_j)^{e_{ij}}}{(y^i)^{e_{ij}} \prod_{j \in N_x} (y^i_j)^{e_{ij}}} \right]^{\frac{1}{\pi_k}}, \quad i \in (M_x - K_x), \quad k \in NRXNE
\]

(2.13.7)
where, \(K_x\) = number of kinetically controlled aqueous complexed species.

The expression for kinetic aqueous complexed species can be derived on the similar lines as that of aqueous components and Eqns. 2.3.1 and 2.3.14.

\[
\frac{\partial x_i}{\partial t} = r_i^a - \lambda_i x_i - \alpha \frac{\partial p}{\partial t} x_i + \frac{1}{\rho_i \phi_s w} \left( Q_{\text{imp}} x_i^{\text{imp}} - Q_{\text{out}}^{\text{aur}} \rho_i x_i \right) - \frac{1}{\rho_i \phi_s w} \frac{\partial \rho_i \phi_s w}{\partial t} x_i, \quad i \in K_x
\]

(2.13.8)

where the contribution from chemical, microbiological and phase change reactions is given by

\[
r_i^{\text{nen}} = \sum_{k=1}^{\text{NRANK}} \left( r_i^{\text{chem}}_{k} + r_i^{\text{gas}}_{k} \right) + \sum_{k=1}^{\text{NRANK}} r_i^{\text{solid}}_{k} + \sum_{k=1}^{\text{NRANK}} r_i^{\text{bio-deg}}_{k} - r_i^{\text{bio-exp}}
\]

(2.13.9)

\[
r_i^{\text{nen}} = \sum_{k=1}^{\text{NRANK}} \frac{V_{ki}^{\text{nen}} - V_{ki}^{\text{chem}}}{\gamma_i} \left( k_i^{\text{chem}} \prod_{j=M}^{\text{chem}} (y_j e_j)^{\text{chem}} - k_i^{\text{bio-deg}} \prod_{j=M}^{\text{bio-deg}} (y_j e_j)^{\text{bio-deg}} \right)
\]

+ \sum_{k=1}^{\text{NRANK}} \frac{V_{ki}^{\text{nen}} - V_{ki}^{\text{chem}}}{\gamma_i} \left( \Gamma_{k,T} I_{pH} s_w \left( \frac{h_k / B_k}{K_{S-k} + h_k / B_k} \right) L_k (y_{Bk} B_k) \right)

+ \sum_{k=1}^{\text{NRANK}} \frac{V_{ki}^{\text{nen}} - V_{ki}^{\text{chem}}}{\gamma_i} \left( \Gamma_{k,T} I_{1k} I_{pH} s_w \left( \frac{S_k}{(K_{S-k} I_{2k}) + S_k} \right) \left( A_k \right) \left( \frac{N_k}{K_{N-k} + N_k} \right) L_k (y_{Bk} B_k) \right)

- \sum_{j=1}^{M} \alpha_{j} x_j \left[ \frac{x_j}{K_{ji} + x_i} \right], \quad i \in K_x
\]

(2.13.10)

The adsorbed equilibrium species can be described as (from Eqn. 2.4.4)
for kinetic adsorbed species (from mole balance and Eqn. 2.3.2)

$$\frac{\partial y_i}{\partial t} = r_i^y - \lambda_i^y y_i - \alpha \frac{\partial p}{\partial t} y_i + \frac{1}{\rho_b} \left( Q_{\text{imp}} y_i^{\text{imp}} \right) - \frac{1}{\rho_b} \frac{\partial p_b}{\partial t} y_i, \quad i \in K_y \tag{2.13.12}$$

The contribution from chemical and microbiological reactions is given by (from Eqns. 2.1.4, 2.4.6, 2.9.8, 2.9.10, 2.9.16, and 2.9.17)

$$r_i^y = \frac{N_{\text{RXN}}}{k=1} r_i^y \left|_{\text{chem}}^{\text{sum}} \right. + \frac{N_{\text{RXN}}}{k=1} r_i^y \left|_{\text{solid}}^{\text{sum}} \right. + \frac{N_{\text{RXN}}}{k=1} r_i^y \left|_{\text{bio-deg}}^{\text{sum}} \right. - r_i^{\text{biorep}}$$

$$= \sum_{k=1}^{N_{\text{RXN}}} \frac{V_{ki}^y - V_{ki}^{'y}}{y_i} \left( k_l \prod_{j \in M} \left( \gamma_j e_j \right)^{\gamma_j} - k_p \prod_{j \in M} \left( \gamma_j e_j \right)^{\gamma_j} \right)$$

$$+ \sum_{k=1}^{N_{\text{RXN}}} \frac{V_{ki}^y - V_{ki}^{'y}}{y_i} \left( \Gamma_{k,T} I_{\text{pH}} S_k \left( \frac{h_k/B_k}{K_{S-k} + h_k/B_k} \right) L_k \left( \gamma_k B_k \right) \right)$$

$$+ \sum_{k=1}^{N_{\text{RXN}}} \frac{V_{ki}^y - V_{ki}^{'y}}{y_i} \left( \Gamma_{k,T} I_{\text{pH}} S_k \left( \frac{S_k}{K_{S-k} + S_k} \right) \left( \frac{A_k}{K_{A,k} + A_k} \right) \left( \frac{N_k}{K_{N-k} + N_k} \right) L_k \left( \gamma_k B_k \right) \right)$$

$$- \sum_{j=1}^{M_k} \alpha_{ji} K_{j} B_{ji} \left[ \frac{y_i}{\gamma_j + y_i} \right], \quad i \in K_y \tag{2.13.13}$$

For equilibrium ion-exchanged species

$$0 = k_k^e \prod_{j \in (N_e + N_e + N_e)} \left( \gamma_j e_j \right)^{\gamma_j} - \prod_{j \in (N_e + N_e + N_e)} \left( \gamma_j e_j \right)^{\gamma_j}, \quad k \in \text{NRXNE} \tag{2.13.14}$$
where one of the species produced in the k-th reaction is an equilibrium controlled ion-exchanged species.

For kinetic ion-exchanged species (from mole balance for species and Eqn. 2.3.3)

\[
\frac{\partial z_i}{\partial t} = r_i^i - \lambda_i z_i - \alpha \frac{\partial p}{\partial t} z_i + \frac{1}{\rho_b} \left( Q_{i_{\text{ion}}} \right) - \frac{1}{\rho_b} \frac{\partial \rho_b}{\partial t} z_i, \quad i \in K_z
\]  

(2.13.15)

where $K_z$ = number of kinetically controlled ion-exchanged species, and

the contribution from chemical and microbiological reactions is given by (from Eqns. 2.1.5, 2.4.2, 2.4.6, 2.9.8, 2.9.10, 2.9.16, and 2.9.17.

\[
r_i^i = \sum_{k=1}^{NRXNK} r_i^{\text{ph}}_{k_i} + \sum_{k=1}^{NBHRXNK} r_i^{\text{solid}}_{k_i} + \sum_{k=1}^{NRXNK} r_i^{\text{bio-deg}}_{k_i} - r_i^{\text{bio-esp}}
\]

\[
= \sum_{k=1}^{NRXNK} \frac{V_{i_k}^* - V_{i_k}'}{\gamma_i} \left( k_i \prod_{j \in M} (y_{j,e})^{y_{i,j}} - k_i \prod_{j \in M} (y_{j,e})^{y_{i,j}} \right)
\]

\[
+ \sum_{k=1}^{NBHRXNK} \frac{V_{i_k}^* - V_{i_k}'}{\gamma_i} \left( \Gamma_{k,T} I_{pH} S_w \left( \frac{h_k / B_k}{K_{S-k} + h_k / B_k} \right) L_k (y_{b_k} B_k) \right)
\]

\[
+ \sum_{k=1}^{NRXNK} \frac{V_{i_k}^* - V_{i_k}'}{\gamma_i} \left( \Gamma_{k,T} I_{pH} S_w \left( \frac{S_k}{K_{S-k} I_{pH} S_k} + \frac{A_k}{K_{A-k} + A_k} \right) \frac{N_k}{K_{N-k} + N_k} \right) L_k (y_{b_k} B_k)
\]

\[
- \sum_{j=1}^{M_a} \alpha_j K_j^d B_j \left[ \frac{z_j}{\kappa_j + z_j} \right], \quad i \in K_z
\]  

(2.13.16)

For equilibrium precipitated species (from Eqn. 2.4.5)

\[
1 = K_k^{eq} \prod_{j \in N_{x_k}} (y_{j,e})^{y_{i,j}}, \quad i \in (M_p - K_p), \quad k \in NRXNE
\]  

(2.13.17)
where \( K_p \) = number of kinetically controlled precipitated species.

For kinetic precipitated species (from mole balance and Eqn. 2.3.4)

\[
\frac{\partial p_i}{\partial t} = r_i^p = r_i^p - \lambda_i^p p_i - \alpha \frac{\partial p}{\partial t} p_i + \frac{1}{\rho_b} \frac{\partial}{\partial t} p_i + \frac{1}{\rho_b} \frac{\partial}{\partial t} p_i, \quad i \in K_p
\] (2.13.18)

where the contribution from chemical and microbiological reactions is given by (from Eqns. 2.1.6, 2.4.2, 2.4.6, 2.9.8, 2.9.10, 2.9.16, and 2.9.17).

\[
r_i^p = \sum_{k=1}^{NRXNK} r_i^p \bigg|_{\text{chem}} + \sum_{k=1}^{NRXNK} r_i^p \bigg|_{\text{deg}} - r_i^\text{bioresp}
\]

\[
= \sum_{k=1}^{NRXNK} \frac{v_i^* - v_i'}{\gamma_i} \left( k_i' \prod_{j=M} \left( \gamma_{j,i} \right) \right) - 1
\]

\[
+ \sum_{k=1}^{NRXNK} \frac{v_i^* - v_i'}{\gamma_i} \left( \Gamma_{k,i} I_{R_{k} I_{M}} \right) \left( \frac{S_k}{K_{S_k} I_{2k}} + S_k \right) \left( \frac{A_k}{K_{A_k} + A_k} \right) \left( \frac{N_k}{K_{N_k} + N_k} \right) L_k \left( \gamma_{M_{k}} B_k \right)
\]

\[
- \sum_{j=1}^{M} \alpha_j K_{j} B \left( \frac{p_i}{K_{j,i} + p_j} \right), \quad i \in K_p
\] (2.13.19)

For the aqueous phase microbiological species (from mole balance and Eqns. 2.3.5 and 2.3.15)

\[
\frac{\partial b_i}{\partial t} = r_i^{bg} - r_i^{bd} - \alpha \frac{\partial p}{\partial t} b_i + r_i^{str} - \frac{1}{\rho_b} \frac{\partial}{\partial t} b_i + \frac{1}{\rho_b} \frac{\partial}{\partial t} b_i + \frac{1}{\rho_b} \left( Q_i^{\text{imp}} - Q_i^{\text{out}} \right)
\] (2.13.20)

where the microbial growth rate is given by (from Eqns. 2.9.8, 2.9.12 and 2.11.7)

\[
r_i^{bg} = \sum_{k=1}^{NRXNK} \frac{v_i^* - v_i'}{\gamma_i} \left( \Gamma_{k,i} I_{R_{k} I_{M}} \right) \left( \frac{h_k / B_k}{K_{S_k} I_{2k} + h_k / B_k} \right) L_k \left( \gamma_{M_{k}} B_k \right)
\]

\[
+ \sum_{k=1}^{NRXNK} \frac{v_i^* - v_i'}{\gamma_i} \left( \Gamma_{k,i} I_{R_{k} I_{M}} \right) \left( \frac{S_k}{K_{S_k} I_{2k} + S_k} \right) \left( \frac{A_k}{K_{A_k} + A_k} \right) \left( \frac{N_k}{K_{N_k} + N_k} \right) L_k \left( \gamma_{M_{k}} B_k \right)
\]
and the microbiological death/decay rate is (from Eqn. 2.9.15)

\[ r_{i}^{bd} = K_{i}^{d} b_{i}, \quad i \in M_{b} \] (2.13.22)

The transfer rate between the aqueous and adsorbed phases is given by (from Eqns. 2.10.2 and 2.10.3)

\[ r_{ij}^{sf} = \frac{(v_{ki}^{*} - v_{ki}^{f})}{\gamma_{i}} k_{k}^{f} (\gamma_{j} b_{j})^{\nu_{ji}} - k_{k}^{b} (\gamma_{j} a_{j})^{\nu_{ji}}, \quad i \in M_{b}, \quad j \in M_{a} \] (2.13.23)

For the adsorbed phase microbiological species (from mole balance and Eqn. 2.3.6)

\[ \frac{\partial a_{i}}{\partial t} = r_{i}^{ag} - r_{i}^{ad} - \alpha \frac{\partial p}{\partial t} a_{i} + \frac{1}{\rho_{b}} (g^{ap} a_{i}^{ap}) + r_{i}^{sf} - \frac{1}{\rho_{b}} \frac{\partial}{\partial t} a_{i}, \quad i \in M_{a} \] (2.13.24)

where the microbial growth rate is (from Eqns. 2.9.8, 2.9.12 and 2.11.7)

\[ r_{i}^{ag} = \sum_{k=1}^{NBRK} \frac{v_{ki}^{*} - v_{ki}^{f}}{\gamma_{i}} \left( r_{k}^{I} I_{pf} s_{w} \left( \frac{h_{k}/B_{k}}{K_{s-k} + h_{k}/B_{k}} \right) \right) L_{k} (\gamma_{e_{k}} B_{k}) + \sum_{k=1}^{NBRK} \frac{v_{ki}^{*} - v_{ki}^{f}}{\gamma_{i}} \left( r_{k}^{I} I_{pf} s_{w} \left( \frac{S_{k}}{(K_{s-k} I_{pf}) + S_{k}} \right) \right) \left( \frac{A_{k}}{K_{a-k} + A_{k}} \right) \left( \frac{N_{k}}{K_{N-k} + N_{k}} \right) L_{k} (\gamma_{e_{k}} B_{k}) \] (2.13.25)

and the microbial death/decay rate is (from Eqn. 2.9.15)

\[ r_{i}^{ad} = K_{i}^{d} a_{i}, \quad i \in M_{a} \] (2.13.26)

and the transfer rate between the aqueous and adsorbed phases is (from Eqns. 2.10.2 and 2.10.3)

\[ r_{ij}^{sf} = \frac{(v_{ki}^{*} - v_{ki}^{f})}{\gamma_{i}} k_{k}^{f} (\gamma_{j} b_{j})^{\nu_{ji}} - k_{k}^{b} (\gamma_{j} a_{j})^{\nu_{ji}}, \quad i \in M_{a}, \quad j \in M_{b} \] (2.13.27)

As described by Salvage and Yeh (1998), a secondary mass balance equations defining total aqueous concentration of each chemical component \( (C_{j}) \), the total sorbed concentration of each
chemical component \( (S_j) \), and the total precipitated concentration of each chemical component \( (P_j) \) are given below:

\[
C_j = \rho_i \phi_{sw} \left( c_j + \sum_{i=1}^{M_i} a_{ij} x_i \right), \quad j \in N_a
\]  
(2.13.28)

\[
S_j = \rho_b \left( \sum_{i=1}^{M_i} a_{ij}^x y_i + \sum_{i=1}^{M_i} a_{ij}^z z_i \right), \quad j \in N_a
\]  
(2.13.29)

\[
P_j = \rho_b \sum_{i=1}^{M_i} a_{ij}^p p_i, \quad j \in N_a
\]  
(2.13.30)

Mass balance equation for water (aqueous) phase saturation (from Eqns. 2.1.42, 2.3.10, and 2.3.17)

\[
A \frac{\partial \rho_i \phi_{sw}}{\partial t} = -\Lambda_w T_w - \alpha \frac{\partial p}{\partial t} T_w - B - \left( \rho_i \phi_{sw} \right) \frac{\partial A}{\partial t}
\]

\[
+ \rho_i \phi_{sw} \left( r_w^{\text{bio}} + \sum_{i=1}^{M_i} a_{iw}^{x} r_i^{\text{bio}} + r_w^{\text{solid}} + \sum_{i=1}^{M_i} a_{iw}^{x} r_i^{\text{solid}_p} + r_w^{\text{gas}} + \sum_{i=1}^{M_i} a_{iw}^{x} r_i^{\text{gas}} \right)
\]

\[
+ \rho_b \left( \sum_{i=1}^{M_i} a_{iw}^{x} r_i^{\text{bio}} + \sum_{i=1}^{M_i} a_{iw}^{x} r_i^{\text{bio}} + \sum_{i=1}^{M_i} a_{iw}^{x} r_i^{\text{bio}} \right)
\]  
(2.13.31)

\[
+ Q^{\text{in}} \left( c_w^{\text{in}} + \sum_{i=1}^{M_i} a_{iw}^{x} x_i^{\text{in}} + \sum_{i=1}^{N_i} a_{iw}^{x} s_i^{\text{in}} + \sum_{i=1}^{M_i} a_{iw}^{x} y_i^{\text{in}} + \sum_{i=1}^{M_i} a_{iw}^{z} z_i^{\text{in}} + \sum_{i=1}^{M_i} a_{iw}^{z} p_i^{\text{in}} \right)
\]

\[
- Q^{\text{out}} \rho_i \left( c_w + \sum_{i=1}^{M_i} a_{iw}^{x} x_i \right)
\]

For solid phase species the mass balance equation for total concentrations of solids components
(From Eqns. 2.1.35, 2.3.11, and 2.3.18 also from 2.1.37 and 2.3.12)

\[
\frac{\partial h^b_i}{\partial t} = -\lambda^b_i h^b_i - (h^b_i)\alpha \frac{\partial p}{\partial t} + r_i^\text{chem} + r_i^\text{solid} \frac{1}{\rho_i \phi s_w} \frac{\partial \rho_i \phi s_w}{\partial t} h^b_i
\]

\[
+ \frac{1}{\rho_i \phi s_w} Q^\text{in}^p (h^b_i)^p - \frac{1}{\phi s_w} Q^\text{out}^p h^b_i, \quad i \in M^b
\]

\[
\frac{\partial h^s_i}{\partial t} = -\lambda^s_i h^s_i - (h^s_i)\alpha \frac{\partial p}{\partial t} + r_i^\text{chem} + r_i^\text{solid} \frac{1}{\rho_b} \frac{\partial \rho_b}{\partial t} h^s_i + \frac{1}{\rho_b} Q^\text{in}^p (h^s_i)^p,
\]

\[i \in M^s\]

The phase change from solid to liquid and physical solid disintegration reactions are kinetic processes. It can be noticed that the solids are represented by independent species only. There are no components as in case of the aqueous phase. As such the kinetic chemical reactions causing disintegration of solids without phase change are part of the Eqns. 1.12.32 and 1.12.33 unlike for aqueous components. The disintegrated fractions would be represented by another solid phase species. Biologically mediated hydrolysis reactions deplete solids species and microbes decay produces may some other species. Bacteria mediated hydrolysis reactions follow the Contois kinetics represented by Eqn. 2.11.6.

The reactions for solids components can be written as under:

\[
r_i^h = \sum_{k=1}^{N M H E N K} r_i^k \big|^{\text{solid} \ p} + \sum_{k=1}^{N M H E N K} r_i^h \big|^{\text{solid} \ p} +
\]

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\[\sum_{k=1}^{N_{\text{species}}} \frac{v_{ki} - v_{ki}'}{\gamma_i} \left( k'_i \prod_{j=M} (y_j e_j)^{e_j} - k''_i \prod_{j=M} (y_j e_j)^{e_j} \right) + \sum_{k=1}^{N_{\text{species}}} \frac{v_{ki}'' - v_{ki}'}{\gamma_i} \left( \Gamma_{k,T} \rho_l s_w \left( \frac{h_i/B_k}{K_{S_i,k} + h_i/B_k} \right) L_v (\gamma_B B_k) \right) \]

\[i \in K_h\] (2.13.34)

For kinetic gas phase components (from Eqns. 2.1.55, 2.3.13, and 2.3.19)

\[
\frac{\partial P_i}{\partial t} = -\frac{T}{\phi(1-s_w)} P_i \frac{\partial}{\partial t} \left[ \frac{\phi(1-s_w)}{RT} \right] - \lambda_P P_i + \frac{RT}{\phi(1-s_w)(MW)} \left( \rho^{\text{gas }} P_i \right)
\]

\[-P_i \left( \alpha \frac{\partial P}{\partial t} + \frac{P_i^{\text{in}} Q_{\text{in}}}{\phi(1-s_w)} - \frac{Q_{\text{out}}}{\phi(1-s_w)} P_i \right) , i \in K_g\] (2.13.35)

where the mass transfer rate between aqueous species and gas phase components is (from Eqn. 2.11.3).

\[\left| \frac{\partial n_i^{\text{gas p}}}{\partial P} \right| = k_L a (x_j - K_{H(j,i)} P_i) \], \(i \in K_g, j \in N_s + M_x\) (2.13.36)

The balance for phase density given by (from Eqns. 2.1.47, 2.1.48, 2.1.53, and 2.1.54)

\[P_i = \frac{1}{c_w M_w + \sum_{j=1}^{N_s} c_j M_j + \sum_{i=1}^{M_y} x_i M_i + \sum_{i=1}^{M_y} h_i^b M_i + \sum_{i=1}^{M_y} a_i M_i}\] (2.13.37)
The heat balance equation for the three phase system can be written from Eqn. (2.1.56) and (2.12.1)

\[
\frac{\partial Q}{\partial t} = \sum_{k=1}^{N_{N\times N\times N}} \omega_k \left( \frac{v'_{ki} - v'_{ki}}{\gamma_i} \right) \Omega_k \left( \gamma_{ki} B_k \right) + M_g + M_q \tag{2.13.40}
\]
3. Numerical Approximation

The concentration of species in all three phases and the total analytical concentrations are solved iteratively in two loops. Figure 3.1 shows the total concentration iterative loop and Figure 3.2 shows the individual species concentration iterative loop. The initial condition is set by the total concentration of the components in the aqueous phase, concentration of solid phase species, and concentration of gas phase species. The total concentration of the aqueous components \((T_j's)\), the total concentration of the adsorbent component \((W_j's)\), the total number of adsorbing sites \((N_{eqi}'s)\), the liquid density \((r_l)\), the solids density \((r_s)\), the gas phase density \((r_g)\), liquid saturation \((s_w)\), and the temperature \((TEMP)\) are calculated using the mass balance equations in the total concentration iterative loop. Using these values of \(T_j's, W_j's, N_{eqi}'s, r_l, r_s, r_g,\) and \(s_w\) the individual species concentrations are computed in individual species concentration iterative loop. At the start of every time step the contributions from kinetic reactions that affect the total component concentration is set to zero. These contributions are updated at the end of computation of individual phase species using Newton-Raphson technique and subsequently used to calculate new values for the total component concentrations.
Compute the values for rate of change of species in all 3 phases due to microbiological and phase change reactions

Solve for $T_j's$, $W_j's$, $N_{eqj}/s$, $r_p$, $r_g$, $s_w$, $TEMP$

Individual species concentration Iterative Loop

Convergent Solution on total Concentration

Proceed to next time step

Figure 3.1 total concentration iterative loop
The application of the Newton-Raphson method to chemical speciation models is relatively straightforward where the residues are computed from the governing equations. The Jacobian is computed by taking the partial differential of the residuals of the governing equations with respect to the species concentration. The formulation of the residuals and Jacobians from the governing equations will be illustrated in the following sections.

3.2 Evaluation of Residuals
The residuals for the component governing equations are calculated during any iteration by substituting the values of species concentrations in the equations given below:

\[
GR_i = R_m = T_m - \rho_p \phi_s w c_m - \rho_p \phi s_w \sum_{k=1}^{M_y} a_{k m}^x x_k - \rho_b \sum_{k=1}^{M_y} a_{k m}^y y_k - \rho_b \sum_{k=1}^{M_y} a_{k m}^z z_k - \rho_b \sum_{k=1}^{M_y} a_{k m}^p p_k
\]

\[
m \in N_a, \quad i = m
\]

(3.2.1)

\[
GR_i = R_m = W^*_{m} - \rho_s \left( s_m + \sum_{k=1}^{M_y} a_{k m}^s y_k \right), \quad m \in N_s, \ i = m + N_a
\]

(3.2.2)

The equilibrium aqueous complexed and adsorbed species are not computed in the matrix solver.

Residuals for all other species are shown below:

For kinetic aqueous complexation species:

\[
GR_i = R_m = \frac{\partial x_m}{\partial t} - r_m^x + \lambda_m^x x_m + \alpha \frac{\partial p}{\partial t} x_m + \frac{Q_{imp}^{imp} x_m^{imp}}{\rho_s \phi s_w} + \frac{Q_{out}^{out} x_m^{out}}{\phi s_w} + \frac{1}{\rho_s \phi s_w} \frac{\partial}{\partial t} \rho_s \phi s_w x_m
\]

\[
m \in K_s, \quad i = m + N
\]

(3.2.3)

where \( N = \) the total number of components, both aqueous and adsorbent, \( (N_a + N_s) \)
For kinetic adsorption:

\[
GR_i = R_m = \frac{\partial y_m}{\partial t} - \nu_m + \frac{\partial p}{\partial t} y_m + \frac{1}{\rho_b} (Q^{\text{inp}} y_m^\text{inp}) + \frac{1}{\rho_b} \frac{\partial \rho_b}{\partial t} y_m
\]

\[m \in K_y, \quad i = m + N + K_x\]  

(3.2.4)

For ion-exchange site equation used for reference species:

\[
GR_i = R_m = N_{eq,j} - \rho_h \left( \sum_{k=NOMZI(j)} \nu_k z_k \right), \quad j \in \text{NSITE}
\]

\[m = \text{reference species for site } j, \quad i = m + N + K_x + K_y\]  

(3.2.5)

for equilibrium ion-exchange:

\[
GR_i = R_m = 0 + \prod_{j = (N_x + M_x + M_z)} (y_{eq,j})^{i_j} - k_{eq}^{i_k} \prod_{j = (N_x + M_x + M_z)} (y_{eq,j})^{i_k}, \quad k \in \text{NRXNE}
\]

\[m \in (M_z - K_z), \quad m \neq \text{Reference ion exchange species}, \quad i = m + N + K_x + K_y\]  

(3.2.6)

For kinetic ion-exchange:

\[
GR_i = R_m = \frac{\partial z_m}{\partial t} - \nu_m z_m + \frac{\partial p}{\partial t} z_m - \frac{1}{\rho_b} (Q^{\text{inp}} z_m^\text{inp}) + \frac{1}{\rho_b} \frac{\partial \rho_b}{\partial t} z_m
\]

\[m \in K_z, \quad m \neq \text{Reference ion exchange species}, \quad i = m + N + K_x + K_y\]  

(3.2.7)

For equilibrium precipitation:

\[
GR_i = R_m = 1 - K_k^{\text{eq}} \prod_{j = N_x} (y_{eq,j})^\nu_j, \quad k \in \text{NRXNE}
\]

\[m \in (M_p - K_p), \quad i = m + N + K_x + K_y + M_z\]  

(3.2.8)

For kinetic precipitation:
\[ GR_m = \frac{\partial p_m}{\partial t} - r_{m}^\text{m} + \lambda_m^\text{c} p_m + \alpha \frac{\partial p}{\partial t} p_m - \frac{1}{\rho_b} \left( Q_{\text{imp}}^{\text{m}} \right) + \frac{1}{\rho_b} \frac{\partial p_b}{\partial t} p_m \]
\[ m \in K_p, \quad i = m + N + K_x + K_y + M_z \quad (3.2.9) \]

For aqueous phase microbial species:

\[ GR_i = \frac{\partial b_m}{\partial t} - r_{m}^{\text{bg}} + r_{m}^{\text{bd}} + \alpha \frac{\partial p}{\partial t} b_m - r_{m}^{\text{swf}} + \frac{1}{\rho_b} \frac{\partial p_b}{\partial t} b_m \]
\[ - \frac{1}{\rho_b} \phi_s \left( Q_{\text{imp}}^{\text{m}} b_m^{\text{imp}} - Q_{\text{out}}^{\text{w}} \rho_i b_m \right) \]
\[ m \in M_b, \quad i = m + N + K_x + K_y + M_z + M_p \quad (3.2.10) \]

For adsorbed microbial species:

\[ GR_i = \frac{\partial d_i}{\partial t} - r_{m}^{\text{ag}} + r_{m}^{\text{ad}} + \alpha \frac{\partial p}{\partial t} a_m - \frac{1}{\rho_b} \left( Q_{\text{imp}}^{\text{a}} a_m^{\text{imp}} \right) - r_{m}^{\text{swf}} + \frac{1}{\rho_b} \frac{\partial p_b}{\partial t} a_m \]
\[ m \in M_a, \quad i = m + N + K_x + K_y + M_z + M_p + M_b \quad (3.2.11) \]

For solid phase kinetic species:

\[ GR_i = \frac{\partial h_m^h}{\partial t} + \lambda_m^h h_m^h + h_m^h \alpha \frac{\partial p}{\partial t} - r_{m}^{\text{chm}} - r_{m}^{\text{solid}} \]
\[ + \frac{1}{\rho_b} \phi_s h_m^b + \frac{1}{\rho_b} \phi_s Q_{\text{imp}}^{\text{b}} h_m^b + \frac{1}{\rho_b} Q_{\text{out}}^{\text{w}} h_m^b, \quad m \in M_h^b \quad (3.2.12) \]
\[ i = m + N + K_x + K_y + M_z + M_p + M_b + M_a \]
\[ GR_i = \frac{\partial h_m^a}{\partial t} \lambda_m^a h_m^a + (h_m^a) \alpha \frac{\partial p}{\partial t} - r_{m}^{\text{chem}} - r_{m}^{\text{solid}} \]
\[ + \frac{1}{\rho_b} \frac{\partial p_b}{\partial t} h_m^a + \frac{1}{\rho_b} Q_{\text{imp}}^{\text{a}} h_m^a, \quad m \in M_h^a, \quad (3.2.13) \]
\[ i = m + N + K_x + K_y + M_z + M_p + M_b + M_a + M_h^b \]
For gas phase species:

\[
GR_i = R_w = \frac{\partial P_i}{\partial t} + \frac{T}{\phi(1-s_w)} P_i \frac{\partial}{\partial t} \left[ \frac{\phi(1-s_w)}{T} \right] + \lambda_i P_i - \frac{RT}{\phi(1-s_w)} \left( r_i^{(\text{os})} \right) \\
+ P_i \left( \alpha \frac{\partial p}{\partial t} \right) - \frac{P_i^{\text{in}}}{\phi(1-s_w)} Q_{\text{in}}^{\text{out}} + \frac{Q_{\text{out}}^{\text{out}}}{\phi(1-s_w)} P_i \ , \ i \in K_g \\
(3.2.14)
\]

\[
i \in M_g \ , \quad i = m + N + K_x + K_y + M_z + M_p + M_b + M_a + M_{b+} + M_{b-}.
\]
3.3 Evaluation of Jacobian elements

3.3.1 Rows for \( N_a \) species:

\[
GJ_{ij} = \frac{\partial R_m}{\partial c_n} = -\rho_s \phi_s \phi_w \sum_{i=1}^{M_x} a_{im}^x \left( \frac{\partial x_i}{\partial c_n} \right) - \rho_b \sum_{i=1}^{M_y} a_{im}^y \left( \frac{\partial y_i}{\partial c_n} \right) - \rho_b \sum_{i=1}^{M_y} a_{im}^y \left( \frac{\partial p_i}{\partial c_n} \right)
\]

\[
= -\rho_s \phi_s \phi_w \delta_{mn} - \rho_s \phi_s \phi_w \sum_{i=1}^{M_x} a_{im}^x \left[ \frac{v_{kn}^x}{v_{kl}^x} \frac{x_i}{c_n} \right] - \rho_b \sum_{i=1}^{M_y} a_{im}^y \left[ \frac{v_{kn}^y}{v_{kl}^y} \frac{y_i}{c_n} \right]
\]

\[
n \in N_a, \quad j = n
\]

where,

\( GJ_{ij} \) is the entry in the i-th row, j-th column of the Jacobian array

\( m = 1, 2, \ldots, N_a, i = m \), corresponding to aqueous components

\( k \in NRXNE \) is the equilibrium reaction defining the formation of equilibrium species ‘ l ’

\[
GJ_{ij} = \frac{\partial R_m}{\partial s_n} = -\rho_b \sum_{i=1}^{M_y} a_{im}^y \left( \frac{\partial y_i}{\partial s_n} \right) = -\rho_b \sum_{i=1}^{M_y} a_{im}^y \left[ \frac{v_{kn}^y}{v_{kl}^y} \frac{y_i}{s_n} \right]
\]

\[
k \in NRXNE, \quad n \in N_s, \quad j = n + N_a
\]
\[ \frac{\partial R_m}{\partial x_n} = -\rho \phi s_w \sum_{l=1}^{M_x} a_{lm}^x \left( \frac{\partial x_l}{\partial x_n} \right) = -\rho \phi s_w \sum_{l=1}^{M_x} a_{lm}^x \delta_{ln} = -\rho \phi s_w a_{nm}^x \quad (3.3.3) \]

\( n \in K_x, \quad j = n + N \)

\[ \frac{\partial R_m}{\partial y_n} = -\rho_b \sum_{l=1}^{M_y} a_{lm}^y \left( \frac{\partial y_l}{\partial y_n} \right) = -\rho_b \sum_{l=1}^{M_y} a_{lm}^y \delta_{ln} = -\rho_b a_{nm}^y \quad (3.3.4) \]

\( n \in K_y, \quad j = n + N + K_x \)

\[ \frac{\partial R_m}{\partial z_n} = -\rho_b \sum_{l=1}^{M_z} a_{lm}^z \left( \frac{\partial z_l}{\partial z_n} \right) = -\rho_b \sum_{l=1}^{M_z} a_{lm}^z \delta_{ln} = -\rho_b a_{nm}^z \quad (3.3.5) \]

\( n \in M_z, \quad j = n + N + K_x + K_y \)

\[ \frac{\partial R_m}{\partial p_n} = -\rho_b \sum_{l=1}^{M_p} a_{lm}^p \left( \frac{\partial p_l}{\partial p_n} \right) = -\rho_b \sum_{l=1}^{M_p} a_{lm}^p \delta_{ln} = -\rho_b a_{nm}^p \quad (3.3.6) \]

\( n \in M_p, \quad j = n + N + K_x + K_y + M_z \)
\[ GJ_{ij} = \frac{\partial R_m}{\partial b_n} = 0 \]  
(3.3.7)

\[ n \in M_b, \quad j = n + N + K_x + K_y + M_z + M_p \]

\[ GJ_{ij} = \frac{\partial R_m}{\partial a_n} = 0 \]  
(3.3.8)

\[ n \in M_a, \quad j = n + N + K_x + K_y + M_z + M_p + M_b \]

\[ GJ_{ij} = \frac{\partial R_m}{\partial h_n^b} = 0 \]  
(3.3.9)

\[ n \in h^b, \quad j = n + N + K_x + K_y + M_z + M_p + M_b + M_a \]

\[ GJ_{ij} = \frac{\partial R_m}{\partial h_n^s} = 0 \]  
(3.3.10)

\[ n \in h^s, \quad j = n + N + K_x + K_y + M_z + M_p + M_b + M_a + h^b \]

\[ GJ_{ij} = \frac{\partial R_m}{\partial P_n} = 0 \]  
(3.3.11)

\[ n \in M_g, \quad j = n + N + K_x + K_y + M_z + M_p + M_b + M_a + h^b + h^s \]
3.3.2 Rows for $N_s$ species

The jacobian for the rows corresponding to the adsorbent component species,

$m = 1, 2, ..., N_s, i = m + N_a$

$$G_{ij} = \frac{\partial R_m}{\partial c_a} = -\rho_b \sum_{i=1}^{M_s} a_{im} \left( \frac{\partial y_i}{\partial c_a} \right) = -\rho_b \sum_{i=1}^{M_s} a_{im} \left( \frac{v'_{kn} y_i}{v'_{ki}} c_n \right), \quad (3.3.12)$$

$$n \in N_a, \ j = n$$

$k \in NRXNE$ is the equilibrium reaction defining the formation of equilibrium species ‘1’

$$G_{ij} = \frac{\partial R_m}{\partial s_n} = -\rho_b \sum_{i=1}^{M_s} a_{im} \left( \frac{\partial y_i}{\partial s_n} \right)$$

$$= -\rho_b \delta_m^a \sum_{i=1}^{M_s} a_{im} \left[ \frac{v'_{kn} y_i}{v'_{ki}} s_n \right] \quad (3.3.13)$$

$$k \in NRXNE, \ n \in N_s, \ j = n + N_a$$

$$G_{ij} = \frac{\partial R_m}{\partial x_n} = 0 \quad n \in K_x, \ j = n + N \quad (3.3.14)$$
\[
G_{ij} = \frac{\partial R_m}{\partial y_n} = -\rho_b \sum_{i=1}^{n} a_{iw}^y \left( \frac{\partial y_i}{\partial s_n} \right) = -\rho_b \sum_{i=1}^{n} a_{iwm}^y \delta_{ln}
\]

\[= -\rho_b a_{nn}^y \quad (3.3.15)\]

\[\ n \in K_y, \ j = n + N + K_x\]

\[
G_{ij} = \frac{\partial R_m}{\partial z_n} = 0, \quad n \in M_y, \ j = n + N + K_x + K_y \quad (3.3.16)
\]

\[
G_{ij} = \frac{\partial R_m}{\partial p_n} = 0, \quad n \in M_p, \ j = n + N + K_x + K_y + M_z \quad (3.3.17)
\]

\[
G_{ij} = \frac{\partial R_m}{\partial b_n} = 0 \quad (3.3.18)
\]

\[\ n \in M_b, \ j = n + N + K_x + K_y + M_z + M_p\]

\[
G_{ij} = \frac{\partial R_m}{\partial a_n} = 0 \quad (3.3.19)
\]

\[\ n \in M_a, \ j = n + N + K_x + K_y + M_z + M_p + M_b\]
\[ G_{J,j} = \frac{\partial R_m}{\partial h_n} = 0 \quad (3.3.20) \]

\[ n \in h^b, \quad j = n + N + K_x + K_y + M_z + M_p + M_b + M_a \]

\[ G_{J,j} = \frac{\partial R_m}{\partial h_n} = 0 \quad (3.3.21) \]

\[ n \in h^s, \quad j = n + N + K_x + K_y + M_z + M_p + M_b + M_a + h^b \]

\[ G_{J,j} = \frac{\partial R_m}{\partial P_n} = 0 \quad (3.3.22) \]

\[ n \in P, \quad j = n + N + K_x + K_y + M_z + M_p + M_b + M_a + h^b + h^s \]

### 3.3.3 Rows for \( K_x \) species

Jacobians for the rows corresponding to the \( K_x \) kinetic complexed species. For the

\[ m = 1, 2, \ldots, K_x \], \( i = m + N \) and \( N = N_a + N_s \)

\[ G_{J,i} = \frac{\partial R_m}{\partial c_n} = \frac{\partial r^x_m}{\partial c_n}, \quad n \in N_a, \quad j = n \quad (3.3.23) \]
\[ GJ_{ij} = \frac{\partial R_m}{\partial s_n} = -\frac{\partial r_m^s}{\partial s_n}, \quad n \in N_z, \quad j = n + N_a \] (3.3.24)

\[ GJ_{ij} = \frac{\partial R_m}{\partial x_n} = -\frac{\partial r_m^s}{\partial x_n} + \left( \frac{1}{\Delta t} + \lambda_n^r + \alpha \frac{\partial n}{\partial t} + \frac{Q_{w}^{\text{out}}}{\phi s_w} + \frac{1}{\rho s_w} \Delta \rho s_w \right) \delta_{mn}, \quad n \in K_x, \quad j = n + N \] (3.3.25)

\[ GJ_{ij} = \frac{\partial R_m}{\partial y_n} = -\frac{\partial r_m^s}{\partial y_n}, \quad n \in K_y, \quad j = n + N + K_x \] (3.3.26)

\[ GJ_{ij} = \frac{\partial R_m}{\partial z_n} = -\frac{\partial r_m^s}{\partial z_n}, \quad n \in M_z, \quad j = n + N + K_x + K_y \] (3.3.27)

\[ GJ_{ij} = \frac{\partial R_m}{\partial p_n} = -\frac{\partial r_m^s}{\partial p_n}, \quad n \in M_p, \quad j = n + N + K_x + K_y + M_z \] (3.3.28)

\[ GJ_{ij} = \frac{\partial R_m}{\partial b_n} = -\frac{\partial r_m^s}{\partial b_n}, \quad n \in M_b, \quad j = n + N + K_x + K_y + M_z + M_p \] (3.3.29)
The partial derivatives of the production / consumption rate terms are evaluated as under:

\[
\begin{align*}
G_{ij} &= \frac{\partial R_{m}}{\partial a_{n}} = -\frac{\partial r_{m}^{x}}{\partial a_{n}}, \quad n \in M_{a}, \quad j = n + N + K_{x} + K_{y} + M_{z} + M_{p} + M_{b} + M_{a} \\
G_{ij} &= \frac{\partial R_{m}}{\partial b_{n}} = -\frac{\partial r_{m}^{x}}{\partial b_{n}}, \quad n \in h^{b}, \quad j = n + N + K_{x} + K_{y} + M_{z} + M_{p} + M_{b} + M_{a} + h^{b} \\
G_{ij} &= \frac{\partial R_{m}}{\partial h_{n}^{s}} = -\frac{\partial r_{m}^{x}}{\partial h_{n}^{s}}, \quad n \in h^{s}, \quad j = n + N + K_{x} + K_{y} + M_{z} + M_{p} + M_{b} + M_{a} + h^{b} + h^{s} \\
G_{ij} &= \frac{\partial R_{m}}{\partial P_{n}} = -\frac{\partial r_{m}^{x}}{\partial P_{n}}, \quad n \in M_{g}, \quad j = n + N + K_{x} + K_{y} + M_{z} + M_{p} + M_{b} + M_{a} + h^{b} + h^{s}
\end{align*}
\] (3.3.30)

\[
\frac{\partial r_{m}^{x}}{\partial e_{n}} = \sum_{k=1}^{NRXNK} \frac{\partial \left( r_{m}^{\text{chem}} \right)_{k}}{\partial e_{n}} + \sum_{k=1}^{NBHRXNK} \frac{\partial \left( r_{m}^{\text{gas}} \right)_{k}}{\partial e_{n}} + \sum_{k=1}^{NRXNK} \frac{\partial \left( r_{m}^{\text{bio}} \right)_{k}}{\partial e_{n}} - \frac{\partial \left( r_{m}^{\text{bioresp}} \right)}{\partial e_{n}}
\]

\[
= \sum_{k=1}^{NRXNK} \frac{\partial \left( v_{k,m}^{'} - v_{k,m}^{'} \right)}{\gamma_{m}} \left( k_{i}^{'} \prod_{i \in M} (\gamma_{i} e_{i})^{y_{i}} - k_{i}^{b} \prod_{i \in M} (\gamma_{i} e_{i})^{y_{i}} \right)
\]

\[
+ \sum_{k=1}^{NBHRXNK} \frac{\partial \left( v_{k,m}^{'} - v_{k,m}^{'} \right)}{\gamma_{m}} \left( \Gamma_{k} \left( r \prod_{i \in M} s_{i} \left( \frac{h_{i} / B_{i}}{K_{S-i} + h_{i} / B_{i}} \right) L_{i} (\gamma_{i} e_{i} B_{i}) \right) \right)
\] (3.3.34)

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Derivatives with respect to \( e_n \) are presented for all species contributing to the Jacobian in the following sub-section.

### 3.3.3.1 Contribution from chemical reactions

For columns \( n \in N_a + N_s \), \( j \in n \), the contribution to the Jacobian from the k-th chemical reaction is:

For \( N_a \) or \( N_s \in r \) (reactant)

\[
\frac{\partial (r_m^{\text{chem}})}{\partial e_n} = \left( \frac{v_{km}^{\gamma_m} - v_{km}^{\gamma_n}}{\gamma_m} \right) k_k \left( \frac{v_{km}^{\gamma_n}}{e_n} \right) \prod_{l=M} (\gamma_l x_l)^{\psi_l} \quad \text{if } r = n
\]  

(3.3.35)

For \( N_a \) or \( N_s \in p \) (product)
From equilibrium complexed or adsorbed species,

From reactant $r \in (M_x - K_x)$ or $(M_y - K_y)$:

$$
\frac{\partial (r_{m}^{\text{chem}}_{\kappa})}{\partial e_{n}} = \left( \frac{V'_{k_{m}} - V'_{k_{m}}}{\gamma_{m}} \right) k^{b}_{k} \left( \frac{V'_{k_{n}}}{e_{n}} \right) \prod_{l \in M} (\gamma_{l} \epsilon_{l})^{\gamma_{l}}
$$

(3.3.36)

where $\kappa \in \text{N RXNE}$ is the equilibrium reaction defining the formation of equilibrium species $r$.

From product $p \in (M_x - K_x)$ or $(M_y - K_y)$:

$$
\frac{\partial (r_{m}^{\text{chem}}_{\kappa})}{\partial e_{n}} = -\left( \frac{V'_{k_{m}} - V'_{k_{m}}}{\gamma_{m}} \right) k^{b}_{k} \left( \frac{V'_{k_{p}}}{e_{n}} \right) \prod_{l \in M} (\gamma_{l} \epsilon_{l})^{\gamma_{l}}
$$

(3.3.37)

where $\kappa \in \text{N RXNE}$ is the equilibrium reaction defining the formation of equilibrium species $p$.

For any other reactant species $r$ or product species $p$, the contribution to the Jacobian in columns $n \in N_{a} + N_{s}$ is zero.
For columns \( n \in K_x + K_y, \quad j = n + N, \) the contribution to the Jacobian from the k-th chemical reaction is given by:

For reactant \( r \in K_x + K_y \):

\[
\frac{\partial (r^\text{chem}_m)_k}{\partial e_n} = \left( \frac{v^*_{km} - v'_{km}}{\gamma_m} \right) k^f \left( \frac{v'_{kn}}{e_n} \right) \prod_{i=0}^{n_f} (\gamma_i e_i)^{\psi_{ii}} \quad \text{if } r = n \tag{3.3.39}
\]

From product \( p \in K_x + K_y \):

\[
\frac{\partial (r^\text{chem}_m)_k}{\partial e_n} = \left( \frac{v^*_{km} - v'_{km}}{\gamma_m} \right) k^b \left( \frac{v^*_{kn}}{e_n} \right) \prod_{i=0}^{n_f} (\gamma_i e_i)^{\psi_{ii}} \quad \text{if } p = n \tag{3.3.40}
\]

For columns \( n \in M_z, \quad j = n + N + K_x + K_y, \) the contribution to the Jacobian from the k-th chemical reaction is:

For reactant \( r \in M_z \):

\[
\frac{\partial (r^\text{chem}_m)_k}{\partial z_n} =
\]
\[
= \left( \frac{v''_{km} - v'_{km}}{\gamma_m} \right)^{k_i} \prod_{l \in M} (\gamma_l \epsilon_l)^{v''_{kn} \left( \frac{1}{z_n} - \gamma_n \right)} \quad \text{if } r = n \quad (3.3.41a)
\]

\[
= \left( \frac{v''_{km} - v'_{km}}{\gamma_m} \right)^{k_i} \prod_{l \in M} (\gamma_l \epsilon_l)^{v''_{kn} \gamma_r} \quad \text{if } r \neq n , n \in NOMZI(i) \quad (3.3.41b)
\]

\[
= 0 \quad \text{if } r \neq n , n \notin NOMZI(i) \quad (3.3.41c)
\]

where \( i \in NSITE \) is the ion exchange site of reaction \( k \)

The derivation of Eqns 3.3.38a, and b were obtained with the assumption that the activity of any ion-exchange species is proportional to its molar concentrations. Also following relation holds true:

Activity of \( i \)-th ion exchange species = \( z_n / s_{T(\beta)} \), \( n \in M_{z(\beta)} \), \( n \notin NOMZI(\beta) \) \( (3.3.41d) \)

And \( s_{T(\beta)} = \sum_{i \in M_{z(\beta)}} z_i \) \( (3.3.41e) \)

For product \( p \in M_z \):

\[
\frac{\partial (r_{\text{chem}}^m)}{\partial z_n} =
\]
\[
\left( \frac{V''_{k,m} - V'_{k,m}}{\gamma_m} \right) k_{l}^{j_{l}} \prod_{l \in M} (\gamma_l e_l)^{\gamma_{i_{l}}} \left( \frac{1}{z_{n} - \gamma} \right) \quad \text{if } p = n \quad (3.3.42a)
\]

\[
\left( \frac{V''_{k,m} - V'_{k,m}}{\gamma_m} \right) k_{l}^{j_{l}} \prod_{l \in M} (\gamma_l e_l)^{\gamma_{i_{l}}} \gamma_{p} \quad \text{if } p \neq n, n \in \text{NOMZI}(i) \quad (3.3.42b)
\]

\[
= 0 \quad \text{if } p \neq n, n \notin \text{NOMZI}(i) \quad (3.3.42c)
\]

for any other reactant or product species, the contribution to the Jacobian for columns \( n \in M_z \) is zero.

For columns \( n \in M_p, j = n + N + K_x + K_y + M_z \), the contribution to the Jacobian from the k-th chemical reaction is zero:

\[
\frac{\partial \left( \rho_{m, k}^{\text{chem}} \right)}{\partial p_n} = 0 \quad (3.3.43)
\]

For columns \( n \in M_b + M_a, j = n + N + K_x + K_y + M_z + M_p \), the contribution to the Jacobian from the k-th chemical reaction is zero:
\[
\frac{\partial (r_{m_k}^{\text{chem}})}{\partial b_n} = 0
\]  
(3.3.44)

\[
\frac{\partial (r_{m_k}^{\text{chem}})}{\partial a_n} = 0
\]  
(3.3.45)

For columns \( n \in h^b + h^s \), \( j = n + N + K_x + K_y + M_z + M_p + M_b + M_a \), the contribution to the Jacobian from the k-th chemical reaction is zero:

\[
\frac{\partial (r_{m_k}^{\text{chem}})}{\partial h_n^b} = 0
\]  
(3.3.46)

\[
\frac{\partial (r_{m_k}^{\text{chem}})}{\partial h_n^s} = 0
\]  
(3.3.47)

For columns \( n \in M_g \), \( j = n + N + K_x + K_y + M_z + M_p + M_b + M_a + h^b + h^s \), will include the contribution from the kinetic reactions involving phase change between aqueous and gas phase.

For reactant \( r \in K_p \)

\[
\frac{\partial (r_{m_k}^{\text{chem}})}{\partial P_n} = 0 \quad \text{if } r = n
\]  
(3.3.48)
3.3.3.2 Contribution from aqueous and gas phase inter-change reactions

The Jacobian terms for this reaction are similar to given later in the gas phase species as per Eqn. 3.3.203 through 3.3.213. The reaction rate is given by Eqn. 3.3.49.

\[
\frac{\partial v^g_m}{\partial g_n} = \sum_{k=1}^{NBRXNK} \frac{\partial}{\partial g_n} \left[ \left( v''_{km} - v'_{km} \right) \left( k_L d(x_i - K_{H,x} P_m) \right) \right]
\]

(3.3.49)

3.3.3.3 Contribution from hydrolysis reaction:

The contribution to the Jacobian from each term in the k-th hydrolysis reaction \((k \in NBHRXNK)\) is:

For columns \(n \in M_a + M_a\), \(j \in n\), the contribution to the Jacobian from the k-th hydrolysis reaction is:

\[
\frac{\partial r_m}{\partial e_n} = \frac{v''_{km} - v'_{km}}{\gamma_m} \left( \Gamma_{k,T} I_{pH} s_w \right) \frac{1}{L_k \left( \gamma_{Bk} \right)} \left( K_{S-k} \frac{B_k}{h_k} + 1 \right), \quad n \in B_k
\]

(3.3.50)

For columns \(n \in h^b + h^c\), \(j \in n\), the contribution to the Jacobian from the k-th hydrolysis reaction is:
For any other species participating in the $k$-th microbiologically mediated hydrolysis reaction, the contribution to the Jacobian. The pH inhibition function $I_{pH}$ and $s_w$ will be used explicitly in the hydrolysis reaction.

3.3.3.4 Contribution from microbiological degradation reaction:

The contribution to the Jacobian from each term in the $k$-th microbial biodegradation reaction ($k \in NBRXNK$) is:

For columns $n \in N_a + N_s$, $j = n$, the contribution to the Jacobian from the $k$-th microbiological reaction is:

If substrate $S_k \in N_a$ or $N_s$ and $S_k \neq I$:

$$
\frac{\partial \left( \hat{r}_{m,k}^{\text{solid}} \right)}{\partial e_n} = \frac{\hat{v}_{km} - \hat{v}_{km}'}{\gamma_m} \left( \Gamma_{s,\mathcal{I}} I_{pH} s_w \right) \left[ \frac{1}{B_k (K_{S-k} + h_k / B_k)} - \frac{h_k / B_k (K_{S-k} + 1/B_k)}{\left( K_{S-k} + h_k / B_k \right)^2} \right] L_k \left( \gamma_B B_k \right),
$$

$$
\left(3.3.51\right)
$$

$$
\frac{\partial \left( \hat{r}_{m,k}^{\text{bio}} \right)}{\partial e_n} = \frac{\hat{v}_{km} - \hat{v}_{km}'}{\gamma_m} \left( \Gamma_{s,\mathcal{I}} I_{pH} s_w \right) \left( \frac{K_{S-k} I_{2k}}{K_{S-k} I_{2k} + S_k} \left( \frac{A_k}{K_{A-k} + A_k} \right) \left( \frac{N_k}{K_{N-k} + N_k} \right) \right) L_k \left( \gamma_B B_k \right)
$$

if $S_k = n$

$$
\left(3.3.52\right)
$$
If electron acceptor $A_k \in N_a$ or $N_s$ and $A_k \neq I$:

$$
\frac{\partial (r_{m_{biodeg}}^{\mathbf{0}})}{\partial e_n} = \frac{v_k'' - v_k'}{\gamma_m} \left( \Gamma_{k,T} I_{1k} L_{pH} \right) \left( \frac{S_k}{K_{S-k} I_{2k} + S_k} \right) \left( \frac{A_k}{K_{A-k} + A_k} \right) L_k (y_{bk} B_k)
$$

if $A_k = n$ \hfill (3.3.53)

If nutrient $N_k \in N_a$ or $N_s$ and $N_k \neq I$:

$$
\frac{\partial (r_{m_{biodeg}}^{\mathbf{0}})}{\partial e_n} = \frac{v_k'' - v_k'}{\gamma_m} \left( \Gamma_{k,T} I_{1k} L_{pH} \right) \left( \frac{S_k}{K_{S-k} I_{2k} + S_k} \right) \left( \frac{A_k}{K_{A-k} + A_k} \right) L_k (y_{bk} B_k)
$$

if $N_k = n$ \hfill (3.3.54)

If inhibitor $I \in N_a$ or $N_s$ and $I \neq S_k$, $I \neq A_k$, $I \neq N_k$, $I \neq B_k$:

$$
\frac{\partial (r_{m_{biodeg}}^{\mathbf{0}})}{\partial e_n} =
$$

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\[
\frac{v'_{km} - v_{km}}{\gamma_m} \left( \Gamma_{k,T} I_{pH} s_w \right) \frac{p}{K_{I1}} \left( 1 + \frac{I}{K_{I1}} \right)^{n-1} \left( \frac{S_k}{K_{S-k} I_{2k} + S_k} \right)\left( \frac{A_k}{K_{A-k} + A_k} \right)\left( \frac{N_k}{K_{N-k} + N_k} \right) L_k(\gamma_{Bk} B_k) -
\]

\[
\frac{v'_{km} - v_{km}}{\gamma_m} \left( \Gamma_{k,T} I_{sT} I_{pH} s_w \right) \frac{S_k qK_{S-k} \left( 1 + \frac{I}{K_{I2}} \right)^{q-1}}{K_{S-k} \left( 1 + \frac{I}{K_{I2}} \right)^{q} + S_k} \left( \frac{A_k}{K_{A-k} + A_k} \right)\left( \frac{N_k}{K_{N-k} + N_k} \right) L_k(\gamma_{Bk} B_k) -
\]

\text{if } I = n
\]

(3.3.55)

If inhibitor \( I \in A \) or \( N_s \) and \( I = S_k, I \neq A_k, I \neq N_k, I \neq B_k \):

\[
\left( \frac{\partial}{\partial e_n} \right)_{k}\left( \frac{v'_{km} - v_{km}}{\gamma_m} \left( \Gamma_{k,T} I_{pH} s_w \right) \frac{p}{K_{I1}} \left( 1 + \frac{I}{K_{I1}} \right)^{n-1} \left( \frac{S_k}{K_{S-k} I_{2k} + S_k} \right)\left( \frac{A_k}{K_{A-k} + A_k} \right)\left( \frac{N_k}{K_{N-k} + N_k} \right) L_k(\gamma_{Bk} B_k) -
\]

\[
\frac{v'_{km} - v_{km}}{\gamma_m} \left( \Gamma_{k,T} I_{sT} I_{pH} s_w \right) K_{S-k} \left( 1 + \frac{I}{K_{I2}} \right)^{q} \left( \frac{S_k qK_{S-k} \left( 1 + \frac{I}{K_{I2}} \right)^{q} + S_k} {K_{S-k} \left( 1 + \frac{I}{K_{I2}} \right)^{q} + S_k} \right) \left( \frac{A_k}{K_{A-k} + A_k} \right)\left( \frac{N_k}{K_{N-k} + N_k} \right) L_k(\gamma_{Bk} B_k) -
\]

\text{if } I = S_k = n
\]

(3.3.56)
If inhibitor $I \in N_a$ or $N_s$ and $I = A_k$, $I \neq S_k$, $I \neq N_k$, $I \neq B_k$:

$$\frac{\partial \left( r_m^{\text{bio-deg}} \right)}{\partial e_n} =$$

$$\frac{v_{km}^* - v_{km}'}{\gamma_m} \left( \Gamma_{k,T} I_{\text{pit}} I_{\text{pit}} S_w \right) \frac{p}{K_{I_1}} \left( 1 + \frac{I}{K_{I_1}} \right)^{p-1} \left( \frac{S_k}{K_{S-k} I_{2k} + S_k} \right) \frac{A_k}{K_{A-k} + A_k} \left( \frac{N_k}{K_{N-k} + N_k} \right) L_k (\gamma_{B_k} B_k) -$$

$$\frac{v_{km}^* - v_{km}'}{\gamma_m} \left( \Gamma_{k,T} I_{\text{pit}} I_{\text{pit}} S_w \right) \frac{S_k q K_{S-k} \left( 1 + \frac{I}{K_{I_2}} \right)^{q-1}}{K_{S-k} \left( 1 + \frac{I}{K_{I_2}} \right) + S_k} \left( \frac{A_k}{K_{A-k} + A_k} \right) \left( \frac{N_k}{K_{N-k} + N_k} \right) L_k (\gamma_{B_k} B_k) +$$

$$\frac{v_{km}^* - v_{km}'}{\gamma_m} \left( \Gamma_{k,T} I_{\text{pit}} I_{\text{pit}} S_w \right) \frac{S_k}{K_{S-k} I_{2k} + S_k} \left( \frac{K_{A-k}}{(K_{A-k} + A_k)^2} \right) \left( \frac{N_k}{K_{N-k} + N_k} \right) L_k (\gamma_{B_k} B_k)$$

if $I = A_k = n$  \hspace{1cm} (3.3.57)

If inhibitor $I \in N_a$ or $N_s$ and $I = N_k$, $I \neq A_k$, $I \neq S_k$, $I \neq B_k$:

$$\frac{\partial \left( r_m^{\text{bio-deg}} \right)}{\partial e_n} =$$

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\[
\begin{aligned}
\frac{v'_{k,m} - v'_{k,m}}{\gamma_m} &= \left( \Gamma_{k,T} I_{pH} S_w \right) \left( \frac{P}{K_{11}} \right) \left( 1 + \frac{I}{K_{11}} \right)^{p-1} \left( \frac{S_k}{K_{S-k} I_{2k} + S_k} \right) \left( \frac{A_k}{K_{A-k} + A_k} \right) \left( \frac{N_k}{K_{S-k} + N_k} \right) L_k (\gamma_{Bl} B_k) - \\
\frac{v''_{k,m} - v''_{k,m}}{\gamma_m} &= \left( \Gamma_{k,T} I_{pH} S_w \right) \left( \frac{S_k q K_{S,M}}{K_{S,M} \left( 1 + \frac{I}{K_{12}} \right)} \right)^{q-1} \left( \frac{A_k}{K_{A-k} + A_k} \right) \left( \frac{N_k}{K_{S,M} + N_k} \right) L_k (\gamma_{Bl} B_k) \\
\frac{v'_{k,m} - v'_{k,m}}{\gamma_m} &= \left( \Gamma_{k,T} I_{pH} S_w \right) \left( \frac{S_k}{K_{S-k} I_{2k} + S_k} \right) \left( \frac{A_k}{K_{A-k} + A_k} \right) \left( \frac{K_{N-M}}{(K_{N-M} + N_k)^2} \right) L_k (\gamma_{Bl} B_k)
\end{aligned}
\]

\text{if } I = N_k = n \quad (3.3.58)

If substrate \( S_k \in \left( M_x - K_x \right) \) or \( \left( M_y - K_y \right) \) i.e. equilibrium complexed or adsorbed species, and \( I \neq S_k \):

\[
\frac{\partial \left( \Gamma_{k,T}^{\text{bio}} \right)}{\partial e_n} = \left[ K_{S-k} I_{2k} \left( \frac{S_k}{K_{S-k} I_{2k} + S_k} \right)^2 \right] \left( \frac{A_k}{K_{A-k} + A_k} \right) \left( \frac{N_k}{K_{S-k} + N_k} \right) L_k (\gamma_{Bl} B_k)
\]

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where \((k \in NBRXNK)\) is the equilibrium reaction defining the formation of equilibrium species \(S_k\).

If electron acceptor \(A_k \in (M_x - K_x)\) or \((M_y - K_y)\) i.e. equilibrium complexed or adsorbed species, and \(S_k \neq I\):

\[
\frac{\partial}{\partial e_n} \left( I_{m}^{\text{bio\,deg}} \right) = \frac{v'_{km} - v'_{km}}{\gamma_m} \left( \Gamma_{k,T} I_{1k} I_{pH} S_w \right) \left( \frac{S_k}{K_{S-k} + S_k} \right) \left[ \frac{K_{A-k} I_{2k} \left( \frac{A_k}{v'_{k,n}} e_n \right)}{\left( K_{A-k} + A_k \right)^2} \right] \left( \frac{N_k}{K_{S-k} + N_k} \right) L_k \left( \gamma_{bh} B_k \right)
\]

(3.3.60)

where \((k \in NBRXNK)\) is the equilibrium reaction defining the formation of equilibrium species \(A_k\).

If nutrient \(N_k \in (M_x - K_x)\) or \((M_y - K_y)\) i.e. equilibrium complexed or adsorbed species, and
\( N_k \neq I: \)

\[
\frac{\partial (r_{m}^{\text{bio,deg}})}{\partial e_{n}} = \left( K_{N-k} \left( \frac{N_k}{v_{k,n}'} \right) \right) \left( \frac{K_{N-k}' - N_k'}{K_{N-k}' + N_k'} \right) L_{k} (\gamma_{Bk} B_k)
\]

if \( v'_{k,n} \neq 0 \) \hspace{2cm} (3.3.61)

where \((k \in NBRXNK)\) is the equilibrium reaction defining the formation of equilibrium species \(N_k\).

If inhibitor \( I \in (M_x - K_x) \) or \((M_y - K_y)\) i.e. equilibrium complexed or adsorbed species, and \( I \neq S_k, I \neq A_k, I \neq N_k: \)

\[
\frac{\partial (r_{m}^{\text{bio,deg}})}{\partial e_{n}} = \left( \frac{K_{K_{11}}}{1 + \frac{I}{K_{11}}} \right) \left( \frac{I}{v_{k,n}'} \right) \left( \frac{S_k}{v_{kl}'} \right) \left( \frac{K_{N-k}'}{K_{N-k} + \frac{N_k}{K_{N-k} + N_k}} \right) L_{k} (\gamma_{Bk} B_k) - \]

213
\[
\frac{v''_{km} - v'_{km}}{\gamma_m} \left( \frac{\Gamma_{k,T} I_{1k} I_{pH} S_w}{K_{i1}} \right) \left( 1 + \frac{I}{K_{l2}} \right)^{q-1} \left( \frac{I}{v''_{kn} e_n} \right) S_k qK_{S-k} \left( 1 + \frac{I}{K_{l2}} \right)^q + S_k \right] \left( \frac{A_k}{K_{A-k} + A_k} \right) \left( \frac{N_k}{K_{N-k} + N_k} \right) L_k (\gamma_{Bk} B_k)
\]

if \( v'_{kn} \neq 0 \)  

(3.3.62)

where \((k \in NBRXNK)\) is the equilibrium reaction defining the formation of equilibrium species \(I\).

If inhibitor \(I = \) substrate \(S_k \in (M_x - K_x)\) or \((M_y - K_y)\) i.e. equilibrium complexed or adsorbed species, \(I \neq A_k, I \neq N_k:\)

\[
\frac{\partial}{\partial e_n} \left( \gamma_{i1}^{biodeg} \right) = -
\]

\[
\frac{v''_{km} - v'_{km}}{\gamma_m} \left( \frac{\Gamma_{k,T} I_{1k} I_{pH} S_w}{K_{i1}} \right) \left( 1 + \frac{I}{K_{l1}} \right)^p \left( \frac{I}{v''_{kn} e_n} \right) S_k qK_{S-k} \left( 1 + \frac{I}{K_{l2}} \right)^q + S_k \right] \left( \frac{A_k}{K_{A-k} + A_k} \right) \left( \frac{N_k}{K_{N-k} + N_k} \right) L_k (\gamma_{Bk} B_k) -
\]

\[
\frac{v''_{km} - v'_{km}}{\gamma_m} \left( \frac{\Gamma_{k,T} I_{1k} I_{pH} S_w}{K_{i1}} \right) \left( 1 + \frac{I}{K_{l2}} \right)^q - qK_{S-k} I_{l2} \left( 1 + \frac{I}{K_{l2}} \right)^q \left( \frac{I}{v''_{kn} e_n} \right) S_k qK_{S-k} \left( 1 + \frac{I}{K_{l2}} \right)^q + S_k \right] \left( \frac{A_k}{K_{A-k} + A_k} \right) \left( \frac{N_k}{K_{N-k} + N_k} \right) L_k (\gamma_{Bk} B_k)
\]

if \( v'_{kn} \neq 0 \)  

(3.3.63)
where \((k \in NBRXNK)\) is the equilibrium reaction defining the formation of equilibrium species 

\[ I = S_k. \]

If inhibitor \(I = \) electron acceptor \(A_k \in (M_x - K_x)\) or \((M_y - K_y)\) i.e. equilibrium complexed or adsorbed species, \(I \neq S_k, I \neq N_k\):

\[
\frac{\partial (r_m^{\text{bio}deg})}{\partial e_n} =
\]

\[
\frac{v_m^* - v_m'}{\gamma_m} (\Gamma_{k,TI_pH,S_w} p) \left( 1 + \frac{I}{K_{11}} \right)^{p-1} \left( \frac{I}{v_{k_1} e_n} \right) \left( \frac{S_k}{K_{S-k,12} + S_k} \right) \left( \frac{A_k}{A_{A-k} + A_k} \right) \left( \frac{N_k}{N_{N-k} + N_k} \right) L_k(\gamma_{Bk} B_k) -
\]

\[
\frac{v_m^* - v_m'}{\gamma_m} \left( \Gamma_{k,TI_pH,S_w} \right) \left( 1 + \frac{I}{K_{12}} \right)^{q-1} \left( \frac{I}{v_{k_2} e_n} \right) \left( \frac{A_k}{A_{A-k} + A_k} \right) \left( \frac{N_k}{N_{N-k} + N_k} \right) L_k(\gamma_{Bk} B_k) +
\]

\[
\left( 1 + \frac{I}{K_{12}} \right)^{2q-1} \left( \frac{I}{v_{k_2} e_n} \right) \left( \frac{A_k}{A_{A-k} + A_k} \right) \left( \frac{N_k}{N_{N-k} + N_k} \right) L_k(\gamma_{Bk} B_k)
\]

if \(v_{k_n} \neq 0\) \hspace{1cm} (3.3.64)

where \((k \in NBRXNK)\) is the equilibrium reaction defining the formation of equilibrium species 

\[ I = A_k. \]
If inhibitor $I = \text{electron acceptor } N_k \in (M_x - K_x)$ or $(M_y - K_y)$ i.e. equilibrium complexed or adsorbed species, $I \neq S_k, I \neq A_k$:

$$
\frac{\partial (r^\text{bio-deg}_m)}{\partial e_n} =
$$

$$
\frac{v_{km}^* - v_{km}'}{\gamma_m} \left( \frac{p}{K_{11}} \right) \left( \frac{1 + I}{K_{12}} \right)^{q-1} \left( \frac{S_k}{K_{2k} + S_k} \right) \left( \frac{A_k}{K_{A-k} + A_k} \right) \left( \frac{N_k}{N_{k-k} + N_k} \right) L_k(y'_{Bk} B_k) -
$$

$$
\frac{v_{km}^* - v_{km}'}{\gamma_m} \left( \frac{S_k q K_{S-k} (1 + I / K_{12})}{K_{S-k} (1 + I / K_{12})^q + S_k} \right) \left( \frac{A_k}{K_{A-k} + A_k} \right) \left( \frac{N_k}{N_{k-k} + N_k} \right) L_k(y'_{Bk} B_k) +
$$

$$
\frac{v_{km}^* - v_{km}'}{\gamma_m} \left( \frac{S_k}{K_{S-k} + S_k} \right) \left( \frac{A_k}{K_{A-k} + A_k} \right) \left[ \frac{K_{N-k}}{v_{km}^* e_n} \right] \left[ \frac{N_k v_{km}'}{v_{km}^* e_n} \right] L_k(y'_{Bk} B_k)
$$

if $v_{km}^* \neq 0$

$$
(3.3.65)
$$

where $(k \in NBRXNK)$ is the equilibrium reaction defining the formation of equilibrium species $I = N_k$.

For any other species participating in the k-th microbial reaction, the contribution to the Jacobian
for columns \( n \in N_u \) or \( N_s \) is zero.

For columns \( n \in K_x + K_y + M_z + M_p \), \( j = n + N \), the contribution to the Jacobian from the k-th microbial degradation reaction is:

If substrate \( S_k \in K_x + K_y + M_z + M_p \) and \( S_k \neq I \):

\[
\frac{\partial (J^{\text{bio-deg}})}{\partial e_n} = \frac{v''_{km} - v'_{km}}{\gamma_m} (\Gamma_{k,T} I_{ik} I_{ph} S_w) \left( \frac{K_{S-k} I_{2k}}{(K_{S-k} I_{2k} + S_k)^2} \right) \left( \frac{A_k}{K_{A-k} + A_k} \right) \left( \frac{N_k}{K_{N-k} + N_k} \right) L_h(y_{B_k} B_k)
\]

if \( S_k = n \) (3.3.66)

If electron acceptor \( A_k \in K_x + K_y + M_z + M_p \) and \( A_k \neq I \):

\[
\frac{\partial (J^{\text{bio-deg}})}{\partial e_n} = \frac{v''_{km} - v'_{km}}{\gamma_m} (\Gamma_{k,T} I_{ik} I_{ph} S_w) \left( \frac{S_k}{K_{S-k} I_{2k} + S_k} \right) \left( \frac{K_{S-k} I_{2k}}{(K_{S-k} I_{2k} + S_k)^2} \right) \left( \frac{A_k}{K_{A-k} + A_k} \right) \left( \frac{N_k}{K_{N-k} + N_k} \right) L_h(y_{B_k} B_k)
\]

if \( A_k = n \) (3.3.67)

If nutrient \( N_k \in K_x + K_y + M_z + M_p \) and \( N_k \neq I \):

217
\[
\frac{\partial (r_{m_k}^{\text{bio deg}})}{\partial e_n} = \frac{\nu_k^* - \nu_k'}{\gamma_m} \left( \Gamma_{k,T} I_{1k} I_{pH} s_w \left( \frac{S_k}{K_{S-k} I_{2k} + S_k} \right) \left( \frac{A_k}{K_{A-k} + A_k} \right) \left( \frac{N_k}{K_{N-k} + N_k} \right) \right) L_k (\gamma_{Bk} B_k) \\
\text{if } N_k = n
\] (3.3.68)

If inhibitor \( I \in K_x + K_y + M_z + M_p \) and \( I \neq S_k, I \neq A_k, I \neq N_k, I \neq B_k \):

\[
\frac{\partial (r_{m_k}^{\text{bio deg}})}{\partial e_n} =
\]

\[
\frac{\nu_k^* - \nu_k'}{\gamma_m} \left( \Gamma_{k,T} I_{1k} I_{pH} s_w \left( 1 + \frac{I}{K_{I1}} \right)^{p-1} \left( \frac{S_k}{K_{S-k} I_{2k} + S_k} \right) \left( \frac{A_k}{K_{A-k} + A_k} \right) \right) \left( \frac{N_k}{K_{N-k} + N_k} \right) L_k (\gamma_{Bk} B_k) -
\]

\[
\frac{\nu_k^* - \nu_k'}{\gamma_m} \left( \Gamma_{k,T} I_{1k} I_{pH} s_w \left( S_k q K_{S-k} \left( 1 + \frac{I}{K_{I2}} \right)^{q-1} \right) \frac{1}{K_{S-k} \left( 1 + \frac{I}{K_{I2}} \right)^q + S_k} \left( \frac{A_k}{K_{A-k} + A_k} \right) \right) \left( \frac{N_k}{K_{N-k} + N_k} \right) L_k (\gamma_{Bk} B_k) \\
\text{if } I = n
\] (3.3.69)

If inhibitor \( I \in K_x + K_y + M_z + M_p \) and \( I = S_k, I \neq A_k, I \neq N_k, I \neq B_k \):

\[
\frac{\partial (r_{m_k}^{\text{bio deg}})}{\partial e_n} =
\]

218
\[
\frac{v''_{km} - v'_{km}}{\gamma_m} \left( \frac{\gamma_{BS}}{K_{BS}} \right) \left( \frac{1 + \frac{I}{K_{I,k}}}{1 + \frac{I}{K_{I,k}}} \right) \left( \frac{S_k}{K_{S,k} I_{1,k} + S_k} \right) \left( \frac{A_k}{K_{A,k} + A_k} \right) \left( \frac{N_k}{K_{N,k} + N_k} \right) L_k (\gamma_{Bl_k} B_k) -
\]

\[
\frac{v''_{km} - v'_{km}}{\gamma_m} \left( \frac{\gamma_{BS}}{K_{BS}} \right) \left( \frac{1 + \frac{I}{K_{I,k}}}{1 + \frac{I}{K_{I,k}}} \right) \left( \frac{S_k}{K_{S,k} I_{1,k} + S_k} \right) \left( \frac{A_k}{K_{A,k} + A_k} \right) \left( \frac{N_k}{K_{N,k} + N_k} \right) L_k (\gamma_{Bl_k} B_k)
\]

\[
\text{if } I = S_k = n
\]

(3.3.70)

If inhibitor \( I \in K_x + K_y + M_z + M_p \) and \( I = N_k, I \neq S_k, I \neq A_k, I \neq B_k \):

\[
\frac{\partial \left( r_{km}^{\text{bio deg}} \right)}{\partial e_n} =
\]

\[
\frac{v''_{km} - v'_{km}}{\gamma_m} \left( \frac{\gamma_{BS}}{K_{BS}} \right) \left( \frac{1 + \frac{I}{K_{I,k}}}{1 + \frac{I}{K_{I,k}}} \right) \left( \frac{S_k}{K_{S,k} I_{1,k} + S_k} \right) \left( \frac{A_k}{K_{A,k} + A_k} \right) \left( \frac{N_k}{K_{N,k} + N_k} \right) L_k (\gamma_{Bl_k} B_k) -
\]

\[
\frac{v''_{km} - v'_{km}}{\gamma_m} \left( \frac{\gamma_{BS}}{K_{BS}} \right) \left( \frac{1 + \frac{I}{K_{I,k}}}{1 + \frac{I}{K_{I,k}}} \right) \left( \frac{S_k}{K_{S,k} I_{1,k} + S_k} \right) \left( \frac{A_k}{K_{A,k} + A_k} \right) \left( \frac{N_k}{K_{N,k} + N_k} \right) L_k (\gamma_{Bl_k} B_k)
\]
\[
\frac{v'_{km} - v''_{km}}{\gamma_m} (\Gamma_{k,T} \Gamma_{1k} I_{pH} s_w) \left( \frac{S_k}{K_{S-k} I_{2k} + S_k} \right) \left( \frac{K_{A-k}}{K_{A-k} + A_k} \right)^2 \left( \frac{N_k}{K_{N-k} N_k} \right) L_h \left( \gamma_{Bk} B_k \right)
\]

if \( I = A_k = n \) \hfill (3.3.71)

If inhibitor \( I \in K_x + K_y + M_z + M_p \) and \( I = N_k, I \neq A_k, I \neq S_k, I \neq B_k \):

\[
\frac{\partial (r^m_{\text{bio-deg}})}{\partial e_n} =
\]

\[
\frac{v'_{km} - v''_{km}}{\gamma_m} (\Gamma_{k,T} \Gamma_{1k} I_{pH} s_w) \frac{p}{K_{11}} \left( 1 + \frac{I}{K_{11}} \right)^{p-1} \left( \frac{S_k}{K_{S-k} I_{2k} + S_k} \right) \left( \frac{A_k}{K_{A-k} + A_k} \right) \left( \frac{N_k}{K_{S-k} N_k} \right) L_h \left( \gamma_{Bk} B_k \right)
\]

\[
\frac{v'_{km} - v''_{km}}{\gamma_m} (\Gamma_{k,T} \Gamma_{1k} I_{pH} s_w) \frac{qK_{S-k}}{K_{S-k} \left( 1 + \frac{I}{K_{12}} \right)^q + S_k} \left( \frac{A_k}{K_{A-k} + A_k} \right) \left( \frac{N_k}{K_{S-k} + N_k} \right) L_h \left( \gamma_{Bk} B_k \right)
\]

\[
\frac{v'_{km} - v''_{km}}{\gamma_m} (\Gamma_{k,T} \Gamma_{1k} I_{pH} s_w) \left( \frac{S_k}{K_{S-k} I_{2k} + S_k} \right) \left( \frac{A_k}{K_{A-k} + A_k} \right) \left( \frac{K_{N-k}}{(K_{N-k} + N_k)^2} \right) L_h \left( \gamma_{Bk} B_k \right)
\]

if \( I = N_k = n \) \hfill (3.3.72)

For any other species participating in the k-th microbial reaction, the contribution to the Jacobian
for columns \( n \in K_x + K_y + M_z + M_p \) is zero.

For column \( n \in M_h + M_a \), \( j = n + N + K_x + K_y + M_z + M_p \), the contribution to the Jacobian from the k-th microbial degradation reaction is:

If \( B_k \neq I \)

\[
\frac{\partial \left( p_m^{\text{bio}} \right)}{\partial e_n} = \frac{v''_{km} - v'_{km}}{\gamma_m} \left( \Gamma_{k,T} I_{pk} I_{pH} S_w \right) \left( \frac{S_k}{K_{S-k} I_{2k} + S_k} \right) \left( \frac{K_{S-k}}{(K_{S-k} + A_k)^2} \right) \left( \frac{N_k}{K_{N-k} + N_k} \right) L_k \delta_{mn}
\]

(3.3.73)

If \( B_k = I \)

\[
\frac{\partial \left( p_m^{\text{bio}} \right)}{\partial e_n} = \frac{v''_{km} - v'_{km}}{\gamma_m} \left( \Gamma_{k,T} I_{pk} I_{pH} S_w \right) \left( \frac{S_k}{K_{S-k} I_{2k} + S_k} \right) \left( \frac{A_k}{K_A + A_k} \right) \left( \frac{N_k}{K_{S-k} + N_k} \right) L_k (\gamma_B B_k) -
\]

\[
\frac{v''_{km} - v'_{km}}{\gamma_m} \left( \Gamma_{k,T} I_{pk} I_{pH} S_w \right) \left( \frac{S_k q K_{S-k} \left( 1 + \frac{1}{K_{I2}} \right)^{q-1}}{K_{S-k} \left( 1 + \frac{1}{K_{I2}} \right)^q + S_k} \right) \left( \frac{A_k}{K_{A-k} + A_k} \right) \left( \frac{N_k}{K_{S-k} + N_k} \right) L_k (\gamma_B B_k)
\]
\[ + \frac{v''_{km} - v'_{km}}{\gamma_m} \left( \Gamma_{k,T} I_{1k} I_p I_{1} g_S \right) \left( \frac{S_k}{K_{S-k} I_{2k} + S_k} \right) \left( \frac{K_{S-k}}{K_{S-k} + A_k} \right) \left( \frac{N_k}{K_{N-k} + N_k} \right) L_k \delta_{mn} \]

If \( I = n \) \hspace{2cm} (3.3.74)

3.3.3.5 Contribution from microbial endogenous respiration

The contribution to the Jacobian from endogenous respiration of the k-th microbial species \( k \in M_B \) is:

For columns \( n \in N_a + N_x + K_x + K_y + M_z + M_p + M_h, \ j = n \), the contribution to the Jacobian from maintenance/ respiration of the k-th microbial species is:

\[ \frac{\partial (r''_{mk}^{biodeg})}{\partial e_n} = \alpha_{km} K_k^d B_k \left( \frac{\kappa_{km}}{\kappa_{km} + x_m} \right) \delta_{mn} \] \hspace{2cm} (3.3.75)

For columns \( n \in M_h + M_a, \ j = N_a + N_x + K_x + K_y + M_z + M_p + M_h \), the contribution to the Jacobian from maintenance/ respiration of the k-th microbial species is:

\[ \frac{\partial (r''_{mk}^{biodeg})}{\partial e_n} = \alpha_{km} K_k^d \left( \frac{x_m}{\kappa_{km} + x_m} \right) \delta_{kn} \] \hspace{2cm} (3.3.76)
3.3.4 Rows for $K_y$ species

The next set of Jacobians, for the kinetic absorbed species, is similar in form to that for the kinetic aqueous complexed species. The jacobian for the rows corresponding to the

Jacobians for the rows corresponding to the $K_y$ kinetic adsorbed species. For the

$m = 1, 2, \ldots, K_y, i = m + N + K_x,$ are:

\[ G_{ij} = \frac{\partial R_m}{\partial c_n} = -\frac{\partial r^y_m}{\partial c_n}, \quad n \in N_a, \quad j = n \quad (3.3.77) \]

\[ G_{ij} = \frac{\partial R_m}{\partial s_n} = -\frac{\partial r^y_m}{\partial s_n}, \quad n \in N_s, \quad j = n + N_a \quad (3.3.78) \]

\[ G_{ij} = \frac{\partial R_m}{\partial x_n} = -\frac{\partial r^y_m}{\partial x_n}, \quad n \in K_x, \quad j = n + N \quad (3.3.79) \]

\[ G_{ij} = \frac{\partial R_m}{\partial y_n} = -\frac{\partial r^y_m}{\partial y_n} + \left( \frac{1}{\Delta t} + \lambda_m^y + \alpha \frac{\partial p}{\partial t} + \frac{1}{\rho_b} \frac{\Delta \rho_b}{\Delta t} \right) \delta_{mn}, \quad (3.3.80) \]

\[ n \in K_y, \quad j = n + N + K_x \]
\[ G_{ij} = \frac{\partial R_m}{\partial z_n} = -\frac{\partial r_m^y}{\partial z_n}, \quad n \in M_y, \quad j = n + N + K_x + K_y \]  (3.3.81)

\[ G_{ij} = \frac{\partial R_m}{\partial p_n} = -\frac{\partial r_m^y}{\partial p_n}, \quad n \in M_p, \quad j = n + N + K_x + K_y + M_z \]  (3.3.82)

\[ G_{ij} = \frac{\partial R_m}{\partial b_n} = -\frac{\partial r_m^y}{\partial b_n}, \quad n \in M_b, \quad j = n + N + K_x + K_y + M_z + M_p \]  (3.3.83)

\[ G_{ij} = \frac{\partial R_m}{\partial a_n} = -\frac{\partial r_m^y}{\partial a_n}, \quad n \in M_a, \quad j = n + N + K_x + K_y + M_z + M_p + M_b \]  (3.3.84)

\[ G_{ij} = \frac{\partial R_m}{\partial h_n^b} = -\frac{\partial r_m^y}{\partial h_n^b}, \quad n \in h^b, \quad j = n + N + K_x + K_y + M_z + M_p + M_b + M_a \]  (3.3.85)

\[ G_{ij} = \frac{\partial R_m}{\partial h_n^b} = -\frac{\partial r_m^y}{\partial h_n^b}, \quad n \in h^b, \quad j = n + N + K_x + K_y + M_z + M_p + M_b + M_a + h^b \]  (3.3.86)

\[ G_{ij} = \frac{\partial R_m}{\partial P_n} = -\frac{\partial r_m^{x^2}}{\partial P_n}, \quad n \in M_g, \quad j = n + N + K_x + K_y + M_z + M_p + M_b + M_a + h^b + h^v \]  (3.3.87)
The partial derivatives of the production / consumption rate terms are evaluated as follows:

\[
\frac{\partial r_{m}^{v}}{\partial e_{n}} = \sum_{k=1}^{NBRXNK} \frac{\partial}{\partial e_{n}} \left( r_{m}^{\text{chem}} \right) + \sum_{k=1}^{NBRXNK} \frac{\partial}{\partial e_{n}} \left( r_{m}^{\text{bio-deg}} \right) - \frac{\partial \left( r_{m}^{\text{bioresp}} \right)}{\partial e_{n}}
\]

\[
= \sum_{k=1}^{NBRXNK} \frac{\partial}{\partial e_{n}} \left[ \frac{v_{k,m}^{v} - v_{k,m}^{v'}}{\gamma_{m}} \left( k_{x}^{l} \prod_{i=M}^{l} (\gamma_{i,e})^{v_{i,i}} - k_{k}^{b} \prod_{i=M}^{l} (\gamma_{i,e})^{v_{i,i}} \right) \right]
\]

\[
+ \sum_{k=1}^{NBRXNK} \frac{\partial}{\partial e_{n}} \left[ \frac{v_{k,m}^{v} - v_{k,m}^{v'}}{\gamma_{m}} \left( \Gamma_{k,t} I_{k,m} I_{pH} S_{w} \left( \frac{S_{k}}{K_{S-k} I_{k,m}^{2}} \right) + S_{k} \right) \left( \frac{A_{k}}{K_{A-k} + A_{k}} \right) \left( \frac{N_{k}}{K_{N-k} + N_{k}} \right) L_{k} \left( \gamma_{k,m} B_{k} \right) \right]
\]

\[
- \sum_{k=1}^{M_{k}} \frac{\partial}{\partial e_{n}} \left[ \alpha_{k,m} K_{i}^{d} B_{k} \left( \frac{x_{m}}{K_{i,m} + x_{m}} \right) \right]
\]

(3.3.88)

As for the kinetic complexed species rows, the partial derivatives of the production / consumption rate terms are evaluated by taking the derivative with respect to \( e_{n} \) term by term to evaluate the contribution to the Jacobian from each species participating in each kinetic reaction. Except for the ion-exchange species, which do not take part in the kinetic adsorbed species reactions, the Jacobian terms from Eqns. 3.3.35 to 3.3.48 for kinetic complexed species can be directly used for kinetic adsorbed species. Similarly, Eqns. 3.3.52 through 3.3.74 can be used to evaluate the contribution of the microbial degradation reactions and microbial endogenous respiration terms to the Jacobian Eqns. 3.3.75 and 3.3.76 for kinetic adsorbed species rows.
3.3.5 Rows for $z_n$ species

The Jacobian terms for the rows of ion-exchange species are $m = 1, 2, \ldots, M_z$, $i = m + N + K_x + K_y$, depend on whether the species $m$ is (1) a “reference” ion-exchange species for one of the ion-exchange sites, (2) an equilibrium controlled ion-exchanged species, or (3) a kinetically controlled ion-exchanged species. The Jacobians for each of these three cases follow as per given in BIOKEMOD:

If species $m$ is the “reference species for an ion exchange site, the residual for this species is given by Eqn. 3.2.5 and the Jacobian for this row is evaluated as follows:

\[
GJ_{ij} = \frac{\partial R_m}{\partial c_n} = 0, \quad n \in N_a, \quad j = n \tag{3.3.89}
\]

\[
GJ_{ij} = \frac{\partial R_m}{\partial s_n} = 0, \quad n \in N_s, \quad j = n + N_a \tag{3.3.90}
\]

\[
GJ_{ij} = \frac{\partial R_m}{\partial x_n} = 0, \quad n \in K_x, \quad j = n + N \tag{3.3.91}
\]

\[
GJ_{ij} = \frac{\partial R_m}{\partial y_n} = 0, \quad n \in K_y, \quad j = n + N + K_x \tag{3.3.92}
\]
\[ G_{ij} = \frac{\partial R_m}{\partial z_n} = -\rho_b \sum_{f=1}^{M_x} v_n h_f, \quad z_n \in \text{NOMZI}(i) \] (3.3.93)

\[ n \in M_y, \quad j = n + N + K_x + K_y \]

\[ G_{ij} = \frac{\partial R_m}{\partial z_n} = 0, \quad z_n \notin \text{NOMZI}(i) \] (3.3.94)

\[ n \in M_y, \quad j = n + N + K_x + K_y \]

\[ G_{ij} = \frac{\partial R_m}{\partial p_n} = 0, \quad n \in M_p, \quad j = n + N + K_x + K_y + M_z \] (3.3.95)

\[ G_{ij} = \frac{\partial R_m}{\partial B_n} = 0, \quad n \in M_b + M_a, \quad j = n + N + K_x + K_y + M_z + M_p \] (3.3.96)

\[ G_{ij} = \frac{\partial R_m}{\partial h_n} = -\rho_b \sum_{k=1}^{M_x} \left( \sum_{l=\text{NOMZI}(j+1)_b}^{\text{NOMZI}(j)_b} v_l z_l \right), \] (3.3.97)

\[ n \in h^b + h^c, \quad j = n + N + K_x + K_y + M_z + M_p + M_b + M_a \]

\[ G_{ij} = \frac{\partial R_m}{\partial p_n} = 0, \quad n \in M_g, \quad j = n + N + K_x + K_y + M_z + M_p + M_b + M_a + h^b + h^c \] (3.3.98)
If species $m$ is an equilibrium controlled ion-exchange species and is not the “reference” species for an ion exchange site, the residual for this species is given by Eqn. 3.2.6 and the Jacobian for this row is evaluated as follows:

For columns $n \in N_a$, $j = n$, the contribution to the Jacobian is:

From reactant $r \in N_a$ in the equilibrium reaction $k$ which defines the formation of species $m$:

$$
\frac{\partial R_m}{\partial e_n} = -K_{eq}^k \left( \frac{v'_{kn}}{c_n} \right) \left( \prod_{l=\{N_x+M_z+M_z\}} (\gamma_l e_l)^{y_{li}} \right) \text{ if } r = n
$$

(3.99)

From product $p \in N_a$ in the equilibrium reaction $k$ which defines the formation of species $m$:

$$
\frac{\partial R_m}{\partial e_n} = \left( \frac{v^p_{kn}}{c_n} \right) \left( \prod_{l=\{N_x+M_z+M_z\}} (\gamma_l e_l)^{y_{li}} \right) \text{ if } p = n
$$

(3.100)

From reactant $r \in (M_x - K_x)$ in the equilibrium reaction $k$ which defines the formation of species $m$:

$$
\frac{\partial R_m}{\partial e_n} = -K_{eq}^k \left( \frac{v'_{kn}}{c_n} \right) \left( \frac{v'_{kr}}{v^p_{kr}} \right) \left( \prod_{l=\{N_x+M_z+M_z\}} (\gamma_l e_l)^{y_{li}} \right) \text{ if } r = n
$$

(3.101)
where \( k \in NRXNE \) is the equilibrium reaction defining the formation of equilibrium species \( r \).

From product \( p \in (M_x - K_x) \) in the equilibrium reaction \( k \) which defines the formation of species \( m \):

\[
\frac{\partial R_m}{\partial e_n} = \left( \frac{V_{kr}^n}{e_n} \right) \left( \frac{V_{kn}'}{V_{kr}'} \right) \prod_{\ell \in (N_x + M_x + M_y)} (\gamma_{e_\ell} v_{ij})^{v_{ij}} \quad \text{if } p = n
\]  

(3.3.102)

For any other reactant species \( r \) or product species \( p \), the contribution to the Jacobian in columns \( n \in N_a \) is zero.

For columns \( n \in N_x, K_x, K_y, j = n + N_a \), the Jacobian entry is zero:

\[
\frac{\partial R_m}{\partial e_n} = 0, \quad n \in N_x, K_x, K_y, j = n + N_a
\]  

(3.3.103)

For columns \( n \in M_z, j = n + N + K_x + K_y \), the contribution to the Jacobian is:

For reactant \( r \in M_z \) in the equilibrium reaction \( k \) which defines the formation of species \( m \):

\[
\frac{\partial R_m}{\partial z_n} = -K_k^{eq} \left( \prod_{\ell \in (N_x + M_x + M_y)} (\gamma_{e_\ell} v_{ij})^{v_{ij}} \right) \frac{1}{\gamma_n} \quad \text{if } r = n
\]  

(3.3.104a)
\[
K_k^{eq} \left( \prod_{i \in \{N_a, M_a, M_z\}} (\gamma_i e_i)^{\psi_i} \right) v_k' \gamma_p \quad \text{if } r \neq n, \; n \in \text{NOMZI}(i) \quad (3.3.104b)
\]

\[
= 0 \quad \text{if } r \neq n, \; n \notin \text{NOMZI}(i) \quad (3.3.104c)
\]

For product \( p \in M_z \) in the equilibrium reaction \( k \) which defines the formation of species \( m \):

\[
\frac{\partial R_m}{\partial z_n} = K_k^{eq} \left( \prod_{i \in \{N_a, M_a, M_z\}} (\gamma_i e_i)^{\psi_i} \right) v_k' \left( \frac{1}{z_n} - \gamma_n \right) \quad \text{if } p = n \quad (3.3.105a)
\]

\[
= K_k^{eq} \left( \prod_{i \in \{N_a, M_a, M_z\}} (\gamma_i e_i)^{\psi_i} \right) v_k' \gamma_p \quad \text{if } p \neq n, \; n \in \text{NOMZI}(i) \quad (3.3.105b)
\]

\[
= 0 \quad \text{if } p \neq n, \; n \notin \text{NOMZI}(i) \quad (3.3.105c)
\]

where \( i \in \text{NSITE} \) is the ion exchange site of reaction \( k \)

For any other reactant or product species, the contribution to the jacobian for columns \( n \in M_z \) is
For columns $n \in M_p$, $j = n + N + K_x + K_y + M_z$, the contribution to the Jacobian is zero.

$$\frac{\partial R_m}{\partial p_n} = 0$$ (3.3.106)

For columns $n \in M_b + M_a$, $j = n + N + K_x + M_z + M_p$, the contribution to the Jacobian is zero.

$$\frac{\partial R_m}{\partial b_n} = 0$$ (3.3.107)

$$\frac{\partial R_m}{\partial a_n} = 0$$ (3.3.108)

For columns $n \in M_h$, $j = n + N + K_x + K_y + M_z + M_p + M_b + M_a$, the contribution to the Jacobian is zero.

$$\frac{\partial R_m}{\partial h_n} = 0$$ (3.3.109)

For columns $n \in M_s$, $j = n + N + K_x + K_y + M_z + M_p + M_b + M_a + M_s$, the contribution to the
Jacobian is zero.

\[
\frac{\partial R_m}{\partial P_n} = 0 \tag{3.3.110}
\]

If species m is kinetic controlled ion-exchanged species and is not a “reference” species, the residual for this row is given by Eqn. 3.2.7 and the Jacobian for this row is evaluated as follows:

\[
G_{J_{ij}} = \frac{\partial R_m}{\partial c_n} = -\frac{\partial r^z_m}{\partial c_n}, \quad n \in N_a, \quad j = n \tag{3.3.111}
\]

\[
G_{J_{ij}} = \frac{\partial R_m}{\partial s_n} = -\frac{\partial r^z_m}{\partial s_n}, \quad n \in N_s, \quad j = n + N_a \tag{3.3.112}
\]

\[
G_{J_{ij}} = \frac{\partial R_m}{\partial x_n} = -\frac{\partial r^z_m}{\partial x_n}, \quad n \in K_x, \quad j = n + N \tag{3.3.113}
\]

\[
G_{J_{ij}} = \frac{\partial R_m}{\partial y_n} = -\frac{\partial r^z_m}{\partial y_n}, \quad n \in K_y, \quad j = n + N + K_x \tag{3.3.114}
\]

\[
G_{J_{ij}} = \frac{\partial R_m}{\partial z_n} = -\frac{\partial r^z_m}{\partial z_n} + \left( \frac{1}{\Delta t} + \dot{\lambda}_m + \alpha \frac{\partial \rho}{\partial t} + \frac{1}{\rho_b} \frac{\Delta \rho_b}{\Delta t} \right) \delta_{mn}, \quad n \in M_y, \quad j = n + N + K_x + K_y \tag{3.3.115}
\]
\[ G_{ij} = \frac{\partial R}{\partial x_i} = -\frac{\partial r}{\partial x_i}, \quad n \in M_p, \quad j = n + K_x + K_y + M_z \] (3.3.116)

\[ G_{ij} = \frac{\partial R}{\partial b_i} = -\frac{\partial r}{\partial b_i}, \quad n \in M_b, \quad j = n + K_x + K_y + M_z + M_p \] (3.3.117)

\[ G_{ij} = \frac{\partial R}{\partial a_i} = -\frac{\partial r}{\partial a_i}, \quad n \in M_a, \quad j = n + K_x + K_y + M_z + M_p + M_b \] (3.3.118)

\[ G_{ij} = \frac{\partial R}{\partial h_i} = -\frac{\partial r}{\partial h_i}, \quad n \in h^b, \quad j = n + K_x + K_y + M_z + M_p + M_b + M_a \] (3.3.119)

\[ G_{ij} = \frac{\partial R}{\partial h_i^a} = -\frac{\partial r}{\partial h_i^a}, \quad n \in h^a, \quad j = n + K_x + K_y + M_z + M_p + M_b + M_a + h^b \] (3.3.120)

\[ G_{ij} = \frac{\partial R}{\partial P_i} = -\frac{\partial r}{\partial P_i}, \quad n \in M_x, \quad j = n + K_x + K_y + M_z + M_p + M_b + M_a + h^b + h^s \] (3.3.121)

Except for the kinetic complexed and adsorbed species, which do not take part in the kinetic ion-exchange reactions, the Jacobian terms from Eqns. 3.3.35 to 3.3.48 for kinetic complexed species
can be directly used for kinetic adsorbed species. Similarly, Eqns. 3.3.52 through 3.3.74 can be used to evaluate the contribution of the microbial degradation reactions and microbial endogenous respiration terms to the Jacobian Eqns. 3.3.75 and 3.3.76 for kinetic ion-exchange species rows. It has to be noted that sorbent component species, adsorbed species or precipitated species do not participate in chemical reactions involving ion exchange, the contribution to the Jacobian from chemical reactions for these columns will be zeros for kinetic ion-exchanged species rows.

3.3.6 Rows for \( M_p \) species

For the rows corresponding to the precipitated species, \( m = 1, \ldots, M_p \), \( i = m + K_x + K_y + M_z \), the Jacobian terms will depend on whether the species is equilibrium or kinetic controlled. For the equilibrium case, the residual equation is 3.2.8 and the Jacobian row \( m \) are:

For columns \( n \in N_a \), \( j = n \):

From reactant \( r \in N_a \) in the equilibrium reaction \( k \) which defines the formation of species \( m \):

\[
\frac{\partial R_m}{\partial e_n} = -K_k^{eq} \left( \frac{v'_{kn}}{c_n} \prod_{i \in M} (\gamma_i e_i)^{\gamma_{ki}} \right) \quad \text{if } r = n \tag{3.3.122}
\]

From reactant \( r \in (M_x - K_x) \) in the equilibrium reaction \( k \) which defines the formation of species \( m \):
\[
\frac{\partial R_m}{\partial c_n} = -K^e_{kl} \left( \frac{v'_{kn} v'_{rm}}{c_n} \right) \left( \prod_{l=1}^{\text{eq}} (\gamma_l e_l)^{v'_{kl}} \right) \quad \text{if } r = n
\] (3.3.123)

For other column, contribution to the Jacobian is zero:

\[
G_{ij} = \frac{\partial R_m}{\partial s_n} = 0, \quad n \in N_x, \quad j = n + N_a
\] (3.3.124)

\[
G_{ij} = \frac{\partial R_m}{\partial x_n} = 0, \quad n \in K_x, \quad j = n + N
\] (3.3.125)

\[
G_{ij} = \frac{\partial R_m}{\partial y_n} = 0, \quad n \in K_y, \quad j = n + N + K_x
\] (3.3.126)

\[
G_{ij} = \frac{\partial R_m}{\partial z_n} = 0, \quad n \in M_y, \quad j = n + N + K_x + K_y
\] (3.3.127)

\[
G_{ij} = \frac{\partial R_m}{\partial p_n} = 0, \quad n \in M_p, \quad j = n + N + K_x + K_y + M_z
\] (3.3.128)

\[
G_{ij} = \frac{\partial R_m}{\partial B_n} = 0, \quad n \in M_b + M_a, \quad j = n + N + K_x + K_y + M_z + M_p
\] (3.3.129)
\[ GJ_{ij} = \frac{\partial R_m}{\partial h_n} = 0, \quad n \in h^h + h^s \quad j = n + N + K_x + K_y + M_z + M_p + M_b + M_a \quad (3.3.130) \]

\[ GJ_{ij} = \frac{\partial R_m}{\partial P_n} = 0, \quad n \in M_g, \quad j = n + N + K_x + K_y + M_z + M_p + M_b + M_a + h^h + h^s \quad (3.3.131) \]

For kinetic precipitated species, the residual equation is 3.2.9 and the Jacobians for row m are:

\[ GJ_{ij} = \frac{\partial R_m}{\partial c_n} = -\frac{\partial r^p_m}{\partial c_n}, \quad n \in N_a, \quad j = n \quad (3.3.132) \]

\[ GJ_{ij} = \frac{\partial R_m}{\partial s_n} = -\frac{\partial r^p_m}{\partial s_n}, \quad n \in N_s, \quad j = n + N_a \quad (3.3.133) \]

\[ GJ_{ij} = \frac{\partial R_m}{\partial x_n} = -\frac{\partial r^p_m}{\partial x_n}, \quad n \in K_x, \quad j = n + N \quad (3.3.134) \]

\[ GJ_{ij} = \frac{\partial R_m}{\partial y_n} = -\frac{\partial r^p_m}{\partial y_n}, \quad n \in K_y, \quad j = n + N + K_x \quad (3.3.135) \]

\[ GJ_{ij} = \frac{\partial R_m}{\partial z_n} = -\frac{\partial r^p_m}{\partial z_n}, \quad n \in M_y, \quad j = n + N + K_x + K_y \quad (3.3.136) \]
\[ GJ_{ij} = \frac{\partial R_m}{\partial p_n} = -\frac{\partial r_m^p}{\partial p_n} + \left( \frac{1}{\Delta t} + \lambda_m^p + \alpha \frac{\partial p}{\partial t} + \frac{1}{\rho_b} \frac{\Delta \rho_b}{\Delta t} \right) \delta_{mn}, \] (3.3.137)

\[ n \in M_p, \ j = n + N + K_x + K_y + M_z \]

\[ GJ_{ij} = \frac{\partial R_m}{\partial b_n} = -\frac{\partial r_m^b}{\partial b_n}, \ n \in M_b, \ j = n + N + K_x + K_y + M_z + M_p \] (3.3.138)

\[ GJ_{ij} = \frac{\partial R_m}{\partial a_n} = -\frac{\partial r_m^a}{\partial a_n}, \ n \in M_a, \ j = n + N + K_x + K_y + M_z + M_p + M_b \] (3.3.139)

\[ GJ_{ij} = \frac{\partial R_m}{\partial h_n^b} = -\frac{\partial r_m^b}{\partial h_n^b}, \ n \in h^b, \ j = n + N + K_x + K_y + M_z + M_p + M_b + M_a \] (3.3.140)

\[ GJ_{ij} = \frac{\partial R_m}{\partial h_n^a} = -\frac{\partial r_m}{\partial h_n^a}, \ n \in h^a, \ j = n + N + K_x + K_y + M_z + M_p + M_b + M_a + h^b \] (3.3.141)

\[ GJ_{ij} = \frac{\partial R_m}{\partial P_n} = -\frac{\partial r_m}{\partial P_n}, \ n \in M_{\rho}, \ j = n + N + K_x + K_y + M_z + M_p + M_b + M_a + h^b + h^a \] (3.3.142)

As done for other kinetic chemical species rows, the partial derivatives of the production/
consumption rate terms are evaluated by taking the partial derivatives terms by term for each species participating in chemical and microbiological reaction. The Jacobian terms from Eqns. 3.3.35 to 3.3.48 for kinetic complexed species can be used for kinetic precipitated species. Similarly, Eqns. 3.3.52 through 3.3.74 can be used to evaluate the contribution of the microbial degradation reactions and microbial endogenous respiration terms to the Jacobian Eqns. 3.3.75 and 3.3.76 for kinetic precipitated species rows. It has to be noted that sorbent component species, adsorbed species or ion-exchanged species do not participate in chemical reactions involving precipitation, the contribution to the Jacobian from chemical reactions for these columns will be zeros for kinetic precipitated species rows.

3.3.7 Rows for \( M_b \) species

For the rows corresponding to the aqueous phase microbial species, \( m = 1, \ldots, M_b \), \( i = m + N + K_x + K_y + M_z + M_p \), the residual equation is 3.2.10 and the Jacobians for row \( m \) are:

\[
GJ_{ij} = \frac{\partial R_m}{\partial c_n} = -\frac{\partial r_m^{bg}}{\partial c_n}, \quad n \in N_a, \quad j = n
\]  

(3.3.143)

\[
GJ_{ij} = \frac{\partial R_m}{\partial s_n} = -\frac{\partial r_m^{bg}}{\partial s_n}, \quad n \in N_s, \quad j = n + N_a
\]  

(3.3.144)

\[
GJ_{ij} = \frac{\partial R_m}{\partial x_n} = -\frac{\partial r_m^{bg}}{\partial x_n}, \quad n \in K_x, \quad j = n + N
\]  

(3.3.145)
\begin{align*}
GJ_{ij} &= \frac{\partial R_m^{bg}}{\partial y_n} = -\frac{\partial r_{x_n}^{bg}}{\partial y_n}, \quad n \in K_y, \ j = n + N + K_x \tag{3.3.146} \\
GJ_{ij} &= \frac{\partial R_m^{bg}}{\partial z_n} = -\frac{\partial r_{y_n}^{bg}}{\partial z_n}, \quad n \in M_y, \ j = n + N + K_x + K_y \tag{3.3.147} \\
GJ_{ij} &= \frac{\partial R_m^{bg}}{\partial p_n} = -\frac{\partial r_{z_n}^{bg}}{\partial p_n}, \quad n \in M_p, \ j = n + N + K_x + K_y + M_z \tag{3.3.148} \\
GJ_{ij} &= \frac{\partial R_m^{bg}}{\partial b_n} = -\frac{\partial r_{y_n}^{fr}}{\partial b_n} - \frac{\partial r_{x_n}^{fr}}{\partial b_n} + \left( \frac{1}{\Delta t} + K_m^d + K_m^d \right) \frac{\partial p}{\partial t} + \frac{1}{\rho \phi s_w} \frac{\partial \rho \phi s_w}{\partial t} + \frac{Q_{out}^{ou}}{\phi s_w} \delta_{mn}, \quad n \in M_b, \ j = n + N + K_x + K_y + M_z + M_p \tag{3.3.149} \\
GJ_{ij} &= \frac{\partial R_m^{bg}}{\partial a_n} = -\frac{\partial r_{y_n}^{fr}}{\partial a_n}, \quad n \in M_a, \ j = n + N + K_x + K_y + M_z + M_p + M_b \tag{3.3.150} \\
GJ_{ij} &= \frac{\partial R_m^{bg}}{\partial h_n^b} = -\frac{\partial r_{y_n}^{bg}}{\partial h_n^b}, \quad n \in h^b, \ j = n + N + K_x + K_y + M_z + M_p + M_b + M_a \tag{3.3.151} \\
GJ_{ij} &= \frac{\partial R_m^{bg}}{\partial h_n} = -\frac{\partial r_{y_n}^{bg}}{\partial h_n}, \quad n \in h', \ j = n + N + K_x + K_y + M_z + M_p + M_b + M_a + h^b \tag{3.3.152}
\end{align*}
The partial derivatives of the microbial growth rate terms are evaluated as follows:

\[
\frac{\partial r_{mg}}{\partial e_n} = \sum_{k=1}^{\text{NBRXNK}} \frac{\partial r_{mg}^k}{\partial e_n} \bigg|_K \tag{3.3.154}
\]

\[
= \sum_{k=1}^{\text{NBRXNK}} \frac{\partial}{\partial e_n} \left[ \frac{v_{km} - v'_{km}}{\gamma_m} \left( \gamma_{m} \left( \frac{S_k}{K_{S-k}} + S_k \right) \left( \frac{A_k}{K_{A-k}} + A_k \right) \left( \frac{N_k}{K_{N-k}} + N_k \right) \right) L_k (v_{bh})^{B_k} \right] \tag{3.3.155}
\]

The derivative with respect to \( e_n \) is taken term by term for each species in each microbiological reaction and their contributions to the Jacobian for row \( m \) are summed. For a given row \( m \), the evaluation of these derivatives is analogous to that outlined for the Jacobians for the kinetic species rows. Eqns 3.3.52 through 3.3.74 can be used to evaluate the microbiological growth contributions in the Jacobian Eqns. 3.3.143 through 3.3.153.

The partial derivatives of the microbial phase transfer terms are evaluated as follows:

\[
\frac{\partial r_{mfr}}{\partial e_n} = \sum_{k=1}^{\text{NBRXNK}} \frac{\partial r_{mfr}^k}{\partial e_n} \bigg|_K \tag{3.3.156}
\]

\[
= \sum_{k=1}^{\text{NBRXNK}} \frac{\partial}{\partial e_n} \left[ \left( \gamma_{m} \right) \left( k_m^f \left( \gamma_{m} \right) \right) \gamma_m' \right] \left( k_m^b \left( \gamma_{m} \right) \right) \gamma_m'^* \left( \gamma_{m} \right) \gamma_m'^* \right] \tag{3.3.157}
\]

\[ j \in M_a \]
For columns \( n \in N_a + N_s + K_x + K_y + M_z + M_p, \ j = n \), the contribution to the Jacobian from the microbial phase transfer reaction is zero.

For columns \( n \in M_h, \ j = n + N_a + N_s + K_x + K_y + M_z + M_p \), the contribution to the Jacobian from the microbial phase transfer reaction is:

\[
\frac{\partial r_{i,j}^{{fr}}}{\partial e_n} = \left( \frac{v_i^n - v_i'}{\gamma_m} \right) k_k v_k m (y_{m,b_m}^{m-1}) \delta_{m,n}
\]

(3.3.156)

3.3.8 Rows for \( M_a \) species

For the rows corresponding to the adsorbed phase microbial species, \( m = 1, \ldots, M_a \), \( i = m + N + K_x + K_y + M_z + M_p + M_h \), the residual equation is 3.2.10 and the Jacobians for row \( m \) are:

\[
G_{ij} = \frac{\partial R_m}{\partial c_n} = -\frac{\partial r_{m,b_g}}{\partial c_n}, \quad n \in N_a, \quad j = n
\]

(3.3.157)

\[
G_{ij} = \frac{\partial R_m}{\partial s_n} = -\frac{\partial r_{m,b_g}}{\partial s_n}, \quad n \in N_s, \quad j = n + N_a
\]

(3.3.158)
\[ G_{ij} = \frac{\partial R_m}{\partial x_n} = -\frac{\partial r_m^{bg}}{\partial x_n}, \quad n \in K_x, \quad j = n + N \]  \hspace{1cm} (3.3.159)

\[ G_{ij} = \frac{\partial R_m}{\partial y_n} = -\frac{\partial r_m^{bg}}{\partial y_n}, \quad n \in K_y, \quad j = n + N + K_x \]  \hspace{1cm} (3.3.160)

\[ G_{ij} = \frac{\partial R_m}{\partial z_n} = -\frac{\partial r_m^{bg}}{\partial z_n}, \quad n \in M_y, \quad j = n + N + K_x + K_y \]  \hspace{1cm} (3.3.161)

\[ G_{ij} = \frac{\partial R_m}{\partial p_n} = -\frac{\partial r_m^{fr}}{\partial p_n}, \quad n \in M_p, \quad j = n + N + K_x + K_y + M_z \]  \hspace{1cm} (3.3.162)

\[ G_{ij} = \frac{\partial R_m}{\partial b_n} = -\frac{\partial r_m^{fr}}{\partial b_n}, \quad n \in M_b, \quad j = n + N + K_x + K_y + M_z + M_p \]  \hspace{1cm} (3.3.163)

\[ G_{ij} = \frac{\partial R_m}{\partial a_n} = -\frac{\partial r_m^{bg}}{\partial a_n} - \frac{\partial r_m^{fr}}{\partial a_n} + \left( \frac{1}{\Delta t} + K_m^d + \alpha \frac{\partial p}{\partial t} + \frac{1}{\rho_b} \frac{\Delta \rho_b}{\Delta t} \right) \delta_{mn}, \quad n \in M_a, \quad j = n + N + K_x + K_y + M_z + M_p + M_h \]  \hspace{1cm} (3.3.164)

\[ G_{ij} = \frac{\partial R_m}{\partial h_n} = -\frac{\partial r_m^{bg}}{\partial h_n}, \quad n \in h^b, \quad j = n + N + K_x + K_y + M_z + M_p + M_b + M_a \]  \hspace{1cm} (3.3.165)
The partial derivatives of the microbiological growth rate and phase transfer terms are evaluated as for the aqueous microbiological species row.

### 3.3.9 Rows for $M_{h^b}$ species

For the rows corresponding to the aqueous phase solids species, $m = 1, \ldots, M_{h^b}$, $i = m + N + K_x + K_y + M_z + M_p + M_b + M_a$, the residual equation is 3.2.10 and the Jacobians for row $m$ are:

\[
G_{ij} = \frac{\partial R_m}{\partial c_n} = -\frac{\partial_r^{bg}}{\partial c_n}, \quad n \in N_a, \quad j = n
\]  

(3.3.168)

\[
G_{ij} = \frac{\partial R_m}{\partial s_n} = -\frac{\partial_r^b}{\partial s_n}, \quad n \in N_s, \quad j = n + N_a
\]  

(3.3.169)
\[ GJ_{ij} = \frac{\partial R_m}{\partial x_n} = -\frac{\partial r_m^h}{\partial x_n}, \quad n \in K_x, \quad j = n + N \]  
(3.3.170)

\[ GJ_{ij} = \frac{\partial R_m}{\partial y_n} = -\frac{\partial r_m^h}{\partial y_n}, \quad n \in K_y, \quad j = n + N + K_x \]  
(3.3.171)

\[ GJ_{ij} = \frac{\partial R_m}{\partial z_n} = -\frac{\partial r_m^h}{\partial z_n}, \quad n \in M_y, \quad j = n + N + K_x + K_y \]  
(3.3.172)

\[ GJ_{ij} = \frac{\partial R_m}{\partial p_n} = -\frac{\partial r_m^h}{\partial p_n}, \quad n \in M_p, \quad j = n + N + K_x + K_y + M_z \]  
(3.3.173)

\[ GJ_{ij} = \frac{\partial R_m}{\partial b_n} = -\frac{\partial r_m^h}{\partial b_n}, \quad n \in M_b, \quad j = n + N + K_x + K_y + M_z + M_p \]  
(3.3.174)

\[ GJ_{ij} = \frac{\partial R_m}{\partial a_n} = -\frac{\partial r_m^h}{\partial a_n}, \quad n \in M_a, \quad j = n + N + K_x + K_y + M_z + M_p + M_b \]  
(3.3.175)

\[ GJ_{ij} = \frac{\partial R_m}{\partial b_n} = -\frac{\partial r_m^h}{\partial b_n} + \left( \frac{1}{\Delta t} + \chi_m^h + \alpha \frac{\partial p}{\partial t} + \frac{Q_{out}}{\phi s_w} + \frac{1}{\rho \phi s_w} \frac{\Delta p \phi s_w}{\Delta t} \right) \delta_{mn}, \quad n \in h^b, \quad j = n + N + K_x + K_y + M_z + M_p + M_b + M_a \]  
(3.3.176)

\[ GJ_{ij} = \frac{\partial R_m}{\partial h_n^s} = -\frac{\partial r_m^h}{\partial h_n^s}, \quad n \in h^s, \quad j = n + N + K_x + K_y + M_z + M_p + M_b + M_a + h^b \]  
(3.3.177)
\[ GJ_{ij} = \frac{\partial R_m}{\partial P_n} = -\frac{\partial r^b_m}{\partial P_n}, \quad n \in M_x, \quad j = n + N + k_x + K_y + M_z + M_p + M_b + M_a + h^b + h' \] (3.3.178)

\[
\frac{\partial r^b_m}{\partial e_n} = \sum_{k=1}^{NRANK} \frac{\partial \left( r^b_{m,k}^{chem} \right)}{\partial e_n} + \sum_{k=1}^{NBHRAV} \frac{\partial \left( r^b_{m,k}^{solid \ P} \right)}{\partial e_n}
\]

\[
= \sum_{k=1}^{NRANK} \frac{\partial}{\partial e_n} \left[ \frac{v^*_{km} - v'_{km}}{\gamma_m} \left( k^f_k \prod_{l \in M \left( \gamma_l e_l \right)^{x_{kl}} - k^b_k \prod_{l \in M \left( \gamma_l e_l \right)^{x_{kl}}} \right) \right]
\]

\[
+ \sum_{k=1}^{NBHRAV} \frac{\partial}{\partial e_n} \left[ \frac{v^*_{km} - v'_{km}}{\gamma_m} \left( \Gamma_{k,T,pH,s_{w,h}} \left( \frac{h_k/B_k}{K_{S-k} + h_k/B_k} \right) L_k \left( \gamma_{bh} B_k \right) \right) \right]
\] (3.3.179)

### 3.3.9.1 Contribution from chemical reactions

These reactions include the non-microbiological hydrolysis reactions and mechanical disintegration of solids to form other solids species.

For \( N_a \in r \) (reactant)

\[
\frac{\partial \left( r^b_{m,k}^{chem} \right)}{\partial e_n} = \left( \frac{v^*_{km} - v'_{km}}{\gamma_m} \right) k^f_k \left( \frac{v'_{kn}}{e_n} \right) \prod_{l \in M \left( \gamma_l e_l \right)^{x_{kl}}} \quad \text{if } r = n
\] (3.3.180)
For $N_a \in p$ (product)

$$\frac{\partial \left( \frac{t_{m|k}^{\text{chem}}}{\partial e_n} \right)}{\partial e_n} = \left( \frac{v''_{km} - v'_{km}}{\gamma_m} \right) k_k \left( \frac{v''_{kn}}{e_n} \right) \prod_{l=1}^{M} (y_l e_l)^{y''_{kl}} \quad \text{if } p = n \quad (3.3.181)$$

For $n \in N_s$

$$\frac{\partial \left( t_{m|k}^{\text{chem}} \right)}{\partial e_n} = 0 \quad (3.3.182)$$

For any other reactant species $r$ or product species $p$, the contribution to the Jacobian in columns $n \in N_a + N_s$ is zero.

From equilibrium complexed species,

For reactant $r \in (M_x - K_x)$

$$\frac{\partial \left( t_{m|k}^{\text{chem}} \right)}{\partial e_n} = \left( \frac{v''_{km} - v'_{km}}{\gamma_m} \right) k_k \left( \frac{v'_{kr}}{e_n} \right) \left( \frac{v'_{kr}}{v''_{km}} \right) \prod_{l=1}^{M} (y_l e_l)^{y''_{kl}} \quad (3.3.183)$$

where $\kappa \in NRXNE$ is the equilibrium reaction defining the formation of equilibrium species $r$. 

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From product \( p \in (M_x - K_x) \):

\[
\frac{\partial (t_{m_k}^{k,\text{chem}})}{\partial e_n} = -\left( \frac{v''_{km} - v'_{km}}{\gamma_m} \right) k_k^h \left( \frac{v''_{kp}}{e_n} \right) \prod_{j=M} (\gamma_j e_j)^{i_j} \]  

(3.3.184)

where \( \kappa \in NRXNE \) is the equilibrium reaction defining the formation of equilibrium species \( p \).

For columns \( n \in K_x \), \( j = n + N \), the contribution to the Jacobian from the \( k \)-th chemical reaction is given by:

For reactant \( r \in K_x \)

\[
\frac{\partial (t_{m_k}^{k,\text{chem}})}{\partial e_n} = \left( \frac{v''_{km} - v'_{km}}{\gamma_m} \right) k_k^f \left( \frac{v'_{kn}}{e_n} \right) \prod_{j=M} (\gamma_j e_j)^{i_j} \quad \text{if} \quad r = n 
\]

(3.3.185)

From product \( p \in K_x \)

\[
\frac{\partial (t_{m_k}^{k,\text{chem}})}{\partial e_n} = -\left( \frac{v''_{km} - v'_{km}}{\gamma_m} \right) k_k^h \left( \frac{v''_{kp}}{e_n} \right) \prod_{j=M} (\gamma_j e_j)^{i_j} \quad \text{if} \quad p = n 
\]

(3.3.186)

For \( n \in K_y \)
\[
\frac{\partial \left( r_{m}^{k,\text{chem}} \right)}{\partial e_{n}} = 0
\]
(3.3.187)

For any other reactant species r or product species p, the contribution to the Jacobian in columns
\( n \in K_x + K_y \) is zero.

For \( n \in M_z \), \( j = n + N + K_x + K_y \), the contribution to the Jacobian from the k-th chemical
reaction is zero:

\[
\frac{\partial \left( r_{m}^{k,\text{chem}} \right)}{\partial e_{n}} = 0
\]
(3.3.188)

For columns \( n \in M_p \), \( j = n + N + K_x + K_y + M_z \), the contribution to the Jacobian from the k-th
chemical reaction is zero:

\[
\frac{\partial \left( r_{m}^{k,\text{chem}} \right)}{\partial p_{n}} = 0
\]
(3.3.189)

For columns \( n \in M_h + M_a \), \( j = n + N + K_x + K_y + M_z + M_p \), the contribution to the Jacobian
from the k-th chemical reaction is zero:

\[
\frac{\partial (r^h_{m|k})}{\partial b_n} = 0 \quad (3.3.190)
\]

\[
\frac{\partial (r^h_{m|k})}{\partial a_n} = 0 \quad (3.3.191)
\]

For columns \( n \in M^h + M^h^* \), \( j = n + N + K_x + K_y + M_x + M_y + M_a, \) the contribution to the Jacobian from the k-th chemical reaction is:

For reactant \( r \in M^h \)

\[
\frac{\partial (r^h_{m|k})}{\partial e_n} = \left( \frac{v''_{km} - v'_{km}}{\gamma_m} \right) k^f \left( \frac{v'_{kn}}{e_n} \right) \prod_{\ell=0}^{M} (\gamma_{i,\ell} e_i)^{\gamma_{i,\ell}} \quad \text{if } r = n \quad (3.3.192)
\]

From product \( p \in M^h \)

\[
\frac{\partial (r^h_{m|k})}{\partial e_n} = -\left( \frac{v''_{km} - v'_{km}}{\gamma_m} \right) k^f \left( \frac{v'_{kn}}{e_n} \right) \prod_{\ell=0}^{M} (\gamma_{i,\ell} e_i)^{\gamma_{i,\ell}} \quad \text{if } p = n \quad (3.3.193)
\]
For columns \( n \in M_g \), \( j = n + N + K_x + K_y + M_z + M_p + M_a + M_{k^b} + M_{k^r} \), the contribution to the Jacobian from the k-th chemical reaction is zero:

\[
\frac{\partial (r^k_{m_k})}{\partial P_n} = 0 \tag{3.3.194}
\]

3.3.9.2 Contribution from microorganisms mediated hydrolysis reaction

\[
\frac{\partial (r^k_{m^p_k})}{\partial C_n} = 0, \quad n \in N_a, \quad j = n \tag{3.3.195}
\]

\[
\frac{\partial (r^k_{m^p_k})}{\partial S_n} = 0, \quad n \in N_x, \quad j = n + N_a \tag{3.3.196}
\]

\[
\frac{\partial (r^k_{m^p_k})}{\partial X_n} = 0, \quad n \in K_x, \quad j = n + N \tag{3.3.197}
\]
\[
\frac{\partial (r_m^{\text{solid } p})}{\partial y_n} = 0, \quad n \in K_y, \ j = n + N + K_x \tag{3.3.198}
\]

\[
\frac{\partial (r_m^{\text{solid } p})}{\partial z_n} = 0, \quad n \in M_y, \ j = n + N + K_x + K_y \tag{3.3.199}
\]

\[
\frac{\partial (r_m^{\text{solid } p})}{\partial p_n} = 0, \quad n \in M_p, \ j = n + N + K_x + K_y + M_z \tag{3.3.200}
\]

For microbial species:
\[
\frac{\partial (r_m^{\text{solid } p})}{\partial e_n} = \frac{v_k'' - v_k'}{\gamma_m} \left( \Gamma_{k,T} I_{pff,sw} \right) \frac{1}{\left( K_{S-k} B_k h_k + 1 \right)^2} L_k (\gamma_{\text{bk}},) \tag{3.3.201}
\]
\[
n \in M_b + M_a, \ j = n + N + K_x + K_y + M_z + M_p
\]

For solid phase species:
\[
\frac{\partial (r_m^{\text{solid } p})}{\partial e_n} = \frac{v_k'' - v_k'}{\gamma_m} \left( \Gamma_{k,T} I_{pff,sw} \right) \left[ \frac{1}{K_{S-k} + \left( h_k / B_k \right)} - h_k / B_k \left( K_{S-k} + 1 / B_k \right) \right] L_k (\gamma_{\text{bk}}, B_k), \tag{3.3.202}
\]
\[
n \in h_k, \ j = n + N + K_x + K_y + M_z + M_p + M_b + M_a
\]
\[ \frac{\partial (I_{m}^{\text{solid}} \cdot p)}{\partial P_n} = 0, \quad n \in M_g, \quad j = n + N + K_x + K_y + M_z + M_p + M_h + M_a + M_h \] (3.3.203)

3.3.10 Rows for gaseous phase species, \( M_g \)

For the rows corresponding to the gaseous species, \( m = 1, 2, \ldots, M_g, \quad j = n + N + K_x + K_y + M_z + M_p + M_h + M_a + M_h \)

For the kinetic gaseous phase species, the residual equation is 3.2.15 and the Jacobians for row \( m \) are:

\[
GJ_{ij} = \frac{\partial R_m}{\partial c_n} = -\frac{\partial r^g_m}{\partial c_n}, \quad n \in N_a, \quad j = n
\] (3.3.204)

\[
GJ_{ij} = \frac{\partial R_m}{\partial s_n} = -\frac{\partial r^g_m}{\partial s_n}, \quad n \in N_s, \quad j = n + N_a
\] (3.3.205)

\[
GJ_{ij} = \frac{\partial R_m}{\partial x_n} = -\frac{\partial r^g_m}{\partial x_n}, \quad n \in K_x, \quad j = n + N
\] (3.3.206)
\[ G_{ij} = \frac{\partial R_m}{\partial y_n} = -\frac{\partial r_{m}^g}{\partial y_n}, \quad n \in K_y, \quad j = n + N + K_x \quad (3.3.207) \]

\[ G_{ij} = \frac{\partial R_m}{\partial z_n} = -\frac{\partial r_{m}^g}{\partial z_n}, \quad n \in M_y, \quad j = n + N + K_x + K_y \quad (3.3.208) \]

\[ G_{ij} = \frac{\partial R_m}{\partial p_n} = -\frac{\partial r_{m}^g}{\partial p_n}, \quad n \in M_p, \quad j = n + N + K_x + K_y + M_z \quad (3.3.209) \]

\[ G_{ij} = \frac{\partial R_m}{\partial b_n} = -\frac{\partial r_{m}^g}{\partial b_n}, \quad n \in M_b, \quad j = n + N + K_x + K_y + M_z + M_p \quad (3.3.210) \]

\[ G_{ij} = \frac{\partial R_m}{\partial a_n} = -\frac{\partial r_{m}^g}{\partial a_n}, \quad n \in M_a, \quad j = n + N + K_x + K_y + M_z + M_p + M_b \quad (3.3.211) \]

\[ G_{ij} = \frac{\partial R_m}{\partial h_n^a} = -\frac{\partial r_{m}^g}{\partial h_n^a}, \quad n \in h^a, \quad j = n + N + K_x + K_y + M_z + M_p + M_b + M_a \quad (3.3.212) \]

\[ G_{ij} = \frac{\partial R_m}{\partial h_n^b} = -\frac{\partial r_{m}^g}{\partial h_n^b}, \quad n \in h^b, \quad j = n + N + K_x + K_y + M_z + M_p + M_b + M_a + h^b \quad (3.3.213) \]

\[ G_{ij} = \frac{\partial R_m}{\partial P_n} = -\frac{RT}{(MW_j)^P} \frac{\partial r_{m}^g}{\partial P_n} \]
\[ + \left[ \frac{1}{\Delta t} + \dot{x}^2 + \alpha \frac{\partial P}{\partial t} + \frac{T}{\phi(1-s_w)} \frac{\Delta [\phi(1-s_w)/T]}{\Delta t} + \frac{Q_{\text{out}}}{\phi(1-s_w)} \right] \delta_{mn}, \quad (3.3.214) \]

\[ n \in M_g, \quad j = n + N + K_x + K_y + M_z + M_p + M_b + M_a + h_b + h^r \]

The partial derivative of the production / consumption rate terms are evaluated as follows:

\[
\frac{\partial r_m^g}{\partial g_n} = \sum_{k=1}^{N_{\text{RXNK}}} \frac{\partial}{\partial g_n} \left[ \frac{\partial}{\partial g_n} \left( \frac{v_{km}^p - v_{km}^i}{\gamma_m} \right) \right] \left( k_i a(x_l - K_{H,k} P_m) \right), \quad m \in K_g, \quad l \in N_x + M_x \quad (3.3.215) \]

For columns \( n \in N_a, \quad j = n : \)

\[
\frac{\partial R_m}{\partial e_n} = \left( k_l a \right) \left( \frac{v_{km}^p - v_{km}^i}{\gamma_m} \right) \delta_{mn} \quad (3.3.216) \]

From columns \( n \in (M_x - K_x) \) in the equilibrium reaction \( \kappa \) which defines the formation of species \( m : \)

\[
\frac{\partial R_m}{\partial c_n} = \left( k_l a \right) \left( \frac{v_{km}^p - v_{km}^i}{\gamma_m} \right) \left( k_l a \right) \delta_{mn} \quad (3.3.217) \]

For other column, contribution to the Jacobian is zero:
\[ G_{ij} = \frac{\partial R_m}{\partial s_n} = 0, \quad n \in N_x, \quad j = n + N_a \] (3.3.218)

\[ G_{ij} = \frac{\partial R_m}{\partial x_n} = 0, \quad n \in K_x, \quad j = n + N \] (3.3.219)

\[ G_{ij} = \frac{\partial R_m}{\partial y_n} = 0, \quad n \in K_y, \quad j = n + N + K_x \] (3.3.220)

\[ G_{ij} = \frac{\partial R_m}{\partial z_n} = 0, \quad n \in M_y, \quad j = n + N + K_x + K_y \] (3.3.221)

\[ G_{ij} = \frac{\partial R_m}{\partial p_n} = 0, \quad n \in M_p, \quad j = n + N + K_x + K_y + M_z \] (3.3.222)

\[ G_{ij} = \frac{\partial R_m}{\partial B_n} = 0, \quad n \in M_b + M_a, \quad j = n + N + K_x + K_y + M_z + M_p \] (3.3.223)

\[ G_{ij} = \frac{\partial R_m}{\partial h_n} = 0, \quad n \in h^0 + h^t \quad j = n + N + K_x + K_y + M_z + M_p + M_b + M_a \] (3.3.224)

\[ G_{ij} = \frac{\partial R_m}{\partial P_n} = \left( k, a \right) \left( \frac{v_{km}^n - v_{km}^t}{\gamma_m^r} \right) K_{ij}^{eq} \delta_{mn}, \] (3.3.225)
3.4 Heat generation

The heat generated in the landfill biodegradation process is mainly due to aerobic respiration in aerobic landfill (Tchobanoglous et al. 1993) and during the acidogenesis step in an anaerobic landfill (El Fadel et al. 1996a). Therefore to accommodate the heat generation process, heat generated in a biological process will be defined as the change in enthalpy per unit formation or consumption of a reaction species of interest. The temperature rise can be given by the Eqn 3.4.1

\[
\Delta H = (c_s m_s + c_i m_i + c_g m_g) \Delta T
\]

(3.4.1)

3.4.1 Evaporation

The landfill gas is saturated with water vapor (Tchobanoglous et al. 1993). This is invariably due to presence of high moisture levels in solid waste and high temperatures. The moisture transfer rates from liquid to gas phase for solid waste landfills are not previously reported in literature. Therefore an empirical approach will be adopted to account for water vapor formation. For a batch reactor simulation, the gas pressure will be allowed to vary from the reactor gas pressure \( P_g \) at the beginning of a time step to a small increment \( (P_g + \Delta P_g) \) at the end of a time step. Generated gas will be removed corresponding to the developed pressure \( \Delta P_g \) to allow reactor gas pressure to be maintained at \( P_g \) for another time step. While coupling this model with the flow
model, the vapor formation rate will equal to the rate of removal of gas out of an elemental volume.
Input Notes:

1. The unit for length, L is ‘cm’, mass, M and time, T could have varying units as long as consistency is maintained.
2. Concentrations for chemical and microbial species are in mass of chemical per mass of phase, moles/g or moles/kg for liquid phase, it is mass/batch volume for solid phase, and gaseous species are expressed as pressure in Atmosphere.
3. Total volume is defined as (Batch volume = Volume of liquid phase + volume of solid phase + volume of gas phase). In addition, headspace volume is optional for gas phase.
4. All thermodynamic equilibrium constants and kinetic rate constants have input values as at 25°C and one Atmosphere.

DATA SET 1: TITLE

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1. NPROB =</td>
<td>Problem number. (Integer 1 to 5)</td>
<td></td>
</tr>
<tr>
<td>2. TITLE =</td>
<td>Array for the title of the problem. (May contain upto 70 characters from column 6 to column 75, followed by three blanks in columns 76 to 78)</td>
<td></td>
</tr>
<tr>
<td>3. IITR =</td>
<td>Integer indicating if iteration table of convergence information to be printed. Input in column 79.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 = yes, 0 =no</td>
<td></td>
</tr>
<tr>
<td>4. ICOND =</td>
<td>Integer indicating if the Jacobian matrix to be printed.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 = yes, 0 =no</td>
<td></td>
</tr>
</tbody>
</table>

DATA SET 2: NUMBER OF COMPONENTS AND SPECIES

258
Two lines per problem are required

### Line 1 (FREE FORMAT) contains following 8 variables

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NONA</td>
<td>Number of aqueous components.</td>
</tr>
<tr>
<td>2</td>
<td>NONS</td>
<td>Number of adsorbent components.</td>
</tr>
<tr>
<td>3</td>
<td>NOMX</td>
<td>Number of complexed species.</td>
</tr>
<tr>
<td>4</td>
<td>NOMY</td>
<td>Number of adsorbent species.</td>
</tr>
<tr>
<td>5</td>
<td>NOMZ</td>
<td>Number of ion-exchange species.</td>
</tr>
<tr>
<td>6</td>
<td>NOMP</td>
<td>Number of species subject to precipitation/dissolution.</td>
</tr>
<tr>
<td>7</td>
<td>NOMB</td>
<td>Number of aqueous microbial species.</td>
</tr>
<tr>
<td>8</td>
<td>NOMA</td>
<td>Number of adsorbed microbial species.</td>
</tr>
</tbody>
</table>

### Line 2 (FREE FORMAT) contains following 3 variables

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NOMHB</td>
<td>Number of solid species suspended in aqueous phase (subject to transport).</td>
</tr>
<tr>
<td>2</td>
<td>NOMHA</td>
<td>Number of solid phase species.</td>
</tr>
<tr>
<td>3</td>
<td>NOG</td>
<td>Number of gas phase species.</td>
</tr>
</tbody>
</table>

---

DATA SET 3: H+, e-, AND IONIC STRENGTH CALCULATION INFORMATION

### Line 1 (FREE FORMAT) contains following 5 variables

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>Description</th>
</tr>
</thead>
</table>
1. **SICOR** = User’s specified ionic strength for computing activity coefficients. (this will be used as a constant ionic strength if the user sets ICOR=1 below).

2. **ICOR** = Is Ionic strength used to correct activity coefficient?  
   0 = no,  
   1 = constant ionic strength is used (value specified by the user)  
   2 = variable ionic strength is used (as calculated by the program)

3. **LNH** = Location of the component-hydrogen ion (H+) among component list (in Data sets 9 and 10)

4. **LNG** = Location of the component without bounds on concentration among component list (in Data sets 9 and 10)

5. **LNE** = Location of the component-electron (e-) among component list (in Data sets 9 and 10)

**DATA SET 4: TEMPERATURE, PRESSURE AND EXPECTED PE AND PH INFORMATION**

Three lines per problem are required

Line 1 (FREE FORMAT) contains following 3 variables

| 1. TEMP | = Absolute temperature in Kelvin. |
| 2. PRESU | = Pressure in Atmosphere |
| 3. TEMPK | = Is effect of temperature considered on microbiological reactions? |
|   |   | 0 = no,  
|   |   | 1 = yes |

Line 2(FREE FORMAT) contains following 3 variables

| 1. | NSIMUL | = If the total gas pressure variable?  
|    |       | 0 = no (maintained at near specified value by user above)  
|    |       | 1 = yes |
| 2. | HSVOL  | = Headspace volume for gas if any, mL |
| 3. | DELPMAX| = Maximum change in the value of pressure, PRESU  
|    |       | A non zero value required if NSIMUL =0 |

Line 3(FREE FORMAT) contains following 3 variables

| 1. | PEMN  | = Expected minimum value of electron potential, pe |
| 2. | PEMX  | = Expected maximum value of electron potential, pe |
| 3. | PEMN  | = Expected minimum value of pH |
| 4. | PEMX  | = Expected maximum value of pH |
DATA SET 5: ADSORPTION INFORMATION

This data set is required if and only if NONS.GT. 0 (NONS from data set 2)

<table>
<thead>
<tr>
<th>Line 1 (FREE FORMAT) contains following 2 variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. NSORB</td>
</tr>
<tr>
<td>2. IADS</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

Note

If IADS = 0, NONS = 1x NSORB
If IADS = 1, NONS = 2x NSORB
If IADS = 2, NONS = 3x NSORB

<table>
<thead>
<tr>
<th>Line 2 TO Line NSORB + 1 (FREE FORMAT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Each line contains the following six variables:</td>
</tr>
<tr>
<td>1. CAP1A(I)</td>
</tr>
<tr>
<td>2. CAP2A(I)</td>
</tr>
<tr>
<td>3. SREAA(I)</td>
</tr>
<tr>
<td>4. LNOA(I)</td>
</tr>
</tbody>
</table>
5. LNBA(I) = Location of the expt(-e*psib/kt) component in the component list for the I-th adsorbing site. (Components are listed in Data Sets 9 and 10) 
(Set = 0 if IADS = 0 or 1)

6. IGAHS(I) = Global species number of the solid phase species associated with the I-th adsorbing site

DATA SET 6: ION-EXCHANGE INFORMATION

This data set is required if and only if NONZ.GT. 0 (NONZ from data set 2)

Line 1(FREE FORMAT) contains following variable

| 1. NSITE | = Number of ion-exchange sites |

Line 2 TO Line NSITE + 1 (FREE FORMAT)

Each line contains the following four variables:

| 1. NOMZI(I) | = Number of ion-exchange species participating in reactions at the I-th exchange site. |
| 2. EC(I) | = Ion-exchange capacity (equivalents/wt of solid species) for the I-th exchange site. |

Note: If the exchanging ions are cationic, enter EC as positive number
If the exchanging ions are anionic, enter EC as negative number
DATA SET 6 (continued)

3. LNI(I) = Indicator for the “reference” ion-exchange species for the I-th site. It gives the location of this “reference” species on the ion-exchanged species list.

4. IGIHS(I) = Global species number of the solid phase species associated with the I-th ion-exchange site.

DATA SET 7: BASIC AND INTEGER PARAMETERS

Three lines are required.

Line 1(FREE FORMAT) contains following variables

1. KSS = Steady state simulation control,
   0 = steady state simulation is desired
   1 = steady state simulation is not desired

2. NOTI = Number of times steps for the simulation

Note: The combination of KSS and NOTI will determine the type of simulation run:
   If KSS = 0 and NOTI = 0, a steady state simulation will be performed
   If KSS = 0 and NOTI > 0, a transient simulation using the steady
If KSS = 1 and NOTI > 0, a transient simulation using user supplied initial conditions will be performed.

Each line contains the following five variables:

<table>
<thead>
<tr>
<th></th>
<th>DELT =</th>
<th>Initial time step size, (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>CHNG =</td>
<td>Time step increment for each of the subsequent time steps, (decimal points)</td>
</tr>
<tr>
<td>3</td>
<td>DELMX =</td>
<td>MAXIMUM TIME STEP SIZE ALLOWED, (t)</td>
</tr>
<tr>
<td>4</td>
<td>TBNG =</td>
<td>Beginning simulation time, (T)</td>
</tr>
<tr>
<td>5</td>
<td>TEND =</td>
<td>Ending simulation time, (T)</td>
</tr>
</tbody>
</table>

Each line contains the following seven variables:

<table>
<thead>
<tr>
<th></th>
<th>OMEGA =</th>
<th>Relaxation parameter for iteration:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0 ~ 1 = under-relaxation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 = exact relaxation,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 ~ 2 = over-relaxation</td>
</tr>
<tr>
<td>2</td>
<td>NITT =</td>
<td>Number of iterations allowed for total concentration solver loop</td>
</tr>
<tr>
<td>3</td>
<td>EPST =</td>
<td>Relative error tolerance for iteration of total concentration solver loop</td>
</tr>
<tr>
<td>4</td>
<td>NPCYL =</td>
<td>Number of cycles allowed for iterating precipitation-dissolution</td>
</tr>
<tr>
<td>5</td>
<td>NITER =</td>
<td>Number of cycles allowed for species concentration solver loop</td>
</tr>
</tbody>
</table>
6. **EPS** = Relative error tolerance for iteration of species concentration solver loop

DATA SET 7 (continued)

7. **CNSTRN** = A factor for the constraint on complex species concentration. No complex species concentration would yield a total component concentration greater than CNSTRN times of the input component concentration

**DATA SET 8: PRINTER AND AUXILIARY STORAGE CONTROL**

Three lines are required.

Line 1 (FREE FORMAT) contains following variables

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>KPR0</strong></td>
<td>Printout control for steady state solution or initial conditions 0 = print nothing 1 = print component information only, 2 = print above plus component species information 3 = print above plus product species information, 4 = print above plus thermodynamic equilibrium constants and stoichiometric coefficients of all product species.</td>
</tr>
<tr>
<td><strong>KPU0</strong></td>
<td>Auxiliary storage output control for steady state solution or initial conditions, 0 = no output on auxiliary device,</td>
</tr>
</tbody>
</table>
1 = output on auxiliary device.

| 3. NTSPRIN | = Number of time steps for which print control and auxiliary storage information required |

Line 2 to line NTSPRIN +1 (FREE FORMAT) contains following variable

| 1. NSPRIN | = Time step for which print control and auxiliary storage information required |

**DATA SET 9: TOTAL AND ANALYTICAL CONCENTRATIONS OF ALL COMPONENTS**

For each component, one line is needed. The NONA aqueous components should be listed first, then the NONS adsorbent components. (NONA and NONS are specified in Data Set 2.

Line 1 FORMAT(A10,D20.12) contains following two variables

If J is one of the NONA aqueous components:

| 1. CNAM(J) | = Component name of the J-th component |
| 2. TOTACP(J) | = Total analytical concentration of the J-th component (moles/total batch volume) |

If J is one of the NONS adsorbent components:

| 1. CNAM(J) | = Component name of the J-th component |
| 2. TOTACP(J) | = Total analytical concentration of the J-th component (number of sites/unit surface are of solid species) |
For each component species, the number of lines required depends on whether the species participates in ion-exchange reactions. If the species does not participate in an ion-exchange reaction, two lines are needed to describe the species. If the species is involved in ion-exchange reactions, three additional lines are needed to describe each ion-exchange site on which this species reacts.

All information relating to one component species is input, then the information for the next component species. Components should be described in the same order used in Data Set 9.

Line 1 FORMAT(A20,I5) is required for each component species and contains two variables:

1. **SPECN(J)** = Name of the J-th component species.
2. **ISCN(J)** = Indicator for the J-th species concentration
   - 0 = species concentration is to be computed
   - 3 = species concentration or activity is fixed

Line 2 – (FREE FORMAT) If J is one of the NONA aqueous components, for each component species and contains five variables

1. **CP(J)** = Initial guess of the J-th component species concentration, (moles/mass of phase)
2. **CS(J)** = Saturation concentration, J-th component species (may be required if component corresponds to highly soluble gas species,
3. VJ(J) = Charge of the J-th component species

4. IONEX = Integer indicating the number of ion exchange sites on which this component species participates in ion-exchange reactions. (set IONEX = 0 if this component)

5. PMV(J) = Partial molar volume of the J-th species (mL/mol)

Line 2 – (FREE FORMAT) If J is one of the NONS aqueous components, for each component specie and contains three variables

1. CP(J) = Initial guess of the J-th component species concentration, (moles/mass of phase)

2. VJ(J) = Charge of the J-th component species

3. IONEX = Integer indicating the number of ion exchange sites on which this component species participates in ion-exchange reactions. (set IONEX = 0 if this component)

The following sub-data set is needed for a component specie only if IONEX is not equal to zero. When IONEX is not equal to 0, this subdata set is repeated IONEX times. For each of the IONEX ion exchange sites on which this component specie is involved in ion-exchange reactions, the following three lines are needed

Line 3 (FREE FORMAT) contains the following variable:
1. **ISITE** = This component species participates in reactions at the ISITE-th ion-exchange site.

---

**DATA SET 10 (continued)**

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Line 4 FORMAT(A20,I5):</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. SPECN(II) = Name of the II-th ion-exchange species resulting from the I-th component species involved in the ISITE-th ion-exchange site reaction.</td>
<td></td>
<td>Note: II is internally arranged according to the order of ion-exchange site.</td>
</tr>
<tr>
<td>2. ISCN(II) = Indicator of the II-th ion-exchange species concentration</td>
<td></td>
<td>0 = species concentration is to be computed,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3 = species concentration is fixed</td>
</tr>
</tbody>
</table>

---

**Line 5 (FREE FORMAT)**

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1. CP(II) = Initial guess of the II-th ion-exchanged species concentration, (moles/mass of solid species)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. AXYZP(I,1) = Stoichiometric coefficient of the first component in the I-th ion exchange species, for use in mass action equation.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. AXYZP(I,2) = Stoichiometric coefficient of the second component in the I-th ion exchange species, for use in mass action equation.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
NON +1 \[ A_{XYZP(I,NON)} \] = Stoichiometric coefficient of the NON-th component in the I-th ion exchange species, for use in mass action equation. (NON is the total number of components in the simulation. NON = NONA + NONS, which are specified in Data set 2).

NON +2 \[ B_{XYZP(I,1)} \] = Stoichiometric coefficient of the first component in the I-th ion exchange species, for use in mole balance equation.

\[ B_{XYZP(I,2)} \] = Stoichiometric coefficient of the second component in the I-th ion exchange species, for use in mole balance equation.

\[ \ldots \] = \ldots

\[ B_{XYZP(I,NON)} \] = Stoichiometric coefficient of the NON-th component in the I-th ion exchange species, for use in mole balance equation.

DATA SET 11: AQUEOUS COMPLEXED SPECIES AND THEIR ION-EXCHANGE SPECIES

This data set is needed only if NOMX .GT. 0. If needed, it is read in similar to DATA SET 10. (NOMX, the number of aqueous complexed species, is specified in Data Set 2).

Line 1 FORMAT(A20,I5) is required for each aqueous complexed specie and contains two variables:

1. \[ SPECN(II) \] = Name of the II-th species or the I-th complexed species.
2. \[ ISCN(II) \] = Indicator for the II-th species concentration
<table>
<thead>
<tr>
<th>DATA SET 11 (continued)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Line 2 (FREE FORMAT) is required for each aqueous complexed specie and contains following variables:</td>
</tr>
<tr>
<td>1. CP(II) = Initial guess of the complexed species concentration, (moles/mass of liquid).</td>
</tr>
<tr>
<td>2. CS(II) = Saturation concentration of the complexed species (may be required if component corresponds to highly soluble gas species, else a very large value could be use as input)</td>
</tr>
<tr>
<td>3. PMV(II) = Partial molar volume of the complexed species (ml/mol)</td>
</tr>
<tr>
<td>4. AXYZP(I,1) = Stoichiometric coefficient of the first component in the I-th complexed species, for use in mass action equation.</td>
</tr>
<tr>
<td>5. AXYZP(I,2) = Stoichiometric coefficient of the second component in the I-th complexed species, for use in mass action equation.</td>
</tr>
<tr>
<td>...</td>
</tr>
<tr>
<td>...</td>
</tr>
<tr>
<td>NON +2 AXYZP(I,NON) = Stoichiometric coefficient of the NON-th component in the I-th complexed species, for use in mass action equation. (NON is the total number of components in the simulation. NON =</td>
</tr>
<tr>
<td>NON +3</td>
</tr>
<tr>
<td>NON +4</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

The following sub-data set is needed for a complexed species only if IONEX is not equal to zero. When IONEX is not equal to 0, this subdata set is repeated IONEX times. For each of the IONEX ion exchange sites on which this component specie is involved in ion-exchange reactions, the following three lines are needed:

Line 3 (FREE FORMAT) contains the following variable:

1. ISITE  = This complexed species participates in reactions at the ISITE-th ion-exchange site.
**Line 4 FORMAT(A20,I5):**

| 1. | SPECN(II) | = | Name of the II-th ion-exchange species resulting from the I-th complexed species involved in the ISITE-th ion-exchange site reaction. Note: II is internally arranged according to the order of ion-exchange site. |

**DATA SET 11 (continued)**

| 2. | ISCN(II) | = | Indicator of the II-th ion-exchange species concentration |
|    |         |   | 0 = species concentration is to be computed, |
|    |         |   | 3 = species concentration is fixed |

**Line 5 (FREE FORMAT)**

| 1. | CP(II) | = | Initial guess of the II-th ion-exchanged species concentration, (moles/mass of solid species) |
| 2. | AXYZP(I,1) | = | Stoichiometric coefficient of the first component in the I-th ion exchange species, for use in mass action equation. |
| 3. | AXYZP(I,2) | = | Stoichiometric coefficient of the second component in the I-th ion exchange species, for use in mass action equation. |
|    |         |   | . . |
|    |         |   | . . |
| NON | AXYZP | = | Stoichiometric coefficient of the NON-th component in the I-th ion exchange species, for use in mass action equation. |
| +1 | (I,NON) |   |   |
NON is the total number of components in the simulation. NON = NONA + NONS, which are specified in Data set 2).

<table>
<thead>
<tr>
<th>NON</th>
<th>BXYZP(I,1)</th>
<th>=  Stoichiometric coefficient of the first component in the I-th ion exchange species, for use in mole balance equation.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>BXYZP(I,2)</td>
<td>=  Stoichiometric coefficient of the second component in the I-th ion exchange species, for use in mole balance equation.</td>
</tr>
<tr>
<td></td>
<td>...</td>
<td></td>
</tr>
<tr>
<td></td>
<td>BXYZP(I,NON)</td>
<td>=  Stoichiometric coefficient of the NON-th component in the I-th ion exchange species, for use in mole balance equation.</td>
</tr>
</tbody>
</table>

**DATA SET 12: ADSORBED SPECIES**

This data set is needed only if NOMY .GT. 0. Two lines per adsorbed species are needed. (NOMY, the number of adsorbed species, is specified in Data Set 2).

Line 1 FORMAT(A20,I5) is required for each adsorbed specie and contains two variables:

<table>
<thead>
<tr>
<th>1.</th>
<th>SPECN(II)</th>
<th>=  Name of the II-th species or the I-th adsorbed species.</th>
</tr>
</thead>
</table>
| 2. | ISCN(II)   |  =  Indicator for the II-th species concentration  
|     |            | 0 = species concentration is to be computed  
|     |            | 3 = species concentration or activity is fixed |

Line 2 (FREE FORMAT) is required for each adsorbed specie and contains following
variables:

<table>
<thead>
<tr>
<th></th>
<th>1. CP(II)</th>
<th>=</th>
<th>Initial guess of the adsorbed species concentration, (moles/mass of solids).</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2. AXYZP(II,1)</td>
<td>=</td>
<td>Stoichiometric coefficient of the first component in the II-th species or in the I-th adsorbed species, for use in mass action equation.</td>
</tr>
<tr>
<td>DATA SET 11 (continued)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. AXYZP(II,2) = Stoichiometric coefficient of the second component in the II-th species or in the I-th adsorbed species, for use in mass action equation.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NON +1 AXYZP(II,NON) = Stoichiometric coefficient of the NON-th component in the II-th species or in the I-th adsorbed species, for use in mass action equation. (NON is the total number of components in the simulation. NON = NONA + NONS, which are specified in Data set 2).</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NON +2 BXYZP(II,1) = Stoichiometric coefficient of the first component in the II-th species or in the I-th adsorbed species, for use in mole balance equation.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
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<td></td>
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</tr>
<tr>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BXYZP(II,2) = Stoichiometric coefficient of the second component in the II-th species or in the I-th adsorbed species, for use in mole balance equation.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
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<td></td>
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<tr>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BXYZP(II,NON) = Stoichiometric coefficient of the NON-th component in the II-th species or in the I-th adsorbed species, for use in mole</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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DATA SET 13: PRECIPITATED SPECIES

This data set is needed only if \texttt{NOMP} \texttt{.GT. 0}. Two lines per adsorbed species are needed. (\texttt{NOMP}, the number of precipitated species, is specified in Data Set 2).

Line 1 \texttt{FORMAT(A20,I5)} is required for each adsorbed specie and contains two variables:

<table>
<thead>
<tr>
<th>1. SPECN(II)</th>
<th>= Name of the II-th species or the I-th precipitated/dissolved species.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2. ISCN(II)</td>
<td>= Indicator for the II-th species concentration</td>
</tr>
<tr>
<td></td>
<td>0 = species concentration is to be computed</td>
</tr>
<tr>
<td></td>
<td>3 = species concentration or activity is fixed</td>
</tr>
</tbody>
</table>

Line 2 (FREE FORMAT) is required for each precipitated species and contains following variables:

| 1. CP(II)    | = Initial guess of the precipitated species concentration,        |
|              | (moles/mass of solids).                                          |
| 2. PKIPD     | = Log 10 of the equilibrium constant for the formation of the II-  |
|              | th precipitated/dissolved species for use in determining          |
|              | solubility.                                                       |
| 3. AXYZP(II,I)| = Stoichiometric coefficient of the first component in the II-th  |
species or in the I-th precipitated/dissolved species, for use in mass action equation.

<table>
<thead>
<tr>
<th>DATA SET 13 (continued)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>4. AXYZP(II,2) = Stoichiometric coefficient of the second component in the II-th species or in the I-th precipitated/dissolved species, for use in mass action equation.</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>NON +2 AXYZP(II,NON) = Stoichiometric coefficient of the NON-th component in the II-th species or in the I-th precipitated/dissolved species, for use in mass action equation. (NON is the total number of components in the simulation. NON = NONA + NONS, which are specified in Data set 2).</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>NON +3 BXYZP(II,1) = Stoichiometric coefficient of the first component in the II-th species or in the I-th precipitated/dissolved species, for use in mole balance equation.</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>BXYZP(II,2) = Stoichiometric coefficient of the second component in the II-th species or in the I-th precipitated/dissolved species, for use in mole balance equation.</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>BXYZP = Stoichiometric coefficient of the NON-th component in the II-</td>
</tr>
</tbody>
</table>
DATA SET 14: MICROBIAL SPECIES

This data set is needed only if NOMB or NOMB .GT. 0. Two lines per species are needed. (the NOMB aqueous microbial species should be listed first then the NOMA adsorbed microbial species (NOMB and NOMA are specified in Data Set 2).

Line 1 FORMAT(A20,I5) is required for each species and contains two variables:

<table>
<thead>
<tr>
<th>SPECN(II)</th>
<th>ISCN(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name of the II-th species</td>
<td>Indicator for the II-th species concentration</td>
</tr>
<tr>
<td>0 = species concentration is to be computed</td>
<td>3 = species concentration or activity is fixed</td>
</tr>
</tbody>
</table>

Line 2 (FREE FORMAT) is required for each precipitated species and contains following variables:

<table>
<thead>
<tr>
<th>CP(II)</th>
<th>PKD</th>
<th>NER</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial value of the II-th microbial species concentration, (moles/mass of phase).</td>
<td>Log 10 of the death/decay constant of the I-th microbial species.</td>
<td>Number of chemical species affected by endogenous respiration of this microbial species.</td>
</tr>
</tbody>
</table>
4. CV(II) = Specific heat capacity of the II-th microbial species, (Joule/mole per degree K)

DATA SET 14 (continued)

The following lines are needed only if NER. GT. 0. Two lines are needed for each of the NER species affected by endogenous respiration.

Line 3 (FREE FORMAT) contains the following variables

1. IGER(II,J) = Global species number of the J-th chemical species affected by endogenous respiration of the II-th microbial species.

Line 4 (FREE FORMAT) contains the following variables

1. ERAIJ = Stoichiometric coefficient for use of the J-th chemical species due to maintenance/decay process this microbial species.

2. ERKIJ = Half saturation constant for the J-th chemical species due to maintenance/decay process this microbial species.

DATA SET 15: SOLID PHASE SPECIES

This data set is needed only if NOMHB or NOMHA .GT. 0. Two lines per species are needed. (the NOMHB solids species suspended in liquid phase should be listed first then the NOMHA solid phase species (NOMHB and NOMHA are specified in Data Set 2).
Line 1 FORMAT(A20,I5) is required for each solid phase species and contains two variables:

<table>
<thead>
<tr>
<th></th>
<th>SPECN(II)</th>
<th>=</th>
<th>Name of the II-th species</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.</td>
<td>ISCN(II)</td>
<td>=</td>
<td>Indicator for the II-th species concentration</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0 = species concentration is to be computed</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3 = species concentration or activity is fixed</td>
</tr>
</tbody>
</table>

Line 2 (FREE FORMAT) is required for each precipitated species and contains following variables:

<table>
<thead>
<tr>
<th></th>
<th>CP(II)</th>
<th>=</th>
<th>Initial value of the II-th solids species concentration, (mass/batch volume).</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.</td>
<td>CV(II)</td>
<td>=</td>
<td>Specific heat capacity of the II-th solids species, (Joule/mass per degree K)</td>
</tr>
</tbody>
</table>

DATA SET 16: GAS PHASE SPECIES

This data set is needed only if NOG .GT. 0. Two lines per species are needed. (NOG, the gas phase species are specified in Data Set 2).

Line 1 FORMAT(A20,I5) is required for each gas phase species and contains two variables:

<table>
<thead>
<tr>
<th></th>
<th>SPECN(II)</th>
<th>=</th>
<th>Name of the II-th species</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.</td>
<td>ISCN(II)</td>
<td>=</td>
<td>Indicator for the II-th species concentration</td>
</tr>
<tr>
<td>0</td>
<td>species concentration is to be computed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>----------------------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>species concentration or activity is fixed</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
DATA SET 16 (continued)

Line 2 (FREE FORMAT) is required for each precipitated species and contains following variables:

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CP(II)</td>
<td>Initial value of concentration of the II-th species, (Atmosphere).</td>
</tr>
<tr>
<td>2</td>
<td>CS(II)</td>
<td>Maximum concentration of the II-th species, (Atmosphere).</td>
</tr>
<tr>
<td>3</td>
<td>CV(II)</td>
<td>Specific heat capacity of the II-th species, (Joule/mole per degree K)</td>
</tr>
<tr>
<td>4</td>
<td>MW(I)</td>
<td>Molecular weight of the I-th gas phase species</td>
</tr>
</tbody>
</table>

DATA SET 17: SOURCE PARAMETERS

Line 1 (FREE FORMAT) contains one variable

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NPROF</td>
<td>Number of species for which source/sink profile are described</td>
</tr>
</tbody>
</table>

Following records are required if NPROF.GT. 0

I-th (I = 1, 2, ..., NPROF) record - FREE FORMAT.

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>IGSPROF(I)</td>
<td>Global species number</td>
</tr>
<tr>
<td>2</td>
<td>NDTPS(I)</td>
<td>Number of records in the source/sink profile</td>
</tr>
<tr>
<td></td>
<td>SSPT(IGSPROF,NDTPS)</td>
<td>Time of the first data point in the I-th profile, (T).</td>
</tr>
<tr>
<td></td>
<td>SSPV(IGSPROF,NDTPS)</td>
<td>mass/time per batch volume</td>
</tr>
</tbody>
</table>
DATA SET 18: REACTION DATA

**NOTE:** Equilibrium chemical reactions involving aqueous complexation, adsorption or precipitation may involve as many reactants as necessary but must be written as the formation of only equilibrium product species. Each equilibrium product species may participate in only one equilibrium reaction.

Ion exchange reactions, weather equilibrium or kinetic, must have one aqueous species and one ion exchanged species both as reactants and as products. The reactant ion exchanged species must be the reference ion exchange species for the site involved. For example:

Aqueous species + Reference Ion-Ex Species $\leftrightarrow$ New Aqueous Species + New Ion-Ex Species

All other kinetic chemical reactions may involve any species as reactants or products.

Microbiological reactions may involve any chemical species as

(a positive value will indicate source and a negative value will indicate sink)
reactants and products. One reactant may be identified as the substrate, one as electron acceptor, one as the nutrient, and one as the inhibitor for use in the Monod kinetic expressions.

Solids disintegration reaction may have one reactant solids species and any number of product solids species

Microbiological solids hydrolysis reaction may involve only one reactant solid phase species and one microbial species with unlimited aqueous phase species

Aqueous phase and gas phase separation reaction may involve only one species in each phase

<table>
<thead>
<tr>
<th>One line is needed specifying the number of chemical reactions in the simulation.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Line 1 (FREE FORMAT) contains the following variable:</td>
</tr>
<tr>
<td>1. NRXN = The number of reactions in this simulation</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>The following subset is needed only if NRXN is greater than zero. For each of the NRXN reactions the following lines are needed.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Line 1 (FREE FORMAT) contains the following variables:</td>
</tr>
<tr>
<td>1. NRTS = The number of reactant species participating in this reaction.</td>
</tr>
</tbody>
</table>
2. **NPDS** = The number of product species participating in this reaction.

3. **KRTYP(I)** = Reaction type of the I-th reaction.
   - 0 if chemical equilibrium,
   - 1 if chemical kinetic by collision theory,
   - 2 if microbial by Monod kinetics,
   - 3 if microbial phase transfer reaction,
   - 4 if solids disintegration kinetic reaction
   - 5 if solids hydrolysis by Contois kinetics
   - 6 if liquid-gas phase mass transfer kinetic reactions

Line 2 (FREE FORMAT) contains the following:

If **KRTYP(I)** =0,

1. **PEQK** = Log10 of the equilibrium constant for this reaction.

If **KRTYP(I)** =1 or 3

1. **PBK** = Log10 of the backward rate constant for this kinetic reaction.
2. **PFK** = Log10 of the forward rate constant for this kinetic reaction.

If **KRTYP(I)** =2,

1. **GRMAXK** = maximum specific growth rate of the i-th reaction, $\mu_{max}$ (1/T).
2. **HSCS** = half saturation constant for the substrate in the i-th reaction, $K_S$, 287
mass/mass of phase (M/M)

3. **HSCA** = half saturation constant for the electron acceptor in the i-th reaction, $K_A$, mass/mass of phase (M/M). (set = 0, if electron acceptor is not required in the reaction).

4. **HSCN** = half saturation constant for the nutrient in the i-th reaction, $K_A$, mass/mass of phase (M/M). (set = 0, if nutrient is not required in the reaction).

5. **HSCL** = half saturation constant for additional limiting nutrient in the i-th reaction, $K_A$, mass/mass of phase (M/M). (set = 0, if additional limiting nutrient is not required in the reaction).

Additional line 2a is required if $KRTYP(I) = 2$,

1. **LOCS** = reactant which is the substrate in the i-th reaction.

2. **LOCA** = reactant which is the electron acceptor in the i-th reaction (set = 0 if not used).

3. **LOCN** = reactant which is the nutrient in the i-th reaction (set = 0 if not used).

4. **LOCL** = reactant which is the additional limiting nutrient in the i-th reaction (set = 0 if not used).

5. **TAUL** = lag time for the i-th reaction (set = 0 if not used).

6. **TAUE** = time to reach exponential growth for the i-th reaction (set = 0 if not used).
Additional line 2b is required if KRTYP(I) = 2,

1. **PHL** = lower inhibiting pH in the i-th reaction (set = 0 if not used).
2. **PHH** = higher inhibiting or the optimum pH in the i-th reaction (set = 0 if not used).
3. **TEMPMAX** = maximum temperature where microorganisms growth ceases in the i-th reaction (set = 0 if not used).
4. **TEMPOPT** = optimum temperature for microorganisms growth in the i-th reaction (set = 0 if not used).
5. **THETAK** = coefficient for calculating temperature effect on microorganisms growth in the i-th reaction (set = 0 if not used).

If KRTYP(I) = 4,

1. **RDK** = maximum specific solids disintegration rate of the i-th reaction, (1/T).
2. **IGSSAN** = Global species number of the solids substrate species in the i-th reactions.

If KRTYP(I) = 5,

1. **RHMXK** = maximum specific solids hydrolysis rate of the i-th reaction, (1/T).
2. **HSCS** = modified half saturation constant for the substrate in the i-th
reaction, $K_H$, mass/mass of phase (M/M)

<table>
<thead>
<tr>
<th>Additional line 2a is required if KRTYP(I) = 5,</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. LOCH = reactant which is the solid substrate in the i-th reaction.</td>
</tr>
<tr>
<td>2. TAUL = lag time for the i-th reaction (set = 0 if not used).</td>
</tr>
<tr>
<td>3. NHYBAC = the global species number of the microbial species affecting the i-th reaction.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Additional line 2b is required if KRTYP(I) = 5,</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. PHL = lower inhibiting pH in the i-th reaction (set = 0 if not used).</td>
</tr>
<tr>
<td>2. PHH = higher inhibiting or the optimum pH in the i-th reaction (set = 0 if not used).</td>
</tr>
<tr>
<td>3. TEMPMAX = maximum temperature where microorganisms growth ceases in the i-th reaction (set = 0 if not used).</td>
</tr>
<tr>
<td>4. TEMPOPT = optimum temperature for microorganisms growth in the i-th reaction (set = 0 if not used).</td>
</tr>
<tr>
<td>5. THETAK = coefficient for calculating temperature effect on microorganism growth in the i-th reaction (set = 0 if not used).</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>If KRTYP(I) = 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. AKH = Henry constant for the i-th reaction, (M/M)(1/PRESURE).</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>2.</td>
</tr>
</tbody>
</table>

Line 3 – (FREE FORMAT) contains the following variables:

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>CXYZP(I,1)</td>
<td>= stoichiometric coefficient of the 1st reactant species in the I-th reaction.</td>
</tr>
<tr>
<td>2.</td>
<td>CXYZP(I,2)</td>
<td>= stoichiometric coefficient of the 2nd reactant species in the I-th reaction.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NRTS</td>
<td>CXYZP(I,NRTS)</td>
<td>= stoichiometric coefficient of the NRTS-th reactant species in the I-th reaction.</td>
</tr>
<tr>
<td>NRTS + 1</td>
<td>DXYZP(I,1)</td>
<td>= stoichiometric coefficient of the 1st product species in the I-th reaction.</td>
</tr>
<tr>
<td></td>
<td>DXYZP(I,2)</td>
<td>= stoichiometric coefficient of the 2nd product species in the I-th reaction.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>DXYZP(I,NPDS)</td>
<td>= stoichiometric coefficient of the NPDS-th product species in the I-th reaction.</td>
</tr>
</tbody>
</table>

Line 4 – (FREE FORMAT) contains the following variables:
1. IGSNRT(I,1) = global species number of the 1st reactant species in the I-th reaction.

2. IGSNRT(I,2) = global species number of the 2nd reactant species in the I-th reaction.

   .

   .

NRTS IGSNRT(I,NRTS) = global species number of the NRTS-th reactant species in the I-th reaction.

NRTS + 1 IGSNPD(I,1) = global species number of the 1st product species in the I-th reaction.

   IGSNPD(I,2) = global species number of the 2nd product species in the I-th reaction.

   .

   .

IGSNPD(I,NPDS) = global species number of the NPDS-th product species in the I-th reaction.

Note: The total, or global number of species in the simulation is

NONA+NONS+NOMX+NOMY+NOMZ+NOMP+NOMB+NOMA+
NOMHB+NOMHS+NOG (All specified in Data Set 2).

if KRTYP(I) = 2 or 5, a fifth line is needed for the following variables
1. **INHIB(I)** = global species number of the inhibitor of the I-th reaction.

2. **HSCINH(1,I)** = growth rate inhibition coefficient for the I-th reaction (parameter $K_{I1}$).

3. **HSCINH(2,I)** = substrate half saturation constant inhibition coefficient for the I-th reaction (parameter $K_{I2}$).

4. **PQ(1,I)** = Fitting parameter for growth rate inhibition of the k-th reaction (parameter p).

5. **PQ(2,I)** = Fitting parameter for substrate half saturation constant inhibition factor in the k-th reaction (parameter q).

**DATA SET 19: WATER/AQUEOUS PHASE DATA**

Two lines are needed

Line 1 (FREE FORMAT) contains the following variables

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>RHOLTHP = Initial bulk liquid density (mass liquid/total batch volume)</td>
</tr>
<tr>
<td>2</td>
<td>CWATP = Initial water concentration (mass water/mass liquid) (often approximated as 55.4 moles/kg liquid)</td>
</tr>
<tr>
<td>3</td>
<td>THP = Initial liquid content (volume of liquid/total batch volume)</td>
</tr>
<tr>
<td>4</td>
<td>PMVW = Partial molar volume of water</td>
</tr>
<tr>
<td>5</td>
<td>CVW = Specific heat capacity of water, (Joule/mass per degree K)</td>
</tr>
</tbody>
</table>

Line 2 (FREE FORMAT) contains (NOMX + MOMY + NOMZ + NOMP) variables
1. \( STCW(I) \) = Stoichiometric coefficient of water in the I-th product species,
   \( I=1, (NOMX + MOMY + NOMZ + NOMP) \)

DATA SET 20: SOLID PHASE DATA

One line is needed

Line 1 (FREE FORMAT) contains the following variables

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>( RHOBP ) = Initial bulk density of solids (mass of solids/total batch volume)</td>
</tr>
<tr>
<td>2.</td>
<td>( IGCG ) = Global species number of first solid phase species to be included in density computation</td>
</tr>
<tr>
<td>3.</td>
<td>( POROSITY ) = Porosity of solids</td>
</tr>
</tbody>
</table>
| 4. | \( KROBC \) = Indicator for the computation of solid phase density  
  0 = density fixed at input value  
  1 = density to be computed |
DATA SET 21: HEAT GENERATION/CONSUMPTION DATA

Temperature change is modeled in BIOKEMOD-3P using coefficients for species produced/consumed in a microbial reaction and relating to the heat generated or consumed.

Line 1 (FREE FORMAT) contains the following variable

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>NHGENFAC = Number of sets of species and reaction data used</td>
</tr>
<tr>
<td></td>
<td>0 = heat generation/consumption ignored</td>
</tr>
</tbody>
</table>

Line 2 (FREE FORMAT) is required if NHFENFAC .GT. 0

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>CVG = Specific heat capacity of gas phase, (Joule/mass per degree K)</td>
</tr>
<tr>
<td>2.</td>
<td>CVS = Specific heat capacity of solid phase, (Joule/mass per degree K)</td>
</tr>
</tbody>
</table>

Following records are required if NHGENFAC.GT. 0

I-th (I = 1, 2, ..., NHGENFAC) record - FREE FORMAT.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>IHEAT(1,I) = Global species number</td>
</tr>
<tr>
<td>2.</td>
<td>IHEAT(1,I) = Microbial reaction in which above species is involved</td>
</tr>
<tr>
<td>3.</td>
<td>DELTAH(I) = Change in heat corresponding to change in IHEAT(1,I) Joule/mole</td>
</tr>
</tbody>
</table>
5.0 References:


Westall, J.C., Zachary, J.L., Morel, F.M.M. (1976). *MINEQL*: a computer program for the calculation of chemical equilibrium composition of aqueous systems. Technical Note 18, Department of Civil Engineering, Massachusetts Institute of Technology, Cambridge, MA.


APPENDIX C:
INPUT AND OUTPUT FILES FOR THE SIMULATION OF ANAEROBIC
BIODEGRADATION OF SOLID WASTE
1 SIMULATION of Solid Waste Degradation

C ******* DATA SET 2: NUMBER OF COMPONENTS AND SPECIES
15 0 8 0 0 9 0 NONA NONS NOMX NOMY NOMZ NOMP NOMB NOMA
0 7 5 NOMHB NOMHS NOG

C ******* DATA SET 3: H+, E-, IONIC STRENGTH AND SORPTION INFORMATION
0 0 1 0 0 SICOR ICOR LNH LNG LNE

C ******* DATA SET 4: TEMPERATURE, PRESSURE, AND EXPECTED PE AND PH
314.15 1.0 0 TEMP PRESSU TEMPK
0 0.250 0.1 NSIMUL QVOL DELPMA
-20.0 20.0 -1.0 20.0 PEMN PEMX PHMN PHMX

C ******* DATA SET 7: BASIC AND INTEGER REAL PARAMETERS
1 1100000 KSS NOTI
0.0001 0.0 0.10 0.0 115 DELT CHNG DELMX TBNG TEND
1.0 30 1.0D-06 1 300 1.0D-09 500.0 OMEGA NITT EPST NPCYL NITER EPS CNSTRN

C ******* DATA SET 8: PRINTER AND AUXILIARY STORAGE CONTROL
4 1 25

1 20000 30000 40000 50000 60000 70000 80000 90000 100000 120000 130000 150000 170000 200000 240000 270000 300000 320000 350000 400000 450000 550000 650000 345000

C ******* DATA SET 9: TOTAL ANALYTICAL CONCENTRATION OF ALL COMPONENTS
H+ -3.9576D-04
HCO3- 3.3162D-05
NH4+ 4.9338D-05
SHAC 2.3215D-04
SHPRO 1.8025D-05
SHBUT 1.6666D-04
<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
<th>Description</th>
<th>Multiplier</th>
<th>Concentration</th>
<th>IONEX</th>
<th>PMV</th>
</tr>
</thead>
<tbody>
<tr>
<td>H+</td>
<td>0</td>
<td></td>
<td>1.00D+03</td>
<td>0.003008</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCO3-</td>
<td>0.5724D-06</td>
<td></td>
<td>1.00D+03</td>
<td>0.062025</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH4+</td>
<td>0.8962D-04</td>
<td></td>
<td>1.00D+03</td>
<td>0.04401</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SHAC</td>
<td>0.1346D-04</td>
<td></td>
<td>1.00D+03</td>
<td>0.06200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SHPRO</td>
<td>0.1364D-05</td>
<td></td>
<td>1.00D+03</td>
<td>0.06200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SHBUT</td>
<td>0.1104D-04</td>
<td></td>
<td>1.00D+03</td>
<td>0.06200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SHVAL</td>
<td>0.9073D-06</td>
<td></td>
<td>1.00D+03</td>
<td>0.06200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SSU</td>
<td>0.3527D-05</td>
<td></td>
<td>1.00D+03</td>
<td>0.003008</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SAA</td>
<td>0.1818D-11</td>
<td></td>
<td>1.00D+03</td>
<td>0.06200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SIN</td>
<td>0.1818D-11</td>
<td></td>
<td>1.00D+03</td>
<td>0.06200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NA+</td>
<td>0.1818D-09</td>
<td></td>
<td>1.00D+03</td>
<td>0.06200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH4*</td>
<td>0.2153D-04</td>
<td></td>
<td>5.00D-05</td>
<td>0.06200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O2*</td>
<td>0.6977D-04</td>
<td></td>
<td>1.00D+03</td>
<td>0.06200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N2*</td>
<td>0.1818D-09</td>
<td></td>
<td>1.00D+03</td>
<td>0.06200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H2*</td>
<td>0.2414D-07</td>
<td></td>
<td>1.00D+03</td>
<td>0.06200</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

C ****** DATA SET 11: COMPLEXED SPECIES AND THEIR ION-EXCHANGED SPECIES

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
<th>Description</th>
<th>Multiplier</th>
<th>Concentration</th>
<th>IONEX</th>
<th>PMV</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH-</td>
<td>0.175D-07</td>
<td></td>
<td>1.00D+03</td>
<td>0.017007</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO3--</td>
<td>0.221D-08</td>
<td></td>
<td>1.00D+03</td>
<td>0.026000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H2CO3*</td>
<td>0.339D-04</td>
<td></td>
<td>5.00D-05</td>
<td>0.026000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SAC-</td>
<td>0.409D-03</td>
<td></td>
<td>1.00D+03</td>
<td>0.026000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SPRO-</td>
<td>0.300</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
0.314D-04  1.00D+03  0.026000    -1  0  0  0  0  0  0  0  0  0  0  0  0  0  0
0 -1  0  0  0  1  0  0  0  0  0  0  0  0  0  0  0  0
SBUT-        0
0.292D-03  1.00D+03  0.026000    -1  0  0  0  0  1  0  0 0 0  0  0  0  0  0
0 -1  0  0  0  0  1  0  0 0  0  0  0  0  0  0  0  0
SVAL-        0
0.219D-04  1.00D+03  0.026000    -1  0  0  0  0  0  1  0 0 0  0  0  0  0  0
0 -1  0  0  0  0  0  1  0 0  0  0  0  0  0  0  0  0
NH3          0
0.880D-07  1.00D+03  0.026000    -1  0  1  0  0  0  0  0 0 0  0  0  0  0  0
0 -1  0  1  0  0  0  0  0 0  0  0  0  0  0  0  0  0
C ******* DATA SET 14: MICROBIAL SPECIES
XHYDRO1      0
0.206D-05  -1.10  1 0 CP(I) PKD NER CV(I)
3
-1  0
XHYDRO2      0
0.867D-05  -1.10  1 0 CP(I) PKD NER CV(I)
3
-1  0
XSU          0
0.116D-14  -0.45  1 0 CP(I) PKD NER CV(I)
3
-1  0
XAA          0
0.116D-14  -0.45  1 0 CP(I) PKD NER CV(I)
3
-1  0
XVAL         0
0.371D-06  -1.50  1 0 CP(I) PKD NER CV(I)
3
-1  0
XBUT         0
0.962D-06  -1.50  1 0 CP(I) PKD NER CV(I)
3
-1  0
XPRO         0
0.817D-07  -1.50  1 0 CP(I) PKD NER CV(I)
3
-1  0
XAC          0
0.168D-05  -1.699  1 0 CP(I) PKD NER CV(I)
3
-1  0
XH2          0
0.108D-05  -1.699  1 0 CP(I) PKD NER CV(I)
3
-1  0
C ******* DATA SET 14B: SOLID PHASE SPECIES
XHCELREDI    0
1.00D-05  0 CP(I) CV(I)
XHCELSLOW    0
0.651D-02  0 CP(I) CV(I)
XCELREDI     0

301
C******** DATA SET 14C: GASEOUS PHASE SPECIES
N2GAS  0.00D0  10.0  0  28  CP(I) CS(I) CV(I) MW(I)
O2GAS  0.00D0  10.0  0  32  CP(I) CS(I) CV(I) MW(I)
CH4GAS 0.431D0 10.0  0  16  CP(I) CS(I) CV(I) MW(I)
CO2GAS 0.492D0  10.0  0  44  CP(I) CS(I) CV(I) MW(I)
H2GAS  0.590D-03  10.0  0   2   CP(I) CS(I) CV(I) MW(I)

C ******* DATA SET 15: SOURCE PARAMETERS
2  NPROF
2  18  IGS PROF, NDTPS
0.0000  0.0000  4.0000  0.000
4.0001 -2.00D-05  5.0000  -2.00D-05
5.0001 -1.00D-05  6.0000  -1.00D-05
6.0001  0.0000  7.0000  0.000
7.0001  0.0000  8.0000  0.000
8.0001  1.00D-07  10.0000  1.00D-07
10.0001  1.00D-07  17.0000  1.00D-07
17.0001  1.00D-07  24.0000  1.00D-07
24.0001  1.00D-07  30.0000  0.10D-06
1  26  IGS PROF, NDTPS
0.0000  0.00  2.0000  2.00D-05
2.0001  2.00D-05  3.0000  4.00D-05
3.0001  4.00D-05  4.0000  1.00D-04
4.0001  5.00D-05  5.0000  5.00D-05
5.0001  5.00D-05  6.0000  6.00D-06
6.0001 -3.00D-06  7.0000  -3.00D-06
7.0001 -3.00D-06  8.0000  -3.00D-06
8.0001 -3.00D-06 10.0000  -3.00D-06
10.0001 -7.00D-06 17.0000  -7.00D-06
17.0001 -5.00D-06 24.0000  -5.00D-06
24.0001 -5.00D-06 30.0000  -5.00D-06
30.0001 -4.00D-06 35.0000  -4.00D-06
35.0001 -3.00D-06 40.0000  -3.00D-06

C ******* DATA SET 16: REACTION DATA
19
1  1  0  NRTS NPDS KRTYP REACTION 1
-14.0  LOGKEQ
-1  1  CXYZP(1,1)  DXYZP(1,1)
1  16  IGS NRT(1,1)
IGSNPD(1,1)
2  1  0  NRTS NPDS KRTYP REACTION 2
-10.32
-1 1 1
1 2 17
IGSNPD(1,1)
2 1 0
6.35
1 1 1
1 2 18
2 1 0
-4.76
-1 1 1
1 4 19
2 1 0
-4.88
-1 1 1
1 5 20
2 1 0
-4.82
-1 1 1
1 6 21
2 1 0
-9.25
-1 1 1
1 3 23
2 6 5

(HYDROLYSIS HEMICELLULOSE)
10.50 2.00d+02
1 0 24
5.00 7.00 343.15 310.15 0.118
PHEL(I),PHH(I),TEMPMAX(I),TEMPOPT(I),THETA(I)
1 6.845d-04
36 3
(CXYZP(I,J),J=1,NRTS), (DXYZP(I,J),J=1,NPDS)
34 3
0 0 0 0
INHIB(I),HSCINH(1,I),HSCINH(2,I),PQ(1,I),PQ(2,I)

1 6 5

(HYDROLYSIS CELULOSE)
10.50 2.00d+02
1 0 25
5.00 7.00 343.15 310.15 0.118
PHEL(I),PHH(I),TEMPMAX(I),TEMPOPT(I),THETA(I)
1 6.693d-04
36 3
(CXYZP(I,J),J=1,NRTS), (DXYZP(I,J),J=1,NPDS)
34 3
0 0 0 0
INHIB(I),HSCINH(1,I),HSCINH(2,I),PQ(1,I),PQ(2,I)

1 6 5

(HYDROLYSIS PROTEIN)
10.50 2.00d+02  RHMXX(I), HSCSAN(1,I)
1 0 24  LOCH,TAUL(I), NHYBAC(I)
5.00 7.00 343.15 310.15 0.118  
  PHH(I), PHL(I), TEMPMAX(I), TEMPOPT(I), THETAK(I)
1 3.476d-03 3.472d-03 3.555d-03 9.273d-03 1.254d-02  
  (CRYZP(I,J),J=1,NRTS), (DYZP(I,J),J=1,NPDS)
37 7 4 5 18 23  
  (IGSNRT(I,J),J=1,NRTS), (IGSNPD(I,J),J=1,NPDS)
0 0 0 0 0  
  INHIB(I), HSCINH(1,I), HSCINH(2,I), PQ(1,I), PQ(2,I)
2 5 2  
  NRTS NPDS KRTYP REACTION 17

(Acetogenesis of Valerate)
1.50 8.00D-07 0 0 0  
  GRMAX HSCSAN(1) HSCSAN(2) HSCSAN(3)
HSCSAN(4)
1 0 0 0 0 0  
  LOCSK LOCAK LOCNK LOCLK TAUL TAUE
5.6 7.0 343.15 310.15 0.069  
  PHL(I), PHH(I) TEMPMAX TEMPOPT THETAK
1 0.065 0.95 0.95 1.90 0.065 0.965 CXYZP(1,I) DXYZP(1,I)
22 3 19 20 15 28 1 IGSNRT(1,I) IGSNPD(1,I)
15 9.00D-07 0 -1 0  
  INHIB(I) HSCINH(1) HSCINH(1) PQ(1) PQ(2)
3 4 2  
  NRTS NPDS KRTYP REACTION 18

(Acetogenesis of Butyrate)
1.60 4.20D-06 0 0 0  
  GRMAX HSCSAN(1) HSCSAN(2) HSCSAN(3)
HSCSAN(4)
1 0 0 0 0 0  
  LOCSK LOCAK LOCNK LOCLK TAUL TAUE
5.6 7.0 343.15 310.15 0.069  
  PHL(I), PHH(I) TEMPMAX TEMPOPT THETAK
1 0.066 0.066 1.868 1.868 0.066 0.934 CXYZP(1,I) DXYZP(1,I)
21 18 3 19 15 29 1 IGSNRT(1,I) IGSNPD(1,I)
15 9.00D-07 0 -1 0  
  INHIB(I) HSCINH(1) HSCINH(1) PQ(1) PQ(2)
2 5 2  
  NRTS NPDS KRTYP REACTION 19

(Acetogenesis of Propionate)
1.50 4.30D-06 0 0 0  
  GRMAX HSCSAN(1) HSCSAN(2) HSCSAN(3)
HSCSAN(4)
1 0 0 0 0 0  
  LOCSK LOCAK LOCNK LOCLK TAUL TAUE
5.6 7.0 343.15 310.15 0.069  
  PHL(I), PHH(I) TEMPMAX TEMPOPT THETAK
1 0.035 0.95 2.85 0.925 0.035 0.910 CXYZP(1,I) DXYZP(1,I)
20 3 19 15 2 30 1 IGSNRT(1,I) IGSNPD(1,I)
15 9.00D-07 0 -1 0  
  INHIB(I) HSCINH(1) HSCINH(1) PQ(1) PQ(2)
3 3 2  
  NRTS NPDS KRTYP REACTION 20

(Acetotrophic Methanogenesis)
1.30 6.00D-05 0 0 0  
  GRMAX HSCSAN(1) HSCSAN(2) HSCSAN(3)
HSCSAN(4)
1 0 0 0 0 0  
  LOCSK LOCAK LOCNK LOCLK TAUL TAUE
5.6 7.0 343.15 310.15 0.069  
  PHL(I), PHH(I) TEMPMAX TEMPOPT THETAK
1 0.03 0.02 0.95 0.95 0.02 CXYZP(1,I) DXYZP(1,I)
19 1 3 12 2 31 IGSNRT(1,I) IGSNPD(1,I)
0 0 0 0 0  
  INHIB(I) HSCINH(1) HSCINH(1) PQ(1) PQ(2)
4 2 2  
  NRTS NPDS KRTYP REACTION 21

(Hydrogenotrophic Methanogenesis)
1.80 8.75D-08 0 0 0  
  GRMAX HSCSAN(1) HSCSAN(2) HSCSAN(3)
HSCSAN(4)
1 0 0 0 0 0  
  LOCSK LOCAK LOCNK LOCLK TAUL TAUE
5.6 7.0 343.15 310.15 0.069  
  PHL(I), PHH(I) TEMPMAX TEMPOPT THETAK
3.833 0.9721 0.96652 5.58d-03 0.9442 5.58d-03 CXYZP(1,I) DXYZP(1,I)
15 2 1 3 12 32 IGSNRT(1,I)
IGSNPD(1,1)
0 0 0 0 0           INHIB(I)  HSCINH(1)  HSCINH(1)  PQ(1)  PQ(2)
1 1 6           NRTS NPDS KRTYP  REACTION 22
3.38D-05 2.50
1 1          KH  KLA
18 43          CXYZP(1,1)  DXYZP(1,1)
1 1 6           IGSNRT(1,1)  IGSNPD(1,1)
1.35D-06 2.00
1 1          KH  KLA
12 42          IGSNRT(1,1)  IGSNPD(1,1)
7.80D-07 2.50
1 1          KH  KLA
15 44          CXYZP(1,1)  DXYZP(1,1)
C ******* DATA SET 17: WATER CONTENT DATA
0.55 55.4 0.55 18.069D-3 0 RHOLTHP CWATP THP PMVW CVW
0 0 0 0 0 0 0 0 0
C ******* DATA SET 18: GRAIN DATA
0.10 33 0.79 1 RHOBP IGCG POROSITY KROBC
C ******* DATA SET 19: HEAT GENERATION DATA
0
0
END OF JOB
Output file as per input

1
PROBLEM 1
SIMULATION of Solid Waste Degradation
IITR = 0, ICOND = 0

C ******* DATA SET 2: NUMBER OF COMPONENTS AND SPECIES

NO. OF AQUEOUS COMPONENTS, NONA . . . . . . . . . . . 15
NO. OF ADSORBENT COMPONENTS, NONS . . . . . . . . . . 0
NO. OF COMPLEXED SPECIES, NOMX . . . . . . . . . . . 8
NO. OF ADSORBED SPECIES, NOMY . . . . . . . . . . . 0
NO. OF ION-EXCHANGED SPECIES, NOMZ . . . . . . . . . 0
NO. OF PRECIPITATED SPECIES, NOMP . . . . . . . . . 0
NO. OF AQUEOUS PHASE MICROBIAL SPECIES, NOMB . . . 9
NO. OF ADSORBED PHASE MICROBIAL SPECIES, NOMA . . . 0
NO. OF AQUEOUS SOLIDS SPECIES, NOMHB . . . . . . . 0
NO. OF ADSORBED PHASE SOLIDS SPECIES, NOMHA . . . 7
NO. OF GASEOUS SPECIES, NOG . . . . . . . . . . . . . 5

NO. OF ALL CHEMICAL COMPONENTS, NON . . . . . . . . . 15
NO. OF CHEMICAL PRODUCT SPECIES, NOPD . . . . . . . 8
NO. OF ALL CHEMICAL SPECIES, NOM . . . . . . . . . . 23
NO. OF ALL MICROBIAL SPECIES, NOB . . . . . . . . . 9
NO. OF ALL SOLIDS SPECIES, NOH . . . . . . . . . . . 7
NO. OF ALL GASEOUS SPECIES, NOG . . . . . . . . . . 5

C ******* DATA SET 3: H+, E-, IONIC STRENGTH AND SORPTION INFORMATION

IONIC STRENGTH USED FOR COMPUTING ACTIVITY COEF. . . 0.000D+00
IS IONIC STRENGTH USED TO CORRECT ACTIVITY COEF. . . 0
LOCATION OF H+ IN THE COMPONENT LIST, LNH . . . . . . 1
LOCATION OF GAS IN THE COMPONENT LIST, LNG . . . . . . 0
LOCATION OF E- IN THE COMPONENT LIST, LNE . . . . . . 0

C ******* DATA SET 4: TEMPERATURE, PRESSURE, AND EXPECTED PE AND PH

ABSOLUTE TEMPERATURE. . . . . . . . . . . . . . . . . . 0.314D+03
PRESSURE . . . . . . . . . . . . . . . . . . . . . . . . 0.100D+01
TEMPERATURE CONTROL PARAMETER 0 OR 1 . . . . . . . . . 0

BATCH REACTOR SIMULATION CONTROL . . . . . . . . . . 0
BATCH REACTOR HEAD-SPACE VOLUME . . . . . . . . . . . 0.250D+00
MAXIMUM ALLOWABLE PRESSURE INCREMENT . . . . . . 0.100D+00

EXPECTED MINIMUM PE, PEMN . . . . . . . . . . . . . . . . -20.0000
EXPECTED MAXIMUM PE, PEMX ................. 20.0000
EXPECTED MINIMUM PH, PHMN ................. -1.0000
EXPECTED MAXIMUM PH, PHMX ................. 20.0000
EXPECTED MINIMUM ELECTRON ACTIVITY .......... 0.1000D-19
EXPECTED MAXIMUM ELECTRON ACTIVITY .......... 0.1000D+21
EXPECTED MINIMUM HYDROGEN ACTIVITY .......... 0.1000D-19
EXPECTED MAXIMUM HYDROGEN ACTIVITY .......... 0.1000D+02

C ******* DATA SET 7: BASIC AND INTEGER REAL PARAMETERS

STATIC SIMULATION CONTROL, KSS ............... 1
NO. OF TIME INCREMENTS (TIME STEPS), NOTI ....... 1100000

TIME STEP SIZE, DELT ......................... 0.100D-03
TIME STEP SIZE CHANGING INCREMENT, CHNG ......... 0.000D+00
MAXIMUM TIME STEP SIZED ALLOWED, DELMX ........... 0.100D+00
BEGINNING SIMULATION TIME, TBNG ............... 0.000D+00
ENDING SIMULATION TIME, TEND .................. 0.115D+03

RELAXATION PARAMETER, OMEGA ................. 0.100D+01
NO. OF ITERATIONS ALLOWED ON TOTAL CONC, NITT .... 30
TOLERANCE FOR ITERATION ON TOTAL CONC, EPST .... 0.100D-05
NO. OF PRECIPITATION CYCLES ALLOWED, NPCYL ....... 1
NO. OF NEWTON RAPHSON ITERATIONS ALLOWED, NITER .... 300
TOLERANCE FOR NEWTON RAPHSON ITERATION, EPS .... 0.100D-08
CONSTRAINT ON THE COMPLEXED SPECIES CONC. ....... 0.500D+03

C ******* DATA SET 8: PRINTER AND AUXILIARY STORAGE CONTROL

C ******* DATA SET 9: TOTAL ANALYTICAL CONCENTRATION OF ALL COMPONENTS

**** INPUT AQUEOUS COMPONENT DATA ****

<table>
<thead>
<tr>
<th>J</th>
<th>COMPONENT NAME</th>
<th>TOTAL COMPONENT CONCENTRATION (MOLES/BATCH VOLUME)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H+</td>
<td>-3.9576D-04</td>
</tr>
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<td>NPDS</td>
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<td>6</td>
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**Reactant Name** | **Global Species No.** | **S.C.**
--- | --- | ---
H+ | 1 | -1.0000
SHBUT | 6 | 1.0000
H+ | 1 | -1.0000
SHVAL | 7 | 1.0000
H+ | 1 | -1.0000
NH4+ | 3 | 0.0007

**Product Name** | **Global Species No.** | **S.C.**
--- | --- | ---
SBUT- | 21 | 1.0000
SVAL- | 22 | 1.0000
NH3 | 23 | 1.0000
XHYDRO1 | 24 | 0.0007
SHBUT | 6 | 0.0033
SHAC | 4 | 0.0046
H2* | 15 | 0.0159
H2CO3* | 18 | 0.0113
H+ | 1 | 0.0007
IRXN = 10,  NRTS = 2,  NPDS = 6,  RXTYP = 5
RHMXK= 0.1050D+02,  HALF SAT CONSTANT= 0.2000D+03
LOCATION OF SOLID SUBSTRATE = 1, LAG TIME = 0.0000D+00
LOCATION OF BACTERIAL SPECIES = 25

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<th>S.C.</th>
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IRXN = 11,  NRTS = 1,  NPDS = 5,  RXTYP = 5
RHMXK= 0.1050D+02,  HALF SAT CONSTANT= 0.2000D+03
LOCATION OF SOLID SUBSTRATE = 1, LAG TIME = 0.0000D+00
LOCATION OF BACTERIAL SPECIES = 24

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IRXN = 12,  NRTS = 2,  NPDS = 5,  RXTYP = 2
GRMAX = 0.1500D+01  GRK = 0.2308D+02

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<th>SUBSTRATE</th>
<th>E- ACCEPTOR</th>
<th>NUTRIENT</th>
</tr>
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<tbody>
<tr>
<td></td>
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<td></td>
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| REACTANT NUMBER :  |             | 1 | 0 | 0 |
| --- | --- | --- | --- |
| HALF SAT CONSTANT = | 0.8000D-06 | 0.0000D+00 | 0.0000D+00 |
| LAG TIME = | 0.0000D+00 | TIME TO EXPONENTIAL GROWTH = | 0.0000D+00 |

<table>
<thead>
<tr>
<th>INHIBITOR SPCS</th>
<th>KI1</th>
<th>KI2</th>
<th>P</th>
<th>Q</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.9000D-06</td>
<td>0.0000D+00</td>
<td>-0.100D+01</td>
<td>0.0000D+00</td>
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<table>
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<th>Reactant Name</th>
<th>Global Species No.</th>
<th>S.C.</th>
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</thead>
<tbody>
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<td>SVAL-</td>
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\begin{verbatim}
2  NH4+                      3                0.0650

J   Product Name      Global Species No.    S.C.
--  --------------------  ------------------   ------
1  SAC-                     19                0.9500   
2  SPRO-                    20                0.9500   
3  H2*                      15                1.9000   
4  XVAL                     28                0.0650   
5  H+                        1                0.9650   

IRXN = 13, NRTS = 3, NPDS = 4, RXTYP = 2
GRMAX = 0.1600D+01 GRK = 0.2424D+02

SUBSTRATE     E- ACCEPTOR   NUTRIENT
-------------     -----------   --------
REACTANT NUMBER :       1             0              0
HALF SAT CONSTANT =   0.4200D-05    0.0000D+00    0.0000D+00
LAG TIME = 0.0000D+00, TIME TO EXPONENTIAL GROWTH = 0.0000D+00

INHIBITOR SPCS        KI1          KI2         P          Q
--------------        ---          ---        ---        ---
15       0.9000D-06   0.0000D+00 -0.100D+01  0.000D+00

1  SBUT-                    21                1.0000   
2  H2CO3*                   18                0.0660   
3  NH4+                      3                0.0660   

IRXN = 14, NRTS = 2, NPDS = 5, RXTYP = 2
GRMAX = 0.1500D+01 GRK = 0.4286D+02

SUBSTRATE     E- ACCEPTOR   NUTRIENT
-------------     -----------   --------
REACTANT NUMBER :       1             0              0
HALF SAT CONSTANT =   0.4300D-05    0.0000D+00    0.0000D+00
LAG TIME = 0.0000D+00, TIME TO EXPONENTIAL GROWTH = 0.0000D+00

INHIBITOR SPCS        KI1          KI2         P          Q
--------------        ---          ---        ---        ---
15       0.9000D-06   0.0000D+00 -0.100D+01  0.000D+00

J   Reactant Name     Global Species No.    S.C.
--  --------------------  ------------------   ------
1  SPRO-                    20                1.0000   

J   Product Name      Global Species No.    S.C.
--  --------------------  ------------------   ------
1  SAC-                     19                1.8680   
2  H2*                      15                1.8680   
3  XBUT                     29                0.0660   
4  H+                        1                0.9340   

IRXN = 14, NRTS = 2, NPDS = 5, RXTYP = 2
GRMAX = 0.1500D+01 GRK = 0.4286D+02

SUBSTRATE     E- ACCEPTOR   NUTRIENT
-------------     -----------   --------
REACTANT NUMBER :       1             0              0
HALF SAT CONSTANT =   0.4300D-05    0.0000D+00    0.0000D+00
LAG TIME = 0.0000D+00, TIME TO EXPONENTIAL GROWTH = 0.0000D+00

INHIBITOR SPCS        KI1          KI2         P          Q
--------------        ---          ---        ---        ---
15       0.9000D-06   0.0000D+00 -0.100D+01  0.000D+00

J   Reactant Name     Global Species No.    S.C.
--  --------------------  ------------------   ------
1  SPRO-                    20                1.0000   
\end{verbatim}
<table>
<thead>
<tr>
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<th>Reactant Name</th>
<th>Global Species No.</th>
<th>S.C.</th>
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<tbody>
<tr>
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<td>0.9500</td>
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<td>XPRO</td>
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<td>5</td>
<td>H+</td>
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IRXN = 15, NRTS = 3, NPDS = 3, RXTYP = 2
GRMAX = 0.1300D+01 GRK = 0.6500D+02

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HALF SAT CONSTANT = 0.0000D+00 0.0000D+00 0.0000D+00

LAG TIME = 0.0000D+00, TIME TO EXPONENTIAL GROWTH = 0.0000D+00

INHIBITOR SPCS KI1 KI2 P Q
------------- --- --- --- ---
0 0.0000D+00 0.0000D+00 0.0000D+00 0.0000D+00

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<th>S.C.</th>
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<tr>
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<td>2</td>
<td>HCO3-</td>
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IRXN = 16, NRTS = 4, NPDS = 2, RXTYP = 2
GRMAX = 0.1800D+01 GRK = 0.3226D+03

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HALF SAT CONSTANT = 0.8750D-07 0.0000D+00 0.0000D+00

LAG TIME = 0.0000D+00, TIME TO EXPONENTIAL GROWTH = 0.0000D+00

INHIBITOR SPCS KI1 KI2 P Q
------------- --- --- --- ---
0 0.0000D+00 0.0000D+00 0.0000D+00 0.0000D+00

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IRXN = 17, NRTS = 1, NPDS = 1, RXTYP = 6

AKH= 0.3380D-04, BKLA= 0.250D+01

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IRXN = 18, NRTS = 1, NPDS = 1, RXTYP = 6

AKH= 0.1350D-05, BKLA= 0.200D+01

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IRXN = 19, NRTS = 1, NPDS = 1, RXTYP = 6

AKH= 0.7800D-06, BKLA= 0.250D+01

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<td>1.0000</td>
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**DATA SET 17: WATER CONTENT DATA**

INITIAL BULK LIQUID DENSITY, RHOLTHP. 0.5500D+00
INITIAL WATER CONCENTRATION, CWATP. 0.5540D+02
INITIAL LIQUID CONTENT, THP 0.5500D+00
PARTIAL MOLAR VOLUME OF WATER, PMVW 0.1807D-01
SPECIFIC HEAT CAPACITY OF WATER 0.0000D+00

STOICHIOMETRY OF WATER IN ALL PRODUCT SPECIES

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<td>6.00</td>
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C ******* DATA SET 18: GRAIN DATA

0

INITIAL BULK SOLID DENSITY, RHOB . . . . . . . 0.1000D+00
GLOBAL SPECIES NUMBER OF SOLIDS GRAIN, IGCG . 33
POROSITY OF SOLIDS , POROSITY . . . . . . . . 0.7900D+00

0
KROBC = 1
SOLIDS DENSITY IS TO BE COMPUTED

1

C ******* DATA SET 19: HEAT GENERATION DATA

0

NHGENFAC = 0 (HEAT GENERATION NOT INCLUDED)

Output file at time = 2.0 day

1

*** WATER, GAS, AND GRAIN DATA AT ITM =**** TIME = 2.0000D+00 ***

WATER CONCENTRATION, CWATP. . . . . . . . . . . 0.55400D+02
LIQUID CONTENT, TH. . . . . . . . . . . . . . 0.55058D+00
BULK LIQUID CONTENT, RHOLTH . . . . . . . . . 0.55000D+00
LIQUID DENSITY, RHOL. . . . . . . . . . . . . 0.99894D+00
GAS CONTENT, GTH. . . . . . . . . . . . . . . 0.23942D+00
TOTAL GAS CONTENT, GASVOL . . . . . . . . . . . 0.48942D+00
GAS DENSITY, RHOG . . . . . . . . . . . . . . 0.99319D-03
GAS PRESSURE, PRESU . . . . . . . . . . . . . 0.10000D+01
GRAIN CONCENTRATION, CGRNP. . . . . . . . . . 0.00000D+00
BULK SOLID DENSITY, RHOB. . . . . . . . . . . . 0.31830D+00
TEMPERATURE, TEMPP. . . . . . . . . . . . . . 0.31415D+03

1

*** COMPONENT OUTPUT AT ITM =**** TIME = 2.0000D+00 ***

(TOTAL CONCENTRATIONS IN MOLES/BATCH VOLUME)

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<th>TOTPC</th>
<th>XLOG</th>
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<td>0.00000D+00</td>
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<td>4.7103D-05</td>
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<td>0.00000D+00</td>
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### Component Species Output

**At ITM = 20000, Time = 2.0000D+00**

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<th>CLOG</th>
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<td>-1.</td>
<td>0.1000D+01</td>
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<td>0.1818D-11</td>
<td>0.</td>
<td>0.1000D+01</td>
<td>-0.1174D+01</td>
</tr>
<tr>
<td>11</td>
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<td>0.1818D-09</td>
<td>0.</td>
<td>0.1000D+01</td>
<td>-0.9740D+01</td>
</tr>
<tr>
<td>12</td>
<td>CH4*</td>
<td>0.5830D-04</td>
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<td>-0.4234D+01</td>
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<tr>
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<td>0.1000D+01</td>
<td>-0.4156D+01</td>
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<tr>
<td>14</td>
<td>N2*</td>
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<tr>
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<td>-0.7216D+01</td>
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</table>

### Product Species Output

**At ITM = 20000, Time = 2.0000D+00**

<table>
<thead>
<tr>
<th>I</th>
<th>SPECIES</th>
<th>CONCEN.</th>
<th>GAMA</th>
<th>VJ</th>
<th>KI</th>
<th>CLOG</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>OH-</td>
<td>0.201D-07</td>
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<tr>
<td>2</td>
<td>CO3--</td>
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<tr>
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### MICROBIAL SPECIES OUTPUT AT ITM = 20000 TIME = 2.0000D+00

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<thead>
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<th>CONCEN.</th>
<th>CLOG</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<tr>
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<td>XSU</td>
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<tr>
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<td>XAA</td>
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<td>7</td>
<td>XPRO</td>
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### SOLIDS SPECIES IN SOLID PHASE OUTPUT AT ITM = 20000 TIME = 2.0000D+00

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<th>CLOG</th>
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</thead>
<tbody>
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<td>XCELREDI</td>
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<td>XCELSLOW</td>
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<td>XPROTREIN</td>
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<td>XSTARCH</td>
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<tr>
<td>7</td>
<td>XINERT</td>
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### GASEOUS SPECIES OUTPUT AT ITM = 20000 TIME = 2.0000D+00

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<thead>
<tr>
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<th>CONCEN.</th>
<th>CLOG</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N2GAS</td>
<td>0.000D+00</td>
<td>-38.0000</td>
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<tr>
<td>2</td>
<td>O2GAS</td>
<td>0.000D+00</td>
<td>-38.0000</td>
</tr>
<tr>
<td>3</td>
<td>CH4GAS</td>
<td>0.535D+00</td>
<td>-0.2715</td>
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<tr>
<td>4</td>
<td>CO2GAS</td>
<td>0.387D+00</td>
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<tr>
<td>5</td>
<td>H2GAS</td>
<td>0.814D-03</td>
<td>-3.0893</td>
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</table>
*** GASEOUS SPECIES OUTPUT AT ITM = 20000 TIME = 2.0000D+00 ***

<table>
<thead>
<tr>
<th>I</th>
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<th>QVOL</th>
</tr>
</thead>
<tbody>
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</tr>
<tr>
<td>2</td>
<td>O2GAS</td>
<td>0.0000D+00</td>
</tr>
<tr>
<td>3</td>
<td>CH4GAS</td>
<td>0.1900D+01</td>
</tr>
<tr>
<td>4</td>
<td>CO2GAS</td>
<td>0.1628D+01</td>
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<tr>
<td>5</td>
<td>H2GAS</td>
<td>0.3025D-02</td>
</tr>
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*** REACTION DATA AT ITM = 20000 TIME = 2.0000D+00 ***

IRXN = 1, LOG KEQ = -14.00, LOG KEQM = -14.00
IRXN = 2, LOG KEQ = -10.32, LOG KEQM = -10.32
IRXN = 3, LOG KEQ =  6.35, LOG KEQM =  6.35
IRXN = 4, LOG KEQ = -4.76, LOG KEQM = -4.76
IRXN = 5, LOG KEQ = -4.88, LOG KEQM = -4.88
IRXN = 6, LOG KEQ = -4.82, LOG KEQM = -4.82
IRXN = 7, LOG KEQ = -4.86, LOG KEQM = -4.86
IRXN = 8, LOG KEQ = -9.25, LOG KEQM = -9.25
IRXN = 9 GRK = 0.1050D+02
IRXN =10 GRK = 0.1050D+02
IRXN =11 GRK = 0.1050D+02
IRXN =12 GRMAX = 0.1500D+01, GRK = 0.2308D+02
IRXN =13 GRMAX = 0.1600D+01, GRK = 0.2424D+02
IRXN =14 GRMAX = 0.1500D+01, GRK = 0.4286D+02
IRXN =15 GRMAX = 0.1300D+01, GRK = 0.6500D+02
IRXN =16 GRMAX = 0.1800D+01, GRK = 0.3226D+03
IRXN =17 BKLA = 0.2500D+01
IRXN =18 BKLA = 0.2000D+01
IRXN =19 BKLA = 0.2500D+01
ITM = 30000, TIME = 0.3000D+01
KTER = 1 ITER = 3 LTER = 3
CONVERGENT SOLUTIONS HAVE BEEN OBTAINED WITH 0 PRECIPITATED SPECIES

Output file at time = 7.0 day

*** WATER, GAS, AND GRAIN DATA AT ITM =**** TIME = 7.0000D+00 ***

WATER CONCENTRATION, CWATP. . . . . . . . . . 0.55400D+02
LIQUID CONTENT, TH. . . . . . . . . . . . . . 0.55058D+00
BULK LIQUID CONTENT, RHOLTH . . . . . . . . . 0.55000D+00
LIQUID DENSITY, RHOL. . . . . . . . . . . . . 0.99895D+00
GAS CONTENT, GTH. . . . . . . . . . . . . . . 0.23942D+00
TOTAL GAS CONTENT, GASVOL . . . . . . . . . . . 0.48942D+00
GAS DENSITY, RHOG . . . . . . . . . . . . . . . 0.10016D-02

321
GAS PRESSURE, PRESU . . . . . . . . . . . . .  0.10000D+01
GRAIN CONCENTRATION, CGRN. . . . . . . . . .  0.00000D+00
BULK SOLID DENSITY, RHOB. . . . . . . . . . .  0.28472D+00
TEMPERATURE, TEMPP. . . . . . . . . . . . . .  0.31415D+03

1

*** COMPONENT OUTPUT AT ITM =**** TIME =  7.0000D+00 ***

(TOTAL CONCENTRATIONS IN MOLES/BATCH VOLUME)

<table>
<thead>
<tr>
<th>J</th>
<th>COMPONENT</th>
<th>TOTAC</th>
<th>TOTDC</th>
<th>TOTSC</th>
<th>TOTPC</th>
<th>XLOG</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>1.5282D-05</td>
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<tr>
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<tr>
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<tr>
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<td>0.0000D+00</td>
<td>-8.5732D+00</td>
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<td>4.5363D-08</td>
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<td>5.3868D-08</td>
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<td>0.0000D+00</td>
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<tr>
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<td>9.1237D-09</td>
<td>9.1237D-09</td>
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<td>0.0000D+00</td>
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</tr>
<tr>
<td>8</td>
<td>SSU</td>
<td>1.9400D-06</td>
<td>1.9400D-06</td>
<td>0.0000D+00</td>
<td>0.0000D+00</td>
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<tr>
<td>9</td>
<td>SAA</td>
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<td>0.0000D+00</td>
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<td>0.0000D+00</td>
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<tr>
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<tr>
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<tr>
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<td>0.0000D+00</td>
<td>-9.7404D+00</td>
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<tr>
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<td>2.3068D-07</td>
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<td>0.0000D+00</td>
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**** COMPONENT SPECIES OUTPUT AT ITM =70000  TIME =  7.0000D+00 ****

(SPECIES CONCENTRATIONS IN MOLES/MASS OF PHASE)

<table>
<thead>
<tr>
<th>I</th>
<th>SPECIES</th>
<th>CONCEN.</th>
<th>VJ</th>
<th>GAMA(I)</th>
<th>CLOG</th>
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</thead>
<tbody>
<tr>
<td>1</td>
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<td>1.</td>
<td>0.1000D+01</td>
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<tr>
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<td>0.3165D-03</td>
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</tr>
<tr>
<td>3</td>
<td>NH4+</td>
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<tr>
<td>4</td>
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</tr>
<tr>
<td>5</td>
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<td>0.</td>
<td>0.1000D+01</td>
<td>-0.9575D+01</td>
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<tr>
<td>6</td>
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<tr>
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<tr>
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<td>SAA</td>
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<td>0.</td>
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<td>-0.1174D+02</td>
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<td>0.</td>
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<td>-0.1174D+02</td>
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<tr>
<td>11</td>
<td>NA+</td>
<td>0.1818D-09</td>
<td>0.</td>
<td>0.1000D+01</td>
<td>-0.9740D+01</td>
</tr>
<tr>
<td>12</td>
<td>CH4*</td>
<td>0.2674D-04</td>
<td>0.</td>
<td>0.1000D+01</td>
<td>-0.4573D+01</td>
</tr>
<tr>
<td>13</td>
<td>O2*</td>
<td>0.6977D-04</td>
<td>0.</td>
<td>0.1000D+01</td>
<td>-0.4156D+01</td>
</tr>
<tr>
<td>14</td>
<td>N2*</td>
<td>0.1818D-09</td>
<td>0.</td>
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<td>-0.9740D+01</td>
</tr>
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**** PRODUCT SPECIES OUTPUT AT ITM =70000 TIME =  7.0000D+00 ****
<table>
<thead>
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<th>SPECIES</th>
<th>CONCEN.</th>
<th>GAMA</th>
<th>VJ</th>
<th>KI</th>
<th>CLOG</th>
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<tr>
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</tbody>
</table>
### Gaseous Species Output at Itm = 70000 Time = 7.0000D+00

<table>
<thead>
<tr>
<th>I</th>
<th>SPECIES</th>
<th>CONCEN.</th>
<th>CLOG</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N2GAS</td>
<td>0.000D+00</td>
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</tr>
<tr>
<td>2</td>
<td>O2GAS</td>
<td>0.000D+00</td>
<td>-38.0000</td>
</tr>
<tr>
<td>3</td>
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<tr>
<td>4</td>
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### Gaseous Species Output at Itm = 70000 Time = 7.0000D+00

<table>
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<th>SPECIES</th>
<th>QVOL</th>
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</thead>
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</tr>
<tr>
<td>2</td>
<td>O2GAS</td>
<td>0.0000D+00</td>
</tr>
<tr>
<td>3</td>
<td>CH4GAS</td>
<td>0.1963D+02</td>
</tr>
<tr>
<td>4</td>
<td>CO2GAS</td>
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</tr>
<tr>
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<td>H2GAS</td>
<td>0.4750D-01</td>
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Output file at time = 20.0 day

*** Water, Gas, and Grain Data at Itm = Time = 2.0000D+01 ***

- WATER CONCENTRATION, CWATP: 0.55400D+02
- LIQUID CONTENT, TH: 0.55058D+00
- BULK LIQUID CONTENT, RHOLTH: 0.55000D+00
- LIQUID DENSITY, RHOL: 0.99894D+00
- GAS CONTENT, GTH: 0.23942D+00
- TOTAL GAS CONTENT, GASVOL: 0.48942D+00
- GAS DENSITY, RHOG: 0.94031D-03
- GAS PRESSURE, PRESU: 0.10000D+01
- GRAIN CONCENTRATION, CGRNP: 0.00000D+00
- BULK SOLID DENSITY, RHOB: 0.21863D+00
**TEMPERATURE, TEMPP. . . . . . . . . . . . . . . . . . . . 0.31415D+03**

1

*** COMPONENT OUTPUT AT ITM =**** TIME = 2.0000D+01 ***

(TOTAL CONCENTRATIONS IN MOLES/BATCH VOLUME)

<table>
<thead>
<tr>
<th>J COMPONENT</th>
<th>TOTAC</th>
<th>TOTDC</th>
<th>TOTSC</th>
<th>TOTPC</th>
<th>XLOG</th>
</tr>
</thead>
<tbody>
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<td>1 H+</td>
<td>7.1150D-06</td>
<td>7.1150D-06</td>
<td>0.0000D+00</td>
<td>0.0000D+00</td>
<td>-7.7512D+00</td>
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<tr>
<td>2 HCO3-</td>
<td>2.5174D-04</td>
<td>2.5174D-04</td>
<td>0.0000D+00</td>
<td>0.0000D+00</td>
<td>-3.3575D+00</td>
</tr>
<tr>
<td>3 NH4+</td>
<td>3.7056D-05</td>
<td>3.7056D-05</td>
<td>0.0000D+00</td>
<td>0.0000D+00</td>
<td>-4.1851D+00</td>
</tr>
<tr>
<td>4 SHAC</td>
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<td>3.1605D-07</td>
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<td>0.0000D+00</td>
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</tr>
<tr>
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<tr>
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</tr>
<tr>
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<tr>
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<td>0.0000D+00</td>
<td>0.0000D+00</td>
<td>-5.4526D+00</td>
</tr>
<tr>
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<td>0.0000D+00</td>
<td>0.0000D+00</td>
<td>-1.1740D+01</td>
</tr>
<tr>
<td>10 SIN</td>
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<td>1.0000D-12</td>
<td>0.0000D+00</td>
<td>0.0000D+00</td>
<td>-1.1740D+01</td>
</tr>
<tr>
<td>11 NA+</td>
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<td>1.0000D-10</td>
<td>0.0000D+00</td>
<td>0.0000D+00</td>
<td>-1.1740D+01</td>
</tr>
<tr>
<td>12 CH4*</td>
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<td>6.3692D-06</td>
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<td>0.0000D+00</td>
<td>-4.9363D+00</td>
</tr>
<tr>
<td>13 O2*</td>
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<td>3.8374D-05</td>
<td>0.0000D+00</td>
<td>0.0000D+00</td>
<td>-4.1563D+00</td>
</tr>
<tr>
<td>14 N2*</td>
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<td>1.0000D-10</td>
<td>0.0000D+00</td>
<td>0.0000D+00</td>
<td>-9.7404D+00</td>
</tr>
<tr>
<td>15 H2*</td>
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<td>0.0000D+00</td>
<td>-6.4051D+00</td>
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*** COMPONENT SPECIES OUTPUT AT ITM =***** TIME = 2.0000D+01 ****

(SPECIES CONCENTRATIONS IN MOLES/MASS OF PHASE)

<table>
<thead>
<tr>
<th>I</th>
<th>SPECIES</th>
<th>CONCEN.</th>
<th>VJ</th>
<th>GAMA(I)</th>
<th>CLOG</th>
</tr>
</thead>
<tbody>
<tr>
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<tr>
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<tr>
<td>3</td>
<td>NH4+</td>
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<tr>
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<tr>
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<tr>
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<td>-0.1016D+02</td>
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<tr>
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<tr>
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<td>0.1000D+01</td>
<td>-0.5453D+01</td>
</tr>
<tr>
<td>9</td>
<td>SAA</td>
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<td>0.1000D+01</td>
<td>-0.1174D+02</td>
</tr>
<tr>
<td>10</td>
<td>SIN</td>
<td>0.1818D-11</td>
<td>0</td>
<td>0.1000D+01</td>
<td>-0.1174D+02</td>
</tr>
<tr>
<td>11</td>
<td>NA+</td>
<td>0.1818D-09</td>
<td>0</td>
<td>0.1000D+01</td>
<td>-0.9740D+01</td>
</tr>
<tr>
<td>12</td>
<td>CH4*</td>
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<tr>
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<td>0.1000D+01</td>
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<tr>
<td>14</td>
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<td>0.1000D+01</td>
<td>-0.9740D+01</td>
</tr>
<tr>
<td>15</td>
<td>H2*</td>
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</tbody>
</table>

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*** PRODUCT SPECIES OUTPUT AT ITM =***** TIME = 2.0000D+01****

<table>
<thead>
<tr>
<th>I</th>
<th>SPECIES</th>
<th>CONCEN.</th>
<th>GAMA</th>
<th>VJ</th>
<th>KI</th>
<th>CLOG</th>
</tr>
</thead>
</table>

325
### MICROBIAL SPECIES OUTPUT AT ITM =***** TIME = 2.0000D+01****

<table>
<thead>
<tr>
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<th>CLOG</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.172D-05</td>
<td>-5.7635</td>
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<tr>
<td>2</td>
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<td>-18.0174</td>
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<tr>
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<tr>
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<tr>
<td>8</td>
<td>XAC</td>
<td>0.239D-04</td>
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<tr>
<td>9</td>
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</table>

### SOLIDS SPECIES IN SOLID PHASE OUTPUT AT ITM =***** TIME = 2.0000D+01****

<table>
<thead>
<tr>
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<th>SPECIES</th>
<th>CONCEN.</th>
<th>CLOG</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>0.100D-04</td>
<td>-5.0000</td>
</tr>
<tr>
<td>2</td>
<td>XHECELSLOW</td>
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</tr>
<tr>
<td>3</td>
<td>XCELREDI</td>
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<td>-5.0000</td>
</tr>
<tr>
<td>4</td>
<td>XCELSLOW</td>
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<tr>
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<td>XSTARCH</td>
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### Gaseous Species Output at ITM = Time = 2.0000D+01

<table>
<thead>
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<th>CONCEN.</th>
<th>CLOG</th>
</tr>
</thead>
<tbody>
<tr>
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<tr>
<td>2</td>
<td>O2GAS</td>
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</tr>
<tr>
<td>3</td>
<td>CH4GAS</td>
<td>0.545D+00</td>
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</tr>
<tr>
<td>4</td>
<td>CO2GAS</td>
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</tr>
<tr>
<td>5</td>
<td>H2GAS</td>
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</tbody>
</table>

### Gaseous Species Output at ITM = Time = 2.0000D+01

<table>
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<tr>
<th>I</th>
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<th>QVOL</th>
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</thead>
<tbody>
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</tr>
<tr>
<td>2</td>
<td>O2GAS</td>
<td>0.0000D+00</td>
</tr>
<tr>
<td>3</td>
<td>CH4GAS</td>
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</tr>
<tr>
<td>4</td>
<td>CO2GAS</td>
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</tr>
<tr>
<td>5</td>
<td>H2GAS</td>
<td>0.2345D+00</td>
</tr>
</tbody>
</table>

Output file at time = 27.0 day

### Component Output at ITM = Time = 2.7000D+01

<table>
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<tr>
<th>J</th>
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<th>TOTAC</th>
<th>TOTDC</th>
<th>TOTSC</th>
<th>TOTPC</th>
<th>XLOG</th>
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</thead>
<tbody>
<tr>
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<tr>
<td>2</td>
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<td>2.8215D-04</td>
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<tr>
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<tr>
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<tr>
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<tr>
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<td>SAA</td>
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<td>0.0000D+00</td>
<td>-1.1740D+01</td>
</tr>
<tr>
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<td>1.0000D-12</td>
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<td>0.0000D+00</td>
<td>-1.1740D+01</td>
</tr>
<tr>
<td>11</td>
<td>NA+</td>
<td>1.0000D-10</td>
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<td>0.0000D+00</td>
<td>0.0000D+00</td>
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</tr>
<tr>
<td>12</td>
<td>CH4*</td>
<td>4.4840D-06</td>
<td>4.4840D-06</td>
<td>0.0000D+00</td>
<td>0.0000D+00</td>
<td>-5.0887D+00</td>
</tr>
<tr>
<td>13</td>
<td>O2*</td>
<td>3.8374D-05</td>
<td>3.8374D-05</td>
<td>0.0000D+00</td>
<td>0.0000D+00</td>
<td>-4.1563D+00</td>
</tr>
</tbody>
</table>
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15 H2*        2.5707D-07  2.5707D-07  0.0000D+00  0.0000D+00 -6.3303D+00

1

*** COMPONENT SPECIES OUTPUT AT ITM =***** TIME =  2.7000D+01 ****

(SPECIES CONCENTRATIONS IN MOLES/MASS OF PHASE)

<table>
<thead>
<tr>
<th>I</th>
<th>SPECIES</th>
<th>CONCEN.</th>
<th>VJ</th>
<th>GAMA(I)</th>
<th>CLOG</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.1000D+01</td>
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<tr>
<td>9</td>
<td>SAA</td>
<td>0.1818D-11</td>
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<td>-0.1174D+02</td>
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<tr>
<td>10</td>
<td>SIN</td>
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<td>0.</td>
<td>0.1000D+01</td>
<td>-0.1174D+02</td>
</tr>
<tr>
<td>11</td>
<td>NA+</td>
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<td>0.</td>
<td>0.1000D+01</td>
<td>-0.9740D+01</td>
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<tr>
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<tr>
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<td>0.</td>
<td>0.1000D+01</td>
<td>-0.4156D+01</td>
</tr>
<tr>
<td>14</td>
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<td>0.1000D+01</td>
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<tr>
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1

*** PRODUCT SPECIES OUTPUT AT ITM =***** TIME =  2.7000D+01 ****

<table>
<thead>
<tr>
<th>I</th>
<th>SPECIES</th>
<th>CONCEN.</th>
<th>GAMA</th>
<th>VJ</th>
<th>KI</th>
<th>CLOG</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>OH-</td>
<td>0.838D-06</td>
<td>1.00D+01</td>
<td>-1.0</td>
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<td>SC = -1.0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0. 0.</td>
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<td>CO3--</td>
<td>0.200D-05</td>
<td>0.10D+01</td>
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<td>H2CO3*</td>
<td>0.133D-04</td>
<td>0.10D+01</td>
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<td>4</td>
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<td>6</td>
<td>SBUT-</td>
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<td>7</td>
<td>SVAL-</td>
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<td>8</td>
<td>NH3</td>
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**Microbial Species Output**

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<thead>
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<th>CONCEN.</th>
<th>CLOG</th>
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<tbody>
<tr>
<td>1</td>
<td>XHYDRO1</td>
<td>0.138D-05</td>
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<td>2</td>
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<td>3</td>
<td>XSU</td>
<td>0.802D-19</td>
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<td>XAA</td>
<td>0.802D-19</td>
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<td>XVAL</td>
<td>0.125D-05</td>
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<td>XBUT</td>
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<td>XPRO</td>
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<td>XAC</td>
<td>0.224D-04</td>
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<td>9</td>
<td>XH2</td>
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**Solids Species in Solid Phase Output**

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<th>CLOG</th>
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<td>0.100D-04</td>
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<td>XCELSLOW</td>
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<td>XCELSLOW</td>
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<td>XPROTREIN</td>
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<td>XSTARCH</td>
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<td>XINERT</td>
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**Gaseous Species Output**

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<th>I</th>
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<tbody>
<tr>
<td>1</td>
<td>N2GAS</td>
<td>0.0000D+00</td>
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<tr>
<td>2</td>
<td>O2GAS</td>
<td>0.0000D+00</td>
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<tr>
<td>3</td>
<td>CH4GAS</td>
<td>0.579D+00</td>
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<td>4</td>
<td>CO2GAS</td>
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<td>H2GAS</td>
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**Gaseous Species Output**

<table>
<thead>
<tr>
<th>I</th>
<th>SPECIES</th>
<th>QVOL</th>
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<tbody>
<tr>
<td>1</td>
<td>N2GAS</td>
<td>0.0000D+00</td>
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<tr>
<td>2</td>
<td>O2GAS</td>
<td>0.0000D+00</td>
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<tr>
<td>3</td>
<td>CH4GAS</td>
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<td>4</td>
<td>CO2GAS</td>
<td>0.1553D+02</td>
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329
<table>
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<tr>
<th>5 H2GAS</th>
<th>0.3296D+00</th>
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<tbody>
<tr>
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APPENDIX D:
INPUT AND OUTPUT FILES FOR THE SIMULATION OF SIMULTANEOUS NITRIFICATION AND DENITRIFICATION
Input file for data at 35 C and 100% oxygen concentration

1 SIMULATION of Solid Waste Degradation

C ******** DATA SET 2: NUMBER OF COMPONENTS AND SPECIES
8 0 5 0 0 0 3 0 NONA NONS NOMX NOMY NOMZ NOMP NOMB NOMA
0 1 3 NOMHB NOMHS NOG

C ******** DATA SET 3: H+, E-, IONIC STRENGTH AND SORPTION INFORMATION
0.0 0 1 0 0 SICOR ICOR LNH LNG LNE

C ******** DATA SET 4: TEMPERATURE, PRESSURE, AND EXPECTED PE AND PH
308.15 1.0 0 TEMP PRESSU TEMPK
1 1.783 0.1 NSIMUL QVOL DELPMAX
-20.0 20.0 -1.0 20.0 PEMN PEMX PHMN PHMX

C ******** DATA SET 7: BASIC AND INTEGER REAL PARAMETERS
1 50000 KSS NOTI
0.0001 0.0 0.10 0.0 5.0 DELT CHNG DELMX TBNG TEND
1.0 30 1.0D-06 1 300 1.0D-09 500.0 OMEGA NITT EPST NPCYL NITER EPS CNSTRN

C ******** DATA SET 8: PRINTER AND AUXILIARY STORAGE CONTROL
4 1 22
1
2
2500
5000
7500
10000
12500
15000
17500
20000
22500
25000
27500
30000
32500
35000
37500
40000
42500
45000
47500
50000

C ******** DATA SET 9: TOTAL ANALYTICAL CONCENTRATION OF ALL COMPONENTS
H+ -1.000D-07
HCO3- 1.400D-05
NH4+ 1.160D-05
NO2- 1.00D-10
NO3- 1.000D-06
CARB 1.00D-09

332
### DATA SET 15: SOURCE PARAMETERS

<table>
<thead>
<tr>
<th>N2GAS</th>
<th>0.95D0 10.0 0 32 CP(I) CS(I) CV(I) MW(I)</th>
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<td>CO2GAS</td>
<td>0.05D0 10.0 0 28 CP(I) CS(I) CV(I) MW(I)</td>
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<td></td>
<td>0.0001D0 10.0 0 44 CP(I) CS(I) CV(I) MW(I)</td>
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### DATA SET 16: REACTION DATA

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<th>NRTS NPDS KRTYP</th>
<th>LOGKEQ</th>
<th>CXYZP(1,1)</th>
<th>DXYZP(1,1)</th>
<th>IGSNRT(1,1)</th>
<th>IGSNPD(1,1)</th>
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<td>0.33 5.00D-07</td>
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### NITROSOMONAS

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<th>HSCSAN(3)</th>
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<tbody>
<tr>
<td>0.42</td>
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### NITROBACTOR

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<tbody>
<tr>
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### DENITRIFICATION 01

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<td>0.33</td>
<td>5.00D-07</td>
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(NITROSOMONAS) 0.42 8.00D-07 0 0 0 GRMAX HSCSAN(1) HSCSAN(2) HSCSAN(3)

(NITROBACTOR) 0.33 5.00D-07 0 0 0 GRMAX HSCSAN(1) HSCSAN(2) HSCSAN(3)

(DENITRIFICATION 01)
2.50 5.00D-08 0 1.00D-06 0          GRMAX  HSCSAN(1) HSCSAN(2)
HSCSAN(3) HSCSAN(4)
1 0 3 0 0 0                     LOCSK LOCAN LOCNL LOCNK LOCLK TAUL TAUE
5.00 8.00 343.15 310.15 0.0 PHH(I),PHL(I),TEMPMAX(I),TEMPOPT(I),THETAK(I)
1.0 0.64 0.24 0.32 0.24 0.80 1.64 0.24
(CXYZP(I,J),J=1,NRTS),(DXYZP(I,J),J=1,NPDS)
6 5 3 8 1 11 9 16
(IGSNRT(I,J),J=1,NRTS),(IGSNPD(I,J),J=1,NPDS)
0 0 0 0 0
INHIB(I),HSCINH(1,I),HSCINH(2,I),PQ(1,I),PQ(2,I)
1 1 6
NRTS NPDS KRTYP REACTION
1.00D-06 100.00
1 1
CXYZP(1,1) DXYZP(1,1)
7 18
IGSNRT(1,1) IGSNPD(1,1)
1 1 6
NRTS NPDS KRTYP REACTION
6.10D-07 80.00
1 1
CXYZP(1,1) DXYZP(1,1)
8 19
IGSNRT(1,1) IGSNPD(1,1)
1 1 6
NRTS NPDS KRTYP REACTION
3.40D-05 30.00
1 1
CXYZP(1,1) DXYZP(1,1)
11 20
IGSNRT(1,1) IGSNPD(1,1)
C ***** DATA SET 17: WATER CONTENT DATA
0.3580 55.4 0.3580 18.069D-3 0 RHOLTHP CWATP THP PMVW CVW
0 0 0 0 0 0 0
C ***** DATA SET 18: GRAIN DATA
0.1795 17 0.55 1 RHOBP IGCG POROSITY KROBC
C ***** DATA SET 19: HEAT GENERATION DATA
0
0

END OF JOB
PROBLEM  1
SIMULATION of Solid Waste Degradation
IITR = 0,  ICOND = 0

C ******* DATA SET 2: NUMBER OF COMPONENTS AND SPECIES

NO. OF AQUEOUS COMPONENTS, NONA  . . . . . . . . . .    8
NO. OF ADSORBENT COMPONENTS, NONS  . . . . . . . . .    0
NO. OF COMPLEXED SPECIES, NOMX  . . . . . . . . . .    5
NO. OF ADSORBED SPECIES, NOMY  . . . . . . . . . .    0
NO. OF ION-EXCHANGED SPECIES, NOMZ  . . . . . . . . .  0
NO. OF PRECIPITATED SPECIES, NOMP  . . . . . . . . .  0
NO. OF AQUEOUS PHASE MICROBIAL SPECIES, NOMB  . . .  3
NO. OF ADSORBED PHASE MICROBIAL SPECIES, NOMA  . . .  0
NO. OF AQUEOUS SOLIDS SPECIES, NOMHS . . . . . . . .  0
NO. OF ADSORBED PHASE SOLIDS SPECIES, NOMHA . . . .  1
NO. OF GASEOUS SPECIES, NOG  . . . . . . . . . . . . .  3

NO. OF ALL CHEMICAL COMPONENTS, NON  . . . . . . . .  8
NO. OF CHEMICAL PRODUCT SPECIES, NOPD . . . . . . .  5
NO. OF ALL CHEMICAL SPECIES, NOM  . . . . . . . . . . 13
NO. OF ALL MICROBIAL SPECIES, NOB  . . . . . . . . .  3
NO. OF ALL SOLIDS SPECIES, NOH  . . . . . . . . . . .  1
NO. OF ALL GASEOUS SPECIES, NOG  . . . . . . . . . .  3

C ******* DATA SET 3: H+, E-, IONIC STRENGTH AND SORPTION INFORMATION

IONIC STRENGTH USED FOR COMPUTING ACTIVITY COEF. . . 0.000D+00
IS IONIC STRENGTH USED TO CORRECT ACTIVITY COEF. . . 0
LOCATION OF H+ IN THE COMPONENT LIST, LNH  . . . . . . 1
LOCATION OF GAS IN THE COMPONENT LIST, LNG  . . . . . 0
LOCATION OF E- IN THE COMPONENT LIST, LNE  . . . . . 0

ABSOLUTE TEMPERATURE  . . . . . . . . . . . . . . . . . 0.308D+03
PRESSURE  . . . . . . . . . . . . . . . . . . . . . . . 0.100D+01
TEMPERATURE CONTROL PARAMETER 0 OR 1  . . . . . . . . 0

BATCH REACTOR SIMULATION CONTROL  . . . . . . . . . . 1
BATCH REACTOR HEAD-SPACE VOLUME . . . . . . . . . . . 0.178D+01
MAXIMUM ALLOWABLE PRESSURE INCREMENT . . . . . . . . 0.100D+00

EXPECTED MINIMUM PE, PEMN  . . . . . . . . . . . . . . . -20.0000
EXPECTED MAXIMUM PE, PEMX .......... 20.0000
EXPECTED MINIMUM PH, PHMN ........... -1.0000
EXPECTED MAXIMUM PH, PHMX ........... 20.0000
EXPECTED MINIMUM ELECTRON ACTIVITY .... 0.1000D-19
EXPECTED MAXIMUM ELECTRON ACTIVITY .... 0.1000D+21
EXPECTED MINIMUM HYDROGEN ACTIVITY .... 0.1000D-19
EXPECTED MAXIMUM HYDROGEN ACTIVITY .... 0.1000D+02

C ******** DATA SET 7: BASIC AND INTEGER REAL PARAMETERS

STATIC SIMULATION CONTROL, KSS ............... 1
NO. OF TIME INCREMENTS (TIME STEPS), NOTI .......... 50000

TIME STEP SIZE, DELT ...................... 0.100D-03
TIME STEP SIZE CHANGING INCREMENT, CHNG .... 0.000D+00
MAXIMUM TIME STEP SIZED ALLOWED, DELMX .... 0.100D+00
BEGINNING SIMULATION TIME, TBNG .......... 0.000D+00
ENDING SIMULATION TIME, TEND .......... 0.500D+01

RELAXATION PARAMETER, OMEGA ............... 0.100D+01
NO. OF ITERATIONS ALLOWED ON TOTAL CONC, NITT .... 30
TOLERANCE FOR ITERATION ON TOTAL CONC, EPST .... 0.100D-05
NO. OF PRECIPITATION CYCLES ALLOWED, NPCYL .... 1
NO. OF NEWTON RAPHSON ITERATIONS ALLOWED, NITER .... 300
TOLERANCE FOR NEWTON RAPHSON ITERATION, EPS .... 0.100D-08
CONSTRAINT ON THE COMPLEXED SPECIES CONC. .... 0.500D+03

C ******** DATA SET 8: PRINTER AND AUXILIARY STORAGE CONTROL

C ******** DATA SET 9: TOTAL ANALYTICAL CONCENTRATION OF ALL COMPONENTS

**** INPUT AQUEOUS COMPONENT DATA ****

<table>
<thead>
<tr>
<th>J</th>
<th>COMPONENT NAME</th>
<th>TOTAL COMPONENT CONCENTRATION (MOLES/BATCH VOLUME)</th>
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<tbody>
<tr>
<td>1</td>
<td>H+</td>
<td>-1.0000D-07</td>
</tr>
<tr>
<td>2</td>
<td>HCO3-</td>
<td>1.4000D-05</td>
</tr>
<tr>
<td>3</td>
<td>NH4+</td>
<td>1.1600D-05</td>
</tr>
<tr>
<td>4</td>
<td>NO2-</td>
<td>1.0000D-10</td>
</tr>
<tr>
<td>5</td>
<td>NO3-</td>
<td>1.0000D-06</td>
</tr>
<tr>
<td>6</td>
<td>CARB</td>
<td>1.0000D-09</td>
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<td>7</td>
<td>O2*</td>
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<tr>
<td>8</td>
<td>N2*</td>
<td>1.0000D-10</td>
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C ******** DATA SET 10: COMPONENT SPECIES AND THEIR ION-EXCHANGED SPECIES

C ******** DATA SET 11: COMPLEXED SPECIES AND THEIR ION-EXCHANGED SPECIES

C ******** DATA SET 14: MICROBIAL SPECIES
**** INPUT SPECIES DATA ****

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<th>I.C.</th>
<th>ISCN</th>
<th>PMV</th>
<th>VJ</th>
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<tr>
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<td>0.174D-07</td>
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<td>0.3008D-02</td>
<td>1.</td>
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<td>S.C. = 1 . 0 . 0 . 0 . 0 . 0 . 0 . 0</td>
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</tr>
<tr>
<td>2</td>
<td>HCO3-</td>
<td>0.160D-04</td>
<td>0</td>
<td>0.6202D-01</td>
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C ******* DATA SET 15: SOURCE PARAMETERS
C ******* DATA SET 16: REACTION DATA

NO. OF REACTIONS, NRXN . . . . . . . 11

IRXN = 1, NRTS = 1, NPDS = 1, RXTYP = 0
LOG KEQ = -14.00

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<th>S.C.</th>
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1  OH-                       9                1.0000
IRXN =  2,  NRTS = 2,  NPDS = 1,  RXTYP = 0
LOG KEQ =  -10.32

J      Reactant Name     Global Species No.    S.C.
--  --------------------  ------------------   ------
1  H+                        1               -1.0000
2  HCO3-                     2                1.0000

J      Product Name      Global Species No.    S.C.
--  --------------------  ------------------   ------
1  CO3--                    10                1.0000

IRXN =  3,  NRTS = 2,  NPDS = 1,  RXTYP = 0
LOG KEQ =   6.35

J      Reactant Name     Global Species No.    S.C.
--  --------------------  ------------------   ------
1  H+                        1                1.0000
2  HCO3-                     2                1.0000

J      Product Name      Global Species No.    S.C.
--  --------------------  ------------------   ------
1  H2CO3*                   11                1.0000

IRXN =  4,  NRTS = 2,  NPDS = 1,  RXTYP = 0
LOG KEQ =   3.44

J      Reactant Name     Global Species No.    S.C.
--  --------------------  ------------------   ------
1  H+                        1                1.0000
2  NO2-                      4                1.0000

J      Product Name      Global Species No.    S.C.
--  --------------------  ------------------   ------
1  HNO2                     12                1.0000

IRXN =  5,  NRTS = 2,  NPDS = 1,  RXTYP = 0
LOG KEQ =  -9.25

J      Reactant Name     Global Species No.    S.C.
--  --------------------  ------------------   ------
1  H+                        1               -1.0000
2  NH4+                      3                1.0000

J      Product Name      Global Species No.    S.C.
--  --------------------  ------------------   ------
1  NH3                      13                1.0000

IRXN =  6,  NRTS = 3,  NPDS = 3,  RXTYP = 2
GRMAX =  0.4200D+00  GRK =  0.4200D+00

SUBSTRATE     E- ACCEPTOR   NUTRIENT
---------     -----------   --------
REACTANT NUMBER :       1             0              0
HALF SAT CONSTANT =   0.8000D-06    0.0000D+00    0.0000D+00
LAG TIME = 0.0000D+00, TIME TO EXPONENTIAL GROWTH = 0.0000D+00

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IRXN = 7, NRTS = 5, NPDS = 2, RXTP = 2

GRMAX = 0.3300D+00  GRK = 0.3300D+00

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HALF SAT CONSTANT = 0.5000D-06  0.0000D+00  0.0000D+00

LAG TIME = 0.0000D+00, TIME TO EXPONENTIAL GROWTH = 0.0000D+00

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GRMAX = 0.2500D+01  GRK = 0.1042D+02

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LAG TIME = 0.0000D+00, TIME TO EXPONENTIAL GROWTH = 0.0000D+00

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AKH= 0.1000D-05, BKLA= 0.100D+03

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IRXN = 10, NRTS = 1, NPDS = 1, RXTYP = 6

AKH= 0.6100D-06, BKLA= 0.800D+02

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IRXN = 11, NRTS = 1, NPDS = 1, RXTYP = 6

AKH= 0.3400D-04, BKLA= 0.300D+02

<table>
<thead>
<tr>
<th>J</th>
<th>Reactant Name</th>
<th>Global Species No.</th>
<th>S.C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H2CO3*</td>
<td>11</td>
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<table>
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<th>Product Name</th>
<th>Global Species No.</th>
<th>S.C.</th>
</tr>
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<tr>
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C******* DATA SET 17: WATER CONTENT DATA

342
INITIAL BULK LIQUID DENSITY, RholTHP. . . . . 0.3580D+00
INITIAL WATER CONCENTRATION, CWATP. . . . . 0.5540D+02
INITIAL LIQUID CONTENT, THP . . . . . . . . . 0.3580D+00
PARTIAL MOLAR VOLUME OF WATER, PMVW . . . . 0.1807D-01
SPECIFIC HEAT CAPACITY OF WATER . . . . . . . 0.0000D+00

STOICHIOMETRY OF WATER IN ALL PRODUCT SPECIES
<table>
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<tr>
<th>I</th>
<th>STCW</th>
<th>I</th>
<th>STCW</th>
<th>I</th>
<th>STCW</th>
<th>I</th>
<th>STCW</th>
<th>I</th>
<th>STCW</th>
</tr>
</thead>
<tbody>
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C ******* DATA SET 18: GRAIN DATA

INITIAL BULK SOLID DENSITY, RhoBP . . . . . . 0.1795D+00
GLOBAL SPECIES NUMBER OF SOLIDS GRAIN, IGCGr . 17
POROSITY OF SOLIDS, POROSITY . . . . . . . . 0.5500D+00

KROBC = 1
SOLIDS DENSITY IS TO BE COMPUTED

C ******* DATA SET 19: HEAT GENERATION DATA

NHGENFAC = 0 (HEAT GENERATION NOT INCLUDED)

Output file at time = 1.0 day

*** WATER, GAS, AND GRAIN DATA AT ITM =**** TIME = 1.0000D+00 ***

WATER CONCENTRATION, CWATP. . . . . . . . . . 0.55400D+02
LIQUID CONTENT, TH. . . . . . . . . . . . . . . 0.35837D+00
BULK LIQUID CONTENT, RHOLTH . . . . . . . . . 0.35800D+00
LIQUID DENSITY, RHOL. . . . . . . . . . . . . . 0.99898D+00

GAS CONTENT, GTH. . . . . . . . . . . . . . . 0.19163D+00
TOTAL GAS CONTENT, GASVOL . . . . . . . . . . 0.19746D+01
GAS DENSITY, RHOG . . . . . . . . . . . . . . 0.12794D-02
GAS PRESSURE, PRESU . . . . . . . . . . . . . 0.10349D+01

GRAIN CONCENTRATION, CGRNP. . . . . . . . . . 0.00000D+00
BULK SOLID DENSITY, RHOB. . . . . . . . . . . 0.40689D+00
TEMPERATURE, TEMPP. . . . . . . . . . . . . . 0.30815D+03
** COMPONENT OUTPUT AT ITM = **** TIME =  1.0000D+00 ****

(TOTAL CONCENTRATIONS IN MOLES/BATCH VOLUME)

<table>
<thead>
<tr>
<th>J</th>
<th>COMPONENT</th>
<th>TOTAC</th>
<th>TOTDC</th>
<th>TOTSC</th>
<th>TOTPC</th>
<th>XLOG</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H+</td>
<td>1.5156D-06</td>
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<tr>
<td>2</td>
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<tr>
<td>3</td>
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<tr>
<td>4</td>
<td>NO2-</td>
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<tr>
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<td>CARB</td>
<td>1.0740D-08</td>
<td>1.0740D-08</td>
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<td>0.0000D+00</td>
<td>-7.5229D+00</td>
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<tr>
<td>7</td>
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<tr>
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** COMPONENT SPECIES OUTPUT AT ITM =10000  TIME =  1.0000D+00 ****

(SPECIES CONCENTRATIONS IN MOLES/MASS OF PHASE)

<table>
<thead>
<tr>
<th>I</th>
<th>SPECIES</th>
<th>CONCEN.</th>
<th>VJ</th>
<th>GAMA(I)</th>
<th>CLOG</th>
</tr>
</thead>
<tbody>
<tr>
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<tr>
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<tr>
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<td>0.1000D+01</td>
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<tr>
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<tr>
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<td>NO3-</td>
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<td>CARB</td>
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** PRODUCT SPECIES OUTPUT AT ITM =10000 TIME =   1.0000D+00****

<table>
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<th>VJ</th>
<th>KI</th>
<th>CLOG</th>
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<tbody>
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344
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**** MICROBIAL SPECIES OUTPUT AT ITM =10000 TIME =  1.0000D+00****

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<th>SPECIES</th>
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<th>CLOG</th>
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</thead>
<tbody>
<tr>
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<td>0.128D-05</td>
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</tr>
<tr>
<td>2</td>
<td>NITROBACTOR</td>
<td>0.161D-06</td>
<td>-6.7920</td>
</tr>
<tr>
<td>3</td>
<td>DENITRIFIER</td>
<td>0.601D-05</td>
<td>-5.2209</td>
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**** SOLIDS SPECIES IN SOLID PHASE OUTPUT AT ITM =10000 TIME = 1.0000D+00****

<table>
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<th>CONCEN.</th>
<th>CLOG</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SOLIDS</td>
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**** GASEOUS SPECIES OUTPUT AT ITM =10000 TIME = 1.0000D+00****

<table>
<thead>
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<th>SPECIES</th>
<th>CONCEN.</th>
<th>CLOG</th>
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<tbody>
<tr>
<td>1</td>
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<td>3</td>
<td>CO2GAS</td>
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**** GASEOUS SPECIES OUTPUT AT ITM =10000 TIME = 1.0000D+00****

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<tbody>
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<td>N2GAS</td>
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<tr>
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Output file at time = 2.25 day

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*** WATER, GAS, AND GRAIN DATA AT ITM =**** TIME = 2.2500D+00 ***

WATER CONCENTRATION, CWATP. . . . . . . . . . . . 0.55400D+02
LIQUID CONTENT, TH. . . . . . . . . . . . . . . . . . 0.35837D+00

345
**BULK LIQUID CONTENT, RHOLTH . . . . . . . . . . . 0.35800D+00**
**LIQUID DENSITY, RHOL . . . . . . . . . . . . . . . 0.99898D+00**

**GAS CONTENT, GTH . . . . . . . . . . . . . . . . . . . . 0.19163D+00**
**TOTAL GAS CONTENT, GASVOL . . . . . . . . . . . . . . . 0.19746D+01**
**GAS DENSITY, RHOG . . . . . . . . . . . . . . . . . . . . 0.12500D-02**
**GAS PRESSURE, PRESU . . . . . . . . . . . . . . . . . . . 0.99700D+00**

**GRAIN CONCENTRATION, CGRNP. . . . . . . . . . . . . . . . 0.00000D+00**
**BULK SOLID DENSITY, RHOB. . . . . . . . . . . . . . . . 0.40689D+00**

**TEMPERATURE, TEMPP. . . . . . . . . . . . . . . . . . . . . 0.30815D+03**

**1**

*** COMPONENT OUTPUT AT ITM =**** TIME = 2.2500D+00 ***

(TOTAL CONCENTRATIONS IN MOLES/BATCH VOLUME)

<table>
<thead>
<tr>
<th>J</th>
<th>COMPONENT</th>
<th>TOTAC</th>
<th>TOTDC</th>
<th>TOTSC</th>
<th>TOTPC</th>
<th>XLOG</th>
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<tr>
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<td>0.0000D+00</td>
<td>-4.7651D+00</td>
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<tr>
<td>3</td>
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<td>4.5415D-07</td>
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<tr>
<td>6</td>
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<td>0.0000D+00</td>
<td>0.0000D+00</td>
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<tr>
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**** COMPONENT SPECIES OUTPUT AT ITM =22500  TIME = 2.2500D+00 ****

(SPECIES CONCENTRATIONS IN MOLES/MASS OF PHASE)

<table>
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<tr>
<th>I</th>
<th>SPECIES</th>
<th>CONCEN.</th>
<th>VJ</th>
<th>GAMA(I)</th>
<th>CLOG</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1.</td>
<td>0.1000D+01</td>
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</tr>
<tr>
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<td>HCO3-</td>
<td>0.1717D-04</td>
<td>-1.</td>
<td>0.1000D+01</td>
<td>-0.4765D+01</td>
</tr>
<tr>
<td>3</td>
<td>NH4+</td>
<td>0.7690D-07</td>
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<td>0.1000D+01</td>
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</tr>
<tr>
<td>4</td>
<td>NO2-</td>
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</tr>
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<td>NO3-</td>
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<tr>
<td>6</td>
<td>CARB</td>
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</tr>
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**** PRODUCT SPECIES OUTPUT AT ITM =22500  TIME = 2.2500D+00****

<table>
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<th>GAMA</th>
<th>VJ</th>
<th>KI</th>
<th>CLOG</th>
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**** MICROBIAL SPECIES OUTPUT AT ITM =22500 TIME = 2.250D00****

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<td>-----------</td>
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<td>NITROSOMONAS</td>
<td>0.132D-05</td>
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<td>2</td>
<td>NITROBACTOR</td>
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<td>DENITRIFIER</td>
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**** SOLIDS SPECIES IN SOLID PHASE OUTPUT AT ITM =22500 TIME = 2.250D00****

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**** GASEOUS SPECIES OUTPUT AT ITM =22500 TIME = 2.250D00****

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<th>SPECIES</th>
<th>CONCEN.</th>
<th>CLOG</th>
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0 1

**** GASEOUS SPECIES OUTPUT AT ITM =22500 TIME = 2.250D00****

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<td>2</td>
<td>N2GAS</td>
<td>0.0000D+00</td>
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<tr>
<td>3</td>
<td>CO2GAS</td>
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347
Output file at time = 3.25 day

1

*** WATER, GAS, AND GRAIN DATA AT ITM =**** TIME =  3.2500D+00 ***

WATER CONCENTRATION, CWATP. . . . . . . . . .  0.55400D+02
LIQUID CONTENT, TH. . . . . . . . . . . . . . .  0.35837D+00
BULK LIQUID CONTENT, RHOLTH . . . . . . . . .  0.35800D+00
LIQUID DENSITY, RHOL. . . . . . . . . . . . . .  0.99898D+00

GAS CONTENT, GTH. . . . . . . . . . . . . . . . . . . . . . .  0.19163D+00
TOTAL GAS CONTENT, GASVOL . . . . . . . . . . .  0.19746D+01
GAS DENSITY, RHOG . . . . . . . . . . . . . . . . . . . . . .  0.12367D-02
GAS PRESSURE, PRESU . . . . . . . . . . . . . . . . . . . . .  0.98597D+00

GRAIN CONCENTRATION, CGRNP. . . . . . . . . . .  0.00000D+00
BULK SOLID DENSITY, RHOB. . . . . . . . . . . . .  0.40689D+00
TEMPERATURE, TEMPP. . . . . . . . . . . . . . . . . . . . .  0.30815D+03

1

*** COMPONENT OUTPUT AT ITM =**** TIME =  3.2500D+00 ***

(TOTAL CONCENTRATIONS IN MOLES/BATCH VOLUME)

<table>
<thead>
<tr>
<th>J</th>
<th>COMPONENT</th>
<th>TOTAC</th>
<th>TOTDC</th>
<th>TOTSC</th>
<th>TOTPC</th>
<th>XLOG</th>
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<tr>
<td>6</td>
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<td>0.0000D+00</td>
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<tr>
<td>7</td>
<td>O2*</td>
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*** COMPONENT SPECIES OUTPUT AT ITM =32500  TIME =  3.2500D+00 ***

(SPECIES CONCENTRATIONS IN MOLES/MASS OF PHASE)

<table>
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<tr>
<th>I</th>
<th>SPECIES</th>
<th>CONCEN.</th>
<th>VJ</th>
<th>GAMA(I)</th>
<th>CLOG</th>
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<tbody>
<tr>
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<td>HCO3-</td>
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<td>0.1000D+01</td>
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<tr>
<td>3</td>
<td>NH4+</td>
<td>0.6523D-07</td>
<td>1.</td>
<td>0.1000D+01</td>
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<tr>
<td>4</td>
<td>NO2-</td>
<td>0.5081D-07</td>
<td>-1.</td>
<td>0.1000D+01</td>
<td>-0.7294D+01</td>
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<tr>
<td>5</td>
<td>NO3-</td>
<td>0.1770D-04</td>
<td>-1.</td>
<td>0.1000D+01</td>
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<tr>
<td>6</td>
<td>CARB</td>
<td>0.3000D-07</td>
<td>0.</td>
<td>0.1000D+01</td>
<td>-0.7523D+01</td>
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<tr>
<td>7</td>
<td>O2*</td>
<td>0.6688D-06</td>
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<td>0.1000D+01</td>
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<td>VJ</td>
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<tr>
<td>OH-</td>
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<tr>
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<tr>
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<td>DENITRIFIER</td>
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<table>
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<tr>
<th>SPECIES</th>
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<th>CLOG</th>
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<tbody>
<tr>
<td>O2GAS</td>
<td>0.690D+00</td>
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</tr>
<tr>
<td>N2GAS</td>
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<tr>
<td>CO2GAS</td>
<td>0.153D+00</td>
<td>-0.8139</td>
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<table>
<thead>
<tr>
<th>SPECIES</th>
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<th>CLOG</th>
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<tr>
<td>SOLIDS</td>
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<thead>
<tr>
<th>SPECIES</th>
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<th>CLOG</th>
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<tr>
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<tr>
<td>N2GAS</td>
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<tr>
<td>CO2GAS</td>
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Output file at time = 5.0 day

*** WATER, GAS, AND GRAIN DATA AT ITM =**** TIME = 5.0000D+00 ***

WATER CONCENTRATION, CWATP. . . . . . . . . . 0.55400D+02
LIQUID CONTENT, TH. . . . . . . . . . . . . . . . . 0.35837D+00
BULK LIQUID CONTENT, RHOLTH . . . . . . . . . 0.35800D+00
LIQUID DENSITY, RHOL. . . . . . . . . . . . . . . 0.99898D+00

GAS CONTENT, GTH. . . . . . . . . . . . . . . . . 0.19163D+00
TOTAL GAS CONTENT, GASVOL . . . . . . . . . . 0.19746D+00
GAS DENSITY, RHOG . . . . . . . . . . . . . . . . 0.12255D-02
GAS PRESSURE, PRESU . . . . . . . . . . . . . . . 0.97614D+00

GRAIN CONCENTRATION, CGRNP. . . . . . . . . . 0.00000D+00
BULK SOLID DENSITY, RHOB. . . . . . . . . . . . 0.40689D+00
TEMPERATURE, TEMPP. . . . . . . . . . . . . . . 0.30815D+03

*** COMPONENT OUTPUT AT ITM =**** TIME = 5.0000D+00 ***

(TOTAL CONCENTRATIONS IN MOLES/BATCH VOLUME)

<table>
<thead>
<tr>
<th>J</th>
<th>COMPONENT</th>
<th>TOTAC</th>
<th>TOTDC</th>
<th>TOTSC</th>
<th>TOTPC</th>
<th>XLOG</th>
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<tr>
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<td>0.0000D+00</td>
<td>-4.7250D+00</td>
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<tr>
<td>6</td>
<td>CARB</td>
<td>1.0740D-08</td>
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<td>0.0000D+00</td>
<td>0.0000D+00</td>
<td>-7.5229D+00</td>
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<td>7</td>
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<td>0.0000D+00</td>
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**** COMPONENT SPECIES OUTPUT AT ITM =50000  TIME = 5.0000D+00 ****
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<th>CONCEN.</th>
<th>VJ</th>
<th>GAMMA (I)</th>
<th>CLOG</th>
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<td>NH4+</td>
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<tr>
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<tr>
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<td>CARB</td>
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<td>0.1000D+01</td>
<td>-0.7523D+01</td>
</tr>
<tr>
<td>7</td>
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*** PRODUCT SPECIES OUTPUT AT ITM =50000 TIME = 5.0000D+00***

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<th>SPECIES</th>
<th>CONCEN.</th>
<th>GAMMA</th>
<th>VJ</th>
<th>KI</th>
<th>CLOG</th>
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<tr>
<td>1</td>
<td>OH-</td>
<td>0.709D-07</td>
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*** MICROBIAL SPECIES OUTPUT AT ITM =50000 TIME = 5.0000D+00***

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<th>CONCEN.</th>
<th>CLOG</th>
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<tbody>
<tr>
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<td>NITROBACTOR</td>
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<td>DENITRIFIER</td>
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*** SOLIDS SPECIES IN SOLID PHASE OUTPUT AT ITM =50000 TIME = 5.0000D+00***

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<tr>
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<th>SPECIES</th>
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<th>CLOG</th>
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<tbody>
<tr>
<td>1</td>
<td>SOLIDS</td>
<td>0.183D+00</td>
<td>-0.7373</td>
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</table>
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<thead>
<tr>
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<th>CLOG</th>
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<tbody>
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<td>N2GAS</td>
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<tr>
<td>CO2GAS</td>
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### Gaseous Species Output at ITM = 50000 Time = 5.0000D+00

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<th>QVOL</th>
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<tr>
<td>N2GAS</td>
<td>0.0000D+00</td>
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<tr>
<td>CO2GAS</td>
<td>0.0000D+00</td>
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</tbody>
</table>