Modelling of Metal Recovery using Sulfate Reducing Bacteria

Simulation in MATLAB and Aspen Plus

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Preface

This master thesis is a part of an MSc in Engineering, Biotechnology from the Faculty of Engineering LTH, Lund University. It is registered with the course code "KMB820" and was performed at the Division of Applied Microbiology, TMB in collaboration with RISE-Research Institutes of Sweden.

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Abstract

This report presents a mathematical kinetic model describing the recovery of metal ions as metal sulfides, using sulfate reducing bacteria (SRB). Metal recovery from industrial waste is a potential beneficial and unused source of metals. The developed kinetic model is implemented and simulated in the computer programs MATLAB R2014b and Aspen Plus V8.8. The MATLAB simulation is performed on the bioreactor, where sulfate reducing bacteria produce hydrogen sulfide. The hydrogen sulfide can be used to precipitate metal ions as metal sulfides in which the metals can be removed and recovered from the industrial waste. The full metal recovery model with precipitation tanks and the bioreactor is simulated in the process simulation program Aspen Plus. A literature study was conducted before the simulation to develop the kinetic model.

The main results from this project are a kinetic growth model for sulfate reducing bacteria implemented in the two computer programs as well as a precipitation model implemented in Aspen Plus. The kinetic model includes inhibition terms for pH and hydrogen sulfide. The models are working and calibrated according to literature data. However, in the future it will be necessary to calibrate the models according to real experimental values for the given process. It can be concluded that simulating processes in computer programs makes it possible to predict how feasible the process is in reality. It can also suggest model designs and critical steps that can be avoided in the future and other potential improvements of the process. This can save a lot of time and resources spent on the process before building it.

The environmental aspects need to be considered since the process produces a lot of toxic hydrogen sulfide. It is therefore important to have an accurate and well established safety routine for this process.

Nomenclature and abbreviations

Table 1: Table of abbreviations, explanations and units used.

Abbreviations	Description	
$ADM1$	Anaerobic Digestion Model No. 1	
$CSTR$	Continuous flow stirred-tank reactor	
IC	Inorganic carbon	
ODE	Ordinary differential equation	
S_{red}	Reduced sulfur	
$aSRB$	Acetate utilizing sulfate reducing bacteria	
$eSRB$	Ethanol utilizing sulfate reducing bacteria	
TCA	Tricarboxylic acid	
Denotation	**Description**	**Units**
a_i	Gas-liquid interphase area for compound *i*	[m^2]
C_0	Initial concentration	[mol L^{-1}]
C_i	Concentration of compound *i*	[mol L^{-1}]
d_e	Bubble diameter	[m]
dt	Time difference	[h]
H_i	Henrys constant for compound *i*	[atm L mol^{-1}]
h	Height of the aqueous phase	[m]
HRT	Hydraulic retention time	[h]
I_{com}	Competitive inhibition	-
I_{non}	Non-competitive inhibition	-
I_{pH}	pH inhibition	-
I_{un}	Un-competitive inhibition	-
$I_{sulfide}$	Hydrogen sulfide inhibition	-
k	Reaction rate constant	[h^{-1} or s^{-1}]
$K_{a,i}$	Acid-base equilibrium coefficient for compound *i*,	[mol L^{-1}]
$k_{A,i}$	Acid bas kinetic parameter for compound *i*,	[mol $L^{-1}h^{-1}$]
$\mathrm{k_{d_i}}$	Decay of biomass for bacteria *i*	[h^{-1}]
K_i	Saturation constant for compound *i*	[mol L^{-1}]
$k_{L,i}$	Mass transfer coefficient for compound *i*	[h^{-1}]
k_m	Monod maximum specific uptake rate	[mol L^{-1} h^{-1}]
m	The order of the reaction	
n	The number of bubbles	-
$N_{2,gas}$	Gas flow of N_2	[L h^{-1}]
p_i	Partial pressure for compound *i*	[atm]
pH	Set pH value	-
pH_{LL}	Lower limit for pH inhibition, complete inhibition	-
pH_{UL}	Upper limit for pH inhibition, no inhibition	-
q_{gas}	Gas flow	[L h^{-1}]
q_i	Flow rate of stream *i*	[L h^{-1}]
R	Gas constant	[atm L mol^{-1} K^{-1}]
S_I	Concentration of inhibitor	[mol L^{-1}]
$S_{i,0}$	Initial concentration of the limiting soluble compound i	[mol L^{-1}]
S_i	Concentration of soluble compound *i*	[mol L^{-1}]

S_i^*	Saturation concentration of soluble compound *i*	[mol L^{-1}]
$S_{i,(l)}$	Concentration of compound *i* in liquid phase	[mol L^{-1}]
S_i^t	Concentration at time t of compound *i*	[mol L^{-1}]
T	Temperature	[K]
U	Rising velocity of bubbles	[m s^{-1}]
V_j	Volume of phase *j*	[L]
v_f	Volumetric flow	[L h^{-1}]
$X_{o,i}$	Initial concentration of insoluble compound *i*	[mol L^{-1}]
X_i	Concentration of insoluble compound *i*	[mol L^{-1}]
$Y_{S,iX}$	Yield of compound *i* on biomass	[mol mol^{-1}]
ΔG^0	Gibbs free energy	[J]
ΔH^0	Entahlpy	[J]
ΔS^0	Entropy	[J K^{-1}]
μ_{max}	Maximum specific growth rate	[h^{-1}]
ρ_i	Rate of reaction for formation of compound *i*	[mol L^{-1} h^{-1}]
ρ_i^t	Mass transfer rate of compound *i*	[mol L^{-1} h^{-1}]

Table 2: A list of the chemicals used in the metal recovery process and the chemical properties. (Aylward, 2013)

Name	**Formula and denotation**	**MW [g mol^{-1}]**	**Density [g cm^{-1}] at 25^0C**	**Dissociation constants, pK_a Solubility products, K_{sp}**
Acetate	CH_3COO^-, Ac	59.04	1.044	pK_a=4.76 (acetic acid)
Biomass	X	24.61		
Carbon dioxide	CO_2	33.07	1.1	$pK_{a,1}$=6.35, $pK_{a,2}$=10.33 Solubility: 1.45 g kg^{-1}
Copper ion	Cu^{2+}	63.55	9.0	
Copper Sulfide	CuS	95.62	4.6	K_{sp} =8·10^{-37}
Ethanol	C_2H_5OH, EtOH	49.07	0.785	
Hydrogen sulfide	H_2S, HS^-, S^{2-}	34.09, 33.08, 32.07	-	$pK_{a,1}$=7.02 $pK_{a,2}$=13.9 Solubility: 3.38 g kg^{-1}
Nitrogen	N_2	28.01	0.8	Solubility: 0.0175 g kg^{-1}
Sodium hydroxide	NaOH	39.9971	2.1	
Sulfate	SO_4^{2-}	96.06	-	
Sulfuric acid	H_2SO_4	98.079	1.8	$pK_{a,1}$<0, $pK_{a,2}$=1.99
Zinc ion	Zn^{2+}	65.41	7.1	
Zinc Sulfide	ZnS	97.48	4.0	K_{sp} =2·10^{-25}/3·10^{-23}

Table of content

1 Introduction

The awareness of environmental problems is constantly rising. A part of building a sustainable society is to take care of resources not yet utilized. One example of an unused resource is industrial waste, which contains a lot of metal residues. These metals can be extracted with various methods, one example is by precipitating the metal ions as metal sulfides. The EU project METGROW+ currently designs a toolbox for metal recovery, to be used by industries with the goal to use industrial waste as an economically beneficial source of metals. The following report will be a small contribution to the METGROW+ project by creating a model for a biological method to recover metals. The metal sulfide precipitation can be done using hydrogen sulfide utilized by bacteria. Biologically produced hydrogen sulfide is more desirable to use than chemically produced sulfide. This is because biological hydrogen sulfide has the potential of being more environmental friendly since the biological systems are renewable and the hydrogen sulfide can be produced in place. The chosen substrate including the carbon source and the electron acceptor used for the biological system could also potentially be taken from waste sources. Modelling is an important tool in process development because it can give more insight into opportunities and critical risks that arise from, in this case, the metal recovery process. It also gives stakeholders the chance to calculate potential profitability when implementing the process in an already existing production. The mathematical model will be used to simulate the bacterial growth in the bioreactor, producing hydrogen sulfide. The model will also be used to simulate the entire process with metal precipitation and production of hydrogen sulfide for which the computer programs, MATLAB and Aspen Plus will be used.

1.1 Aim

The aim of this project is to create a mathematical model describing a metal recovery process including metal sulfide precipitation and a biologically produced hydrogen as a contribution to the METGROW+ project. The model should be easily accessible and easy to use and therefore the model will be implemented in process simulation tools. The aim is for the model to include a bacterial growth model describing the kinetic relationships for sulfate reducing bacteria producing hydrogen sulfide as well as a model describing the chemical precipitation of metal sulfides. The two simulations of the model will be evaluated using literature data and connected to a whole metal recovery system.

1.2 Scope

This project will focus on modelling of the production of hydrogen sulfide in the bioreactor and the precipitation of metals in the precipitation tanks. The entire process does not exist in reality and no experimental data will be accessible for comparison. Therefore, less focus will be on actual flows and the design of equipment. The goal is to obtain a fully functioning model describing the process and not to optimize the process. The design of the model should hopefully give the opportunity to adapt it to real processes in the future.

The start of the process will be a leach stream including dissolved metal ions and not the untreated industrial waste with bound metal residues. The metal ions in the leach stream can further react and create precipitated metal sulfides. The end of the process will be the created metal sulfides, no further purification will be considered. Due to time limitations, this project

will not include costs for the process, nor energy or flow optimizations. It will also not include a fully developed plan for waste management, just a brief suggestion of important things to consider. Within the scope, a model with the potential of future optimization of current processes of metal recovery will be created. The metals of focus will be copper and zinc. The models will be evaluated using literature data and by conducting a sensitivity analysis to investigate the most important parameters and variables.

1.3 Disposition

The following report consists of six main chapters. It starts with a short background describing the different prerequisites for the project. This is followed by a theory part, where all significant theoretical materials are presented. Examples of important theoretical materials are description of the metabolic pathways in a bacterial system, equations for bacterial growth, equations describing the metal precipitation and process parameters. The method describes the literature search, developed mathematical model and the implementation of the model in computer software. The results and discussion for the model formulation is presented after the method. It includes simulations evaluations and a process chart for the Aspen simulation. This part also contains a sensitivity analysis for each simulation to verify the models. This is followed by a reflection in which future improvements to the model and environmental issues are treated. The report ends with a conclusion.

2 Background

In this section, the EU-project METGROW+, will be briefly described together with a more detailed description of the process. Some parameters are set as prerequisites for the process and some are to be decided as a result from the model.

2.1 METGROW+

This project is a part of a larger EU-project, METGROW+, that focuses on developing new systems for metal recovery in Europe. METGROW+ was initiated because there are unused resources in waste streams today that are disposed of in landfills. One such resource is metals, which are important to remove from an environmental point of view and recover because of a shortage of metals as a raw material. One goal for the new metallurgy systems approach developed in the METGROW+ project is to completely remove metals from industrial waste, including both critical and base metals. To achieve this goal, the METGROW+ project is developing different possibilities and systems to fit particular requirements for companies in the need of metal recovery from their waste streams. Therefore, METGROW+ is creating a "New Metallurgical Systems" Toolbox that will include unit operations for pretreatment, metal extraction, metal recovery and matrix conversion for low grade ores and industrial wastes. The toolbox will also enable optimal coupling of the unit operations.

Different parts of the METGROW+ project are developed by different partners around Europe and the focus for RISE (former SP) is the bio-precipitation method using sulfate reducing bacteria. The bio-precipitation task in METGROW+ can be summarized as using the ability of microorganisms to perform redox reactions that lead to precipitation of metals from the formed reduced substances. This is described as advantageous because less chemicals are needed and high yields and product stability can be achieved. Other METGROW+ partners that also work on this particular task are VTT in Finland and University of Gent in Belgium.

2.2 The metal recovery process

This part will present the metal recovery process with inlet streams, bioreactor, precipitation of metal sulfides and outlet streams.

2.2.1 The process setup

The metal precipitation uses hydrogen sulfide as a precipitation agent and a reaction occurs between this compound and the dissolved metal forming metal sulfides. These metal sulfides have a very low solubility at the ambient conditions and this reaction can therefore be considered to be irreversible (Tokuda et al., 2008). The precipitation will be performed in different tanks with different pH to enable selective precipitation. This is possible because different metals react with the hydrogen sulfide at different pH. The idea is to produce the hydrogen sulfide for the precipitation process from sulfate reducing bacteria performing redox reactions of sulfate in a separate bioreactor. The hydrogen sulfide is produced as a gas and will be sparged into the precipitation tank. There will also be dissolved hydrogen sulfide in the liquid that will be used in the precipitation units run at higher pH. The solid metal sulfides will be separated after each tank and be further treated and purified in a downstream process.

The basic structure for the bioprecipitation process to be modelled in this project can be seen in Figure 1.

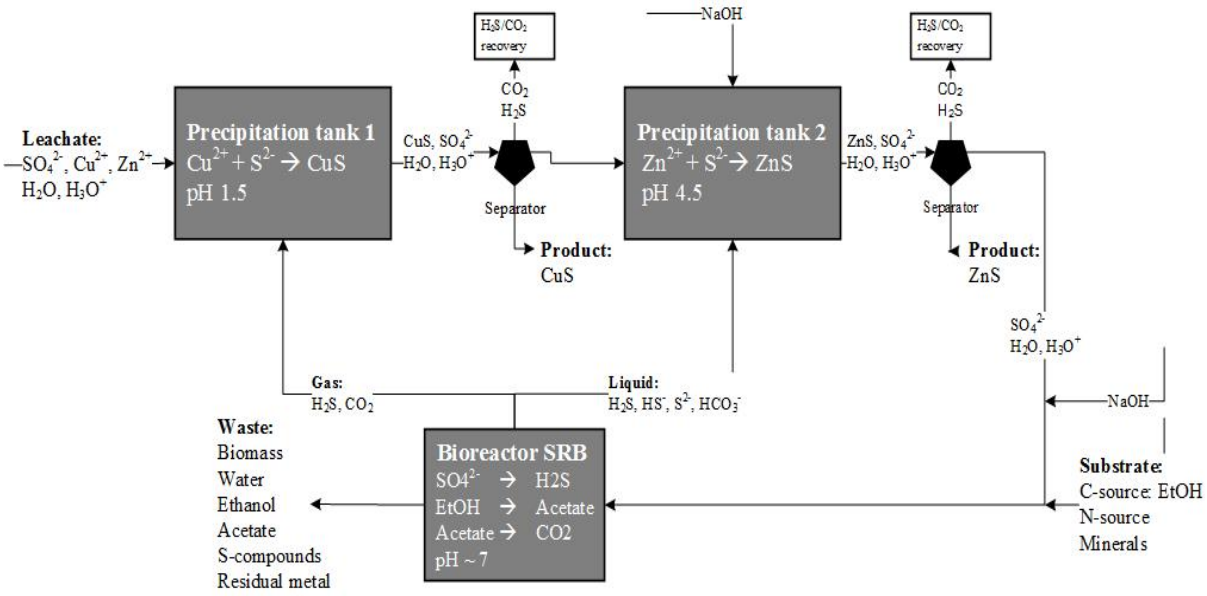

Figure 1: The process setup for the recovery of metal sulfides from industrial waste using hydrogen sulfide produced from SRB.

The process will be designed in continuous mode where some form of mixing will occur in the tanks. All the process units are shown as squared blocks in Figure 1. The solid separators are assumed to be cyclones and some form of filter is used to separate the biomass from the liquid stream after the bioreactor.

The process modelled in this project starts with an inflow of a stream where the metals are already in the form of metal ions. This stream is referred to as the leachate in this report. This stream can be directly used in the precipitation tank without pre-treatments. Thus, the industrial process stream has already been treated with sulfuric acid, H_2SO_4 to release the metal ions from a bound state when entering the process. The substrate stream is the stream that contains the additional compounds, like the carbon source, that the bacteria need for growth and produce the hydrogen sulfide. The sulfate will already be present in the leachate. The NaOH stream is an additional inflow to the precipitation tanks required for keeping the pH in the tanks constant and to ensure a selective precipitation. There is also an NaOH stream to adjust the pH before the bioreactor.

The outflows from the process are the semi-pure metal sulfide streams, a waste stream from the liquid separation after the bioreactor and gas purges from the recirculation of the gases in the system. Neither the waste management, the purification of metal sulfides nor the gas purification will be included in the model.

2.2.2 Process conditions

The microorganisms used for hydrogen sulfide production are Sulfate Reducing Bacteria (SRB). Some of the process conditions used in this model were decided by the supervisors

before the start of this project, the carbon source for the microorganism for instance is ethanol. The other conditions will either be decided before the project is initiated to limit the literature search or investigated during the course of the project and the optimal ones will be presented as results.

The metals of focus have been decided to be zinc and copper based on the METGROW+ project plan where these are defined as economically important metals. The model will however be adjustable to other metals. All the tanks are treated as continous-flow stirred tank reactors (CSTR) or batch reactors, ambient conditions will be used for the precipitation tanks and the temperature will be optimized for the bioreactor according to literature data. H_2SO_4 is the assumed chemical for the leaching step and will therefore give a low pH in the leach stream. The chemical used for pH increase will be NaOH. Other chemicals used in the system are NH_3 as nitrogen source for the bacteria and N_2 as stripping gas.

The composition for the leach stream will be obtained from literature data. It will later be possible to calibrate the model to experimental data within the METGROW+ project, but these results will not be accessible before the end of this project. The kinetic parameters for the model will be based on literature values and the model will also be compared and calibrated to experimental values found in literature.

3 Theory

In this section, the basis for the model formation will be presented, followed by the important process parameters affecting the model. The bioreactor and precipitation tanks are described in different sections. To get a deeper understanding of how the bacteria influences the hydrogen sulfide production, the relevant metabolic pathways will be presented.

3.1 The biological system used in the model

SRB use anaerobic respiration, in which the electrons released from the ethanol conversion are transferred through an electron transport chain and accepted by the non-oxygen terminal electron acceptor. In SRB this is sulfate and the SRB are obligate anaerobes, meaning they can only carry out anaerobic respiration and the environment should be kept strictly free from oxygen (Willey et al. 2008). The doubling time for the SRB genus *Desulfobacter* is around 20 hours on acetate and sulfate at 33°C, (Brandt and Ingvorsen 1997) which is quite long comparing to 0.35 hour for *E. coli* in 40°C (Willey et al. 2008). The important pathways for hydrogen sulfide production, which are sulfate reduction and ethanol/acetate degradation and the connection between these, will be presented in this section. However, the metabolism is not fully defined and therefore the pathway will be a combination of different sources and some part are still unkown.

3.1.1 Building the biomass

Ethanol and acetate are used as carbon sources by the SRB, which means that a part of the carbon source goes to cell mass formation. The cell also needs a nitrogen source, phosphorus and trace elements like different vitamins and minerals. The compound relationship for the buildup of biomass is shown in Equation (3.1) and (3.2).

$$C_2H_5OH + NH_4 \rightarrow CH_{1,8}O_{0,5}N_{0,2} \quad (3.1)$$

$$C\ source + N\ source + P\ source + Trace\ elements \rightarrow Biomass \quad (3.2)$$

Sometimes yeast extract is added as a supplement to the substrate, which works as an additional carbon source for bacterial growth. Yeast extract is used to enrich the media in several of the studies for data used in this report (Kremer et al., 1988, Caffreyet et al., 2007, Keller et al., 2014). The acetate to ethanol ratio has shown to be one with the usage of yeast extract Nagpal et al., (2000), showing that the yeast extract is used as a carbon source instead of ethanol.

3.1.2 Metabolic pathway for sulfate reduction

As mentioned before, SRB use sulfate as a terminal electron acceptor. These types of anaerobic microorganisms reduce sulfate with the dissimilatory sulfate reduction pathway where sulfate is converted to hydrogen sulfide (Willey et al., 2008, Keller et al., 2014). Despite the term SRB – sulfate reducing bacteria, there are both archaea and bacteria that are capable of this type of metabolic pathway (Keller et al., 2014). Sulfate reduction takes place in the cytoplasm (Thauer et al., 2007) and therefore the sulfate ion must be transported into the cell. The strain *Desulfovibrio* uses eight electrons and eight protons to reduce sulfate to sulfide. This reaction is shown in Equation. (3.3) (Thauer et al., 2007, Willey et al., 2008).

$$SO_4^{2-} + 8e^- + 8H^+ \rightarrow S^{2-} + 4H_2O \quad (3.3)$$

The reduction of sulfate occurs in three steps. The first step is the activation of sulfate, this reaction is endogenous and requires energy in the form of ATP. The next two reactions are exogenous and occurs with the help of electrons from the electron donor used as substrate. All these enzymatic reactions occur in the cytoplasm of the cell with the help of soluble enzymes (Barton et al., 2014) and a more detailed view can be seen in Figure 2.

3.1.3 Metabolic pathway for ethanol degradation

Ethanol is taken up by the cell and converted into acetaldehyde by alcohol dehydrogenase, which is believed to be the only ethanol oxidizing enzyme in sulfate reducing bacteria (Haveman et al., 2003). The acetaldehyde is oxidized to acetate as the end product and one possible enzyme catalyzing this reaction is aldehyde dehydrogenase. The reduction of NAD^+ to NADH occurs in the process and there is also a generation of electrons and protons that can be used for energy production and sulfate reduction (Ramos et al., 2015). The electrons and the hydrogen ions are the links between the carbon source degradation and the sulfate conversion.

The ethanol to sulfide molar ratio is 1:0.5 because ethanol to acetate donates 4 electrons while sulfate to sulfide conversion requires 8 electrons. The total stoichiometric reaction for when ethanol is used as substrate and sulfate as terminal electron acceptor is shown in Equation (3.4) (Nagpal et al. 2000).

$$C_2H_5OH + 0.5SO_4^{2-} \rightarrow 0.5H_2S + CH_3COO^- + H_2O \quad (3.4)$$

3.1.4 Metabolic pathway for acetate degradation

The incomplete oxidation of ethanol yields acetate as a product and not carbon dioxide, which would be the case for complete oxidation. There are sulfate reducers that use acetate as a carbon source and as an electron donor (Nagpal et al., 2000, Laanbroek et al., 1983). When having a SRB mix present in the bioreactor, there is a possibility to oxidize the acetate to carbon dioxide with other sulfate reducers. In a study by Laanbroek et al., (1984) The acetate can be oxidized into carbon dioxide through the acetyl-CoA pathway, one example of a bacterium using this pathway is *Desulfobacca acetoxidants* (Goevert and Conrad, 2008). Not all SRB uses the same pathway for acetate oxidation, another pathway is tricarboxylic acid (TCA) cycle, used by for example *Desulfobacter postgatei* with pyruvate as an intermediate (Gebhardt et al., 1983). There are no other anaerobe bacteria than SRB that oxidizes acetate through the TCA-cycle. There is a stoichiometric relationship of 1:1 between acetate degradation and sulfate consumption (Goevert and Conrad, 2008). The reaction for oxidation of acetate is shown in Equation (3.5) (Schauder et al., 1986).

$$CH_3COO^- + SO_4^{2-} + 3H^+ \rightarrow H_2S + 2CO_2 + 2H_2O \quad (3.5)$$

3.1.5 Electron transfer and energy generation

The transport of electrons in the cell is important for the sulfate reduction. The electron transfer trough the membrane occurs with the help of cytochrome c and membrane bound enzymes active in the electron transport chain. Electrons are transported to enable the sulfate reduction. Transport of electrons around the cell is possible with the help of proteins, one of these proteins is the electron donor, ferredoxin (Fd) (Ramos et al., 2015).

To enable the reactions described in this section, transfer of energy is needed. Energy in the cell is packaged in the form of ATP. In SRB, ATP is not believed to be synthesized in substrate level phosphorylation as in many other biological systems but instead through the cycling of protons, creating a proton motive force. In the conversion of ethanol to acetate by alcohol dehydrogenase and aldehyde dehydrogenase proton production takes place. These molecules are transferred over the membrane and an electron gradient is created when the hydrogen is ionized by the oxidation by periplasmic hydrogenases, Figure 2, (Haveman et al. 2003, (Caffrey et al., 2007). The movement of protons back to the cytoplasm occurs over the membrane, with chemotaxis through the ATP synthase that forms ATP from ADP and phosphate. Three protons are needed for one ATP formation (Willey et al., 2008).

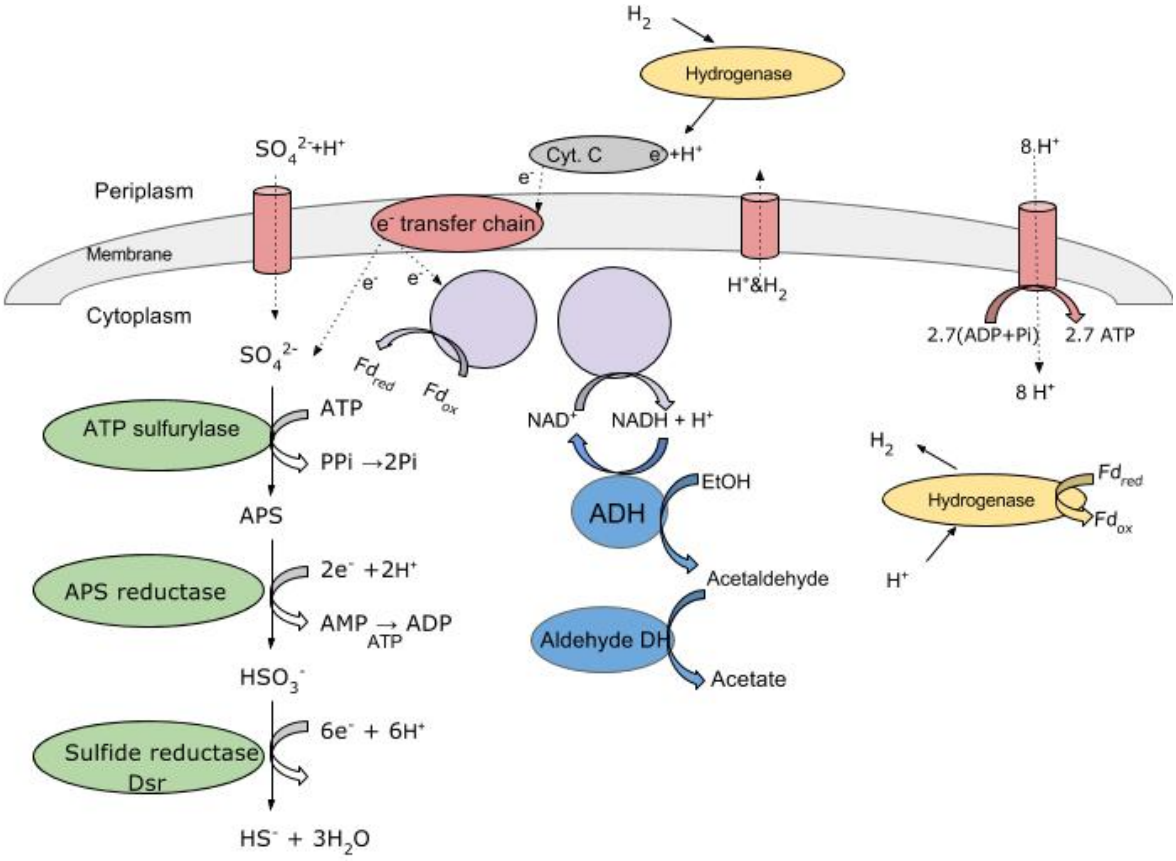

Figure 2: A simplified schematic overview for the most important metabolic pathways relevant for modeling the biological system with ethanol as a substrate. All circles represent enzymes, the dotted lines represent transport and the full lines represent reactions in the cell. Cyt. C is cytochrome C and ADH stands for alcohol dehydrogenase. The exact pathway varies between different strains of SRB (Ramos et al., 2003, Haveman et al., 2003, Caffrey et al., 2007, Willey et al., 2008)

3.2 Modelling of the bioreactor

An important factor when modelling the bioreactor is to find the kinetic relationships for the substrate degradation and product formation. Also, coproducts need to be investigated and inhibitory factors need to be found. This model is based on the ADM1 model developed for biogas production with methanogenic bacteria (Batstone et al., 2002). The model is further based on the extensions made by Barrera et al., (2013) and Fedorovich et al., (2003) for SRB.

3.2.1 Mass balances

The main principle for this process is that the substrate is consumed to produce product and to build biomass according to Figure 3.

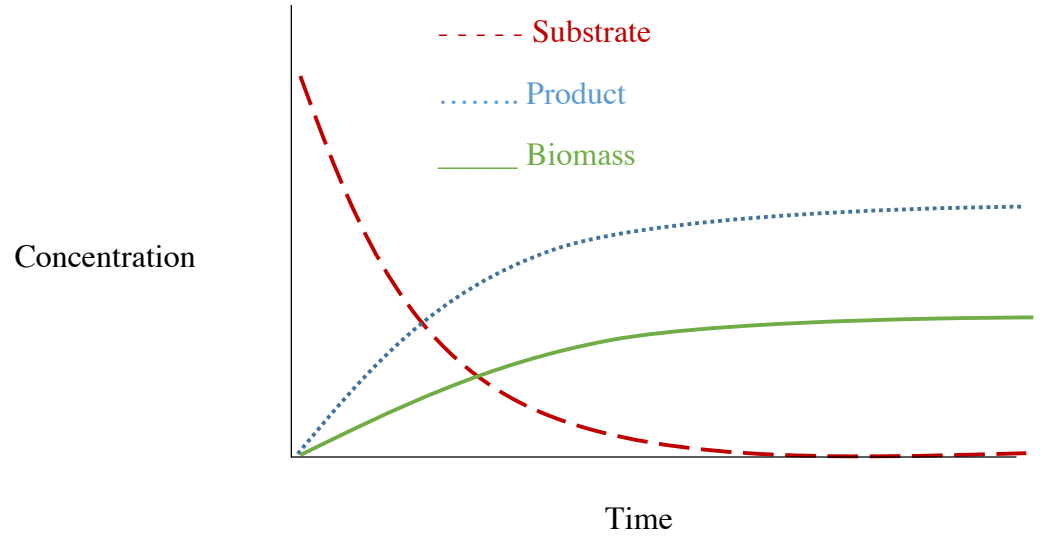

Figure 3: Substrate uptake, product and biomass formation.

To describe how this is done mass balances for the reactions of a continuous flow stirred-tank reactor (CSTR) can be developed according to the model presented in the book by Villadsen et al. (2011). A general way of describing the mass balance for a substance in a CSTR is according to Equation (3.6).

$$Accumulation = inflow - outflow + produced - consumed \quad (3.6)$$

Accumulation is the change in the amount of a substance over time. The inflow/outflow is the amount of the substance of interest that enters/exits the reactor per time unit. The change between produced and consumed describe the results of the reactions occurring inside the tank. The general equation for a dynamic mass balance in a CSTR can be further expressed as in Equation (3.7).

$$\frac{d(C_i)}{dt} = \frac{q_{feed}}{V} C_{i,feed} - \frac{q_{exit}}{V} C_{i,exit} + \rho(C_i) * X \quad (3.7)$$

Where C_i represent the concentration of the substance of interest, i. V is the volume of the tank, q is the flow rate, $\rho(C_i)$ is the production rate after substituting the consumption and X is the amount of biomass catalyzing the chemical reactions.

The different kinetic rates can be summarized into a rate equation matrix in which it is possible to see the relationship between substrate uptake, product formation, biomass formation and bacterial decay. Other factors affecting the rate like inhibition can also be included in this matrix. The developed rate equation matrix will follow the basic principle used in Batstone et al. (2002) and will be presented with the developed dynamic mass balances for the SRB growth in the Method.

A simplified model of how to construct a rate equation matrix is shown in Table 3. Equation (3.8) and (3.9) describes the uptake of substance A and the production of B and C. This is

connected to the uptake of B to produce D and E. The developed dynamic mass balances for the SRB growth in this system will be presented in the Method.

$$4A \xrightarrow{\rho_A} 2B + 2C \quad (3.8)$$

$$2B \xrightarrow{\rho_B} D + E \quad (3.9)$$

Table 3: Simple rate equation matrix model, showing the relationship between uptake of substance and the product formation and what rate equation correspond to each reaction.

Substance	A	B	C	D	E	Rate ρ_i
Uptake of A	-4	2	2			ρ_A
Uptake of B		-2		1	1	ρ_B

3.2.2 Mass transfer

The mass transfer rates will often be lower than the maximum reaction rate in the multiphase system according to Villadsen et al. (2011). It leads to smaller actual rates than what could have been expected from the kinetics. This mass transfer can occur between two liquid phases, solid and liquid phases, or liquid and gas phases.

The effectiveness of the mass transfer in the gas-liquid phases is usually described by the volumetric mass transfer coefficient (k_La). The term consists of the mass transfer coefficient k_L and the specific area, a. The limiting mass transfer rate is the mass transfer in the stagnant film layer between the liquid and the gaseous phase. The driving force for the molecules to go into the gaseous phase is the concentration gradient, according to Fick's first law describing the tendency for substances to diffuse from a place with high concentration of molecules to a place with lower concentration of molecules (Villadsen et al., 2011).

The volumetric mass transfer rate (ρ_i^t) can be calculated as the product of the k_La and the driving force of the system, which is the difference between the saturation concentration of solubles of the compound S_i^* and the actual concentration of the compound in the liquid phase, S_i, see Equation (3.10) (Villadsen et al., 2011).

$$\rho_A^t = k_L a\left(S_i^* - S_{i,(l)}\right) \quad (3.10)$$

The S_i^* can be calculated from Henry's law according to Nagpal et al., (2000), se Equation (3.11).

$$S_i^* = p_i/H_i \quad (3.11)$$

Henrys constant, H_i, is temperature dependent, p_i is the partial pressure for the substance *i*, in gaseous phase, which can be calculated through the ideal gas law.

The hydrogen sulfide is produced as a gas in the liquid. A part of this gas will dissolve in the liquid and some will be transported through the liquid and up to the precipitation tanks. Mass transfer will therefore occur between the liquid phase and the gas phase. If ideal mixing is assumed in the liquid phase there should always be H_2S molecules near the film layer that can be transported to the gaseous phase. Mixing is therefore important for the process, mixing is

the process in which homogeneity of a solution is achieved (Villadsen et al., 2011). The hydrogen sulfide has high solubility at high pH and a considerable amount of the product will be dissolved in the liquid and this will also be the case for carbon dioxide, see Table 2. The high amount of dissolved product will be a limiting factor for the process if only the gas is transferred from the bioreactor to the precipitation tanks and not also the liquid. It would mean that the amount of hydrogen sulfide produced would not correspond to the amount of hydrogen sulfide accessible for the precipitation of metal sulfides. Therefore, both gas and liquid should be used in the precipitation tanks and mass transfer must be taken into consideration to describe the system accurately.

The concentration gradient is always present as long as the gaseous form of H_2S is constantly removed from the tank. The mass transfer rate is considered by addition of the volumetric mass transfer rate (ρ_i^t) to the dynamic mass balances. The same theory applies for the carbon dioxide produced by the acetate-utilizing SRB. The developed equation for the mass transfer rates of the process will be presented in the Method.

3.2.3 Relationships describing inhibition

A low H_2S amount in the precipitation tank is not always due to mass transfer limitations described above, but can also be due to inhibition of the SRB, resulting in lower production rates. There are many kinds of inhibition of bacterial growth and different reasons for inhibition are suggested in literature. First, the substrate can inhibit the bacteria and lower the growth potential. There is also a possibility that the product, here H_2S can inhibit the bacterial growth and lower the growth rate at a certain concentration of product.

The basis for the model is the ADM1 developed by Batstone et al. (2002). The model is used and modified by many other researchers. Fedorovich et al. (2003) uses the ADM1 model from Batstone et al. (2002) for the implementation of inhibition into the uptake rate. Both a model for pH inhibition and sulfide inhibition is presented. The basis for the model is Monod kinetics and it is extended with the inhibition terms, which can be seen in Equation (3.12).

$$\rho_i = \frac{\mu_{max} S_i}{K_S + S_i} * \frac{S_{SO_4^{2-}}}{K_{SO_4^{2-}} + S_{SO_4^{2-}}} X * I_{pH} * I_{sulfide}, i = EtOH \; or \; Ac \tag{3.12}$$

The AMD1 model by Batstone et al. (2002) describes three different inhibition models which can be added to the equation above, competitive, uncompetitive and non-competitive according to Equations (3.13) to (3.15).

Non-competitive: $$I_{non} = \frac{1}{1 + \frac{S_I}{K_I}} \tag{3.13}$$

Uncompetitive: $$I_{un} = \frac{k_m X S_i}{K_S + S_i\left(1 + \frac{K_I}{S_I}\right)} \tag{3.14}$$

Competitive: $$I_{com} = \frac{k_m X S_i}{K_s\left(1 + \frac{S_I}{K_I}\right) + S_i} \tag{3.15}$$

Competitive inhibition means that the inhibitor binds to the active site on the enzyme and this hinders the substrate to bind to the active site. In non-competitive the inhibitor binds to an

allosteric site and change the conformation of the enzyme. This means that the substrate cannot bind to the active site anymore, since it does not fit. In uncompetitive inhibition, the inhibitor instead binds to the formed enzyme-substrate complex and hinder it from further reaction (Strelow et al., 2012).

3.2.3.1 Product inhibition from H_2S

Kaksonen et al. (2004) investigated the sulfide toxicity effect on SRB. They found that the model best describing the sulfide inhibition was a noncompetitive inhibition model. It is suggested that the noncompetitive inhibition can be regarded as a type of mixed inhibition where the inhibitor decreases μ_{max} but does not alter k_m (Kaksonen et al., 2004), (Maillacheruvu and Parkin, 1996) and (Okabe et al., 1995). According to Kaksonen et al. (2004) it is a general assumption that the main toxic form of sulfide is the un-dissociated hydrogen sulfide. This since only uncharged molecules can permeate the cell membrane and not HS^- and S^{2-} (Oude Elferink et al., 1994). In an aqueous environment, the form of sulfide varies depending on the pH, it can be S^{2-}, HS^- or dissolved H_2S. The free hydrogen sulfide is causing a toxic and inhibitory effect on the bacteria and this effect is hence dependent of the pH in the surrounding medium (Utgikar et al., 2002) and (Kalyuzhnyi et al., 1997). H_2S inhibition is reversible and the bacteria can recover metabolic activity again when the H_2S is removed (van Houten et al. (1994).

Many extensions of the ADM1 model by Batstone et al. (2002) has been developed to describe the product inhibition from hydrogen sulfide. Fedorovich et al. (2003) proposed a first order equation according to Equation (3.16).

$$I_{sulfide} = 1 - \frac{H_2S}{K_I} \tag{3.16}$$

The expression has a limitation because the inhibition will become negative if the H_2S concentration is larger than K_I.

Equation (3.17) is describing the non-competitive inhibition and is defined by Knobel and Lewis (2002).

$$I_{sulfide} = \frac{1}{1+\frac{S_I}{K_I}} \tag{3.17}$$

Poinapen and Ekama (2010) found that the first-order and non-competitive inhibition functions had negative values and instability in the inhibition function when the concentration of the H_2S was above the K_I value, $S_I > K_I$. They therefore suggested a function, which reaches zero more gradually with an increasing concentration of H_2S and should be more stable. This function can be used with high H_2S concentrations, see Equation (3.18).

$$I_{sulfide} = e^{\left[-\left(\frac{S_I}{0.60056K_I}\right)^2\right]} \tag{3.18}$$

From the sources above it seems reasonable to assume that the inhibition from hydrogen sulfide is non-competitive. The inhibition mechanism can be explained as the following. The first inhibition that occurs is on the growth rate of the bacteria. Then the product formation will also be inhibited, even for those bacteria that actually have been able to grow during the inhibited

conditions. H_2S will be transported into the bacterial cell when it is present in the solution. Only the un-dissociated form can pass the cell membrane (O'Flaherty et al., 1998). The H_2S will decrease the pH inside the cell. This is not desirable and the bacteria then need to actively transport the hydrogen sulfide back to the outer environment and over the cell membrane, which requires ATP. Hence the bacteria will grow less with the presence of H_2S. It will also produce less H_2S in the presence of H_2S. The H_2S does not bind to an active site or hinder the formation of product in any other way, more than it requires energy to increase the pH inside the bacterial cell and actively transport the H_2S over the cell membrane. The equations that can describe the pH inhibition are presented in the next section.

3.2.3.2 pH inhibition

pH inhibition can occur when the pH affects the ion state of hydrogen sulfide and results in a higher concentration of the un-dissociated H_2S than it would at other pH values. Batstone et al. (2002) presents two pH inhibition expressions, one for a combination of high and low pH inhibition presented in Equation (3.19).

$$I_{pH} = \frac{1+2*10^{0.5(pH_{LL}-pH_{UL})}}{1+10^{(pH-pH_{UL})}+10^{(pH_{LL}-pH)}} \tag{3.19}$$

The pH_{LL} is the lower limit where the organisms are 50 % inhibited and the pH_{UL} is the upper limit where the organisms are 50 % inhibited respectively.

The other model for pH inhibition that Batstone et al. (2002) describes is used when only low pH inhibition occurs, shown in Equation (3.20) and (3.21).

$$I_{pH} = \exp\left(-3\left(\frac{(pH-pH_{UL})}{pH_{UL}-pH_{LL}}\right)^2\right)\Big|_{pH<pH_{UL}} \tag{3.20}$$

$$I = 1|_{pH>pH_{UL}} \tag{3.21}$$

Here, the pH_{UL} and pH_{LL} correspond to points where the organisms are not inhibited at all or completely inhibited respectively.

3.2.3.3 Substrate inhibition

The substrates can cause inhibition of the bacteria growth. Reis et al. (1990) claims that inhibition of SRB growth can occur from un-dissociated acetate. The authors also mention the effect of sulfate on the SRB, here high concentration of sulfate can inhibit SRB activity.

3.2.3.4 Metal and metal sulfide inhibition

If the precipitation of metal sulfides is not fully accomplished, some of the metal ions could possibly be re-circulated to the bioreactor. Here, the metal ions can react with the formed hydrogen sulfide and create metal sulfides in the bioreactor. This is not desirable since the metal sulfides can inhibit the SRB. Heavy metals can have different effect on SRB, depending on the concentration of the metal. It can have an enhancing effect in low concentration, but could also act as an inhibitor if present in high concentration. The metals can become toxic to microorganisms since they can deactivate enzymes in the bacterial cell. This is achieved through denaturation of proteins and/or deactivation of functional groups. Metals can also

compete with important cations. Studies have shown that even metal sulfides can inhibit the activity of SRB. The inhibition seems to act external on the bacterial cell (Utgikar et al., 2002).

The metal sulfides should not participate in the biochemical reaction since they are insoluble. It was therefore suggested that the inhibition caused by metal sulfides were due to a physical hindrance of the bacteria. The metal sulfide precipitate acts as a barrier, which could prevent the access of the electron donor-acceptor pair to the active bacterial site, or enzyme that catalyze the sulfate reduction (Utgikar et al., 2002). It is important to establish a plan for how to remove the potentially formed metal sulfides in the bioreactor to eliminate the inhibition of the SRB growth.

3.2.3.5 Other inhibition factors

Another inhibition factor for SRB growth is oxygen. This effect is reversible and the activity of the bacteria can be restored when the oxygen is removed. SRB can tolerate low levels of oxygen (Nagpal et al., 2000a). An anaerobic reactor is simulated in this project and to ensure anaerobic conditions it is assumed that the bioreactor is sparged with N_2 gas.

Other microorganisms that work at similar conditions as sulfate reducers and use the same substrate can outcompete SRB. Microorganisms that also oxidize acetate using the acetyl-CoA/carbon monoxide dehydrogenase pathway are acetogenic methanogens (Goevert and Conrad 2008). Methanogens in general can often live in the same environment as SRB. However, it is shown that SRB outcompete methanogens if there is a sufficient amount of sulfate present. A COD to SO_4^{2-} ratio of around 0.6 is the critical value SRB to outcompete the growth of methanogens (de Smul et al., 1997 and Brand et al., 2014). If there is a limited amount of sulfate, then growth of methanogens can be favored on acetate (Brand et al., 2014).

3.2.4 Possible alternative conditions for the bioreactor

The system investigated in this report can be altered in different ways. There is a large variety of sulfate reducing bacteria with different qualifications. This gives the possibility of using different substrates and operational conditions in the system. These differences will be investigated in this section of the theory.

3.2.4.1 Different strains of sulfate reducing bacteria

There are different strains of bacteria using sulfate as an electron acceptor. There are for example thermophilic sulfate reducers that can survive temperatures of up to 55ºC (Vallero et al., 2003). There are also strains that survive more salinity than ambient sulfate reducers, for example *Desulfobacter halotolerans* (Vallero et al., 2005); they can survive NaCl concentrations of 0.5-13 wt./vol% (Brandt and Ingvorsen, 1997). There are also differences in sulfate reduction abilities between strains (Laanbroek et al., 1984). The study by Laanbroek et al. (1984) showed that *Desulfovibrio baculatus* and *Desulfobulbus propionicus* could not oxidize acetate. This indicates the need for specialized acetate oxidizers, acetotrophic SRB in addition to the ethanol oxidizing strains (de Smul et al., 1997). There are however strains that oxidizes both ethanol and acetate, for example *Desulfobacter postgatei* (Laanbroek et al., 1984) and *Desulfonacter halotolerance* (Vallero et al., 2005).

3.2.4.2 Substrate investigation

Bacteria need an electron acceptor and donor, a carbon source, nitrogen source, vitamins and minerals to grow and survive. SRB uses anaerobic respiration where organic compounds are oxidized using sulfate as a terminal electron acceptor (Pereira et al., 2011).

There are numerous possible electron donors such as hydrogen, acetate, methanol and ethanol (Moosa et al., 2002). It is decided that ethanol will be used within the METGROW+ project. However, it is of interest to consider and discuss the advantages and disadvantages of different kinds of substrates. A short description of some potential substrates follows below and is summarized in Table 4.

Ethanol is a relatively cheap raw material and has high availability (Nagpal et al., 2000a). One negative aspect of the use of ethanol is the low growth rate for the SRB (Liamleam and Annachhatre, 2007). Methanol is cost effective and has high availability (Dijkhuizen et al., 1985). However, growth of SRB is slow and the temperature chosen is significant. The highest rate of sulfate reduction can be obtained at higher temperatures around 65 °C (Weijma et al., 2000). Acetate is another option, even though it has many disadvantages and is not the first choice as an externally added substrate to the bioreactor. This substance is an intermediate state in the oxidation of ethanol to CO_2 and H_2O, which means that there will be two possible electron donors accessible if ethanol is used as a substrate (Liamleam and Annachhatre, 2007). Lactate is a widely used carbon source by most SRB species (Al-Zuhair et al., 2008). Lactate is preferable to use for the start-up of a process since it gives a high growth yield for the SRB. It will however result in high operational cost, when used in large-scale operations (Nagpal et al., 2000a).

Table 4: Examples of different substrate used for SRB growth, describing the most important positive and negative aspects.

Substrate	Positive	Negative
Ethanol	Cheap and high availability	Low growth rate
Methanol	Cost effective and high availability	Low growth rate and temperature dependent
Acetate	Intermediate state in ethanol oxidation	Low growth rate
Lactate	High growth rate	Expensive

3.3 Metal sulfide precipitation model

Precipitation is described as the process where two soluble species can form a solid product through a chemical reaction. Precipitation occurs at a fast rate and with a high recovery yield, it is sometimes referred to as reactive crystallization (Lewis et al., 2015). The fast rate and high yield makes this method suitable when metals should be removed and recovered from waste streams.

The formation of metal sulfides is suitable for the metal recovery application because the precipitates are non-soluble, which decreases the risk of metals leaking into the environment. Also, different metal ions precipitate at different pH resulting in the possibility for selective

recovery of metals in a waste stream with mixed content. Furthermore, sulfide have a high reactivity resulting in a low retention time in the precipitation tank. H_2S as a precipitation agent has shown a higher selectivity between precipitates compared to using for example Na_2S. (Tokuda et al., 2008)

It is advantageous to produce the hydrogen sulfide separate from the precipitation because this allows the pH to be optimized depending on the precipitates and the biological systems separately. For the precipitation this results in the possibility of using a multi tank system with a gradual increase of pH in each tank. The pH specificity of the metal sulfides can hence be used for continuous separation after each tank instead of downstream separation after the precipitation unit.

The precipitation in this process will occur between the sparged hydrogen sulfide in gas phase and the metal ions in the liquid phase. Therefore, the mass transfer step between gas and liquid must be considered in addition to the chemical reaction in the precipitation tank model. The mass transfer will be dependent on diffusion and the rate of mixing in the tank (Lewis et al., 2015). The precipitation efficiency depends on the surrounding environment in the form of pH and temperature. It also depends on the ratio between metal ions and hydrogen sulfide (Choi et al., 2006).

The stoichiometric ratio for precipitation of copper and zinc to hydrogen sulfide is 1:1. The rate of precipitation however, increases with increased sulfide concentration (Choi et al., 2006). This is further proved by Tokuda et al., (2008) where a higher hydrogen sulfide flow resulted in faster precipitation rates for copper. The diameter of the gas bubble decreases with increased H_2S flow and this results in a higher mass transfer.

3.3.1 Principle steps in the precipitation tank

The rate of formation of metal sulfide precipitates is dependent on different principles. The mass transfer rate for the reactive species to come in contact with each other, the chemical reaction rate and the rate of precipitation of the reacted compound.

A picture of how the precipitation occurs in the tank according to Higbie's theory can be seen in Figure 4. It shows how the hydrogen sulfide first moves to the surface of the gas-liquid interface from the gas phase in the bubble, 1. Then the hydrogen sulfide diffuses from the interphase over to the reaction zone, 2. The metal ion diffuses to the reaction zone, 3 and the chemical reaction can occur between the two species, 4. After the reaction, the formed metal sulfide precipitates away from the reaction zone, 5 (Mishra and Kapoor, 1978).

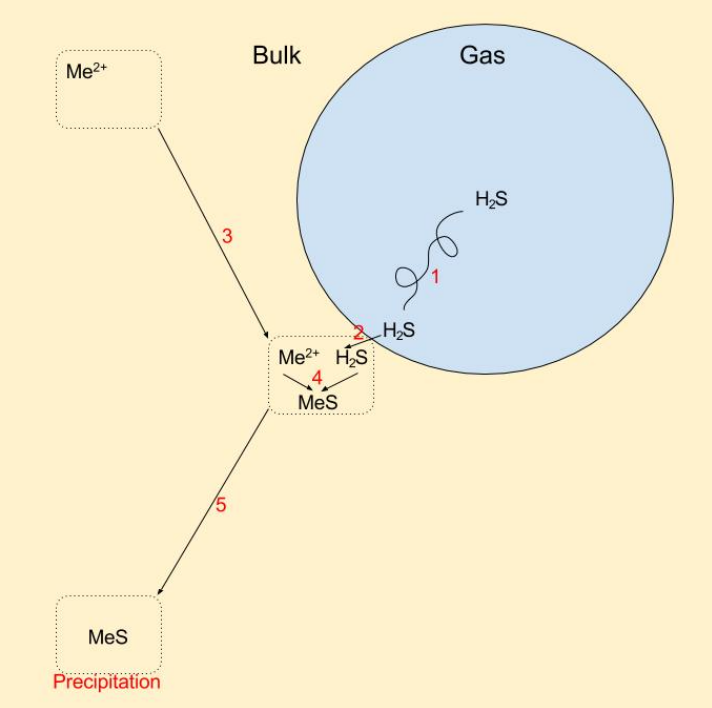

Figure 4: The steps of metal precipitation according to Higbie's theory, the figre is inspired by the article by (Mishra and Kapoor, 1978).

3.3.2 Metal sulfide formation rates

The rate of metal sulfide formation can be limited either by the chemical reaction rate or the mixing rate for the compounds. The time constant of precipitation based on the chemical reaction, ρ can be described by the reaction rate constant, k, the initial concentration of the limiting reagent, S_{A0} and the order of the reaction, m see Equation (3.22) (Lewis et al., 2015).

$$\rho = \frac{1}{k*(S_{A0})^{m-1}} \tag{3.22}$$

Mixing rate affects the reaction rate by increasing the probability of the reagents to have contact with each other. Mixing occurs on different scales in a tank. On the largest scale the dispersion of sparged gas and homogenization of the fluid in the tank can be described. Mixing can also be described locally on a smaller scale at for example the inlet where the fluid in the tank is mixed with the feed. The homogenization on molecular scale can be described through diffusion of the molecules in the tank (Lewis et al., 2015). The importance of mixing and mass transport makes the reactor design an important factor when designing an efficient precipitation process (Al-Tarazi et al. 2003). To see if the rate of formation of the precipitate depends on the mixing rate or the chemical formation rate, comparison between these should be done for the system.

The time limiting factor for the metal sulfide formation is mixing in form of diffusion of the reactants into the reaction zone according to (Mishra and Kapoor, 1978). This is because the chemical reaction occurs instantaneously when the species come in contact with each other (Tokuda et al., 2008). Several researchers have used Higbie's theory to describe the mass transport rate of the reactants to the reaction zone. This rate, which equals the metal ion removal rate over time is described in Equation (3.23) to (3.25) (Tokuda et al., 2008, Mishra and Kapoor 1976, Oktaybas et al., 1994).

$$\frac{dX_{MeS}^{t}}{dt} = \rho^{t} = \frac{a}{V} k_L (S_{Me^{2+}}^{t} + S_{H_2S}^{*}) \quad (3.23)$$

Where a is the gas-liquid interfacial area in m^2, k_L is the mass-transfer coefficient in m s^{-1} and V is the volume in m^3 in the aqueous phase. $S_{Me^{2+}}^{t}$ is the concentration at time t of the metal ions and $S_{H_2S}^{0}$ is the concentration of hydrogen sulfide at equilibrium at the system conditions. The gas-liquid interfacial area is defined in Equation (3.24) (Tokuda et al., 2008).

$$a = n\pi \, d_e^2 \frac{h}{U} \quad (3.24)$$

Where n is the number of bubbles per second, h is the height of the aqueous phase in m, U is the rising velocity of bubbles in s^{-1} and d_e is the bubble diameter in m.

The reaction rate constant, k can be used to calculate the mass transfer coefficient, see Equation (3.25).

$$k = \frac{a}{V} * k_L \quad (3.25)$$

The reaction kinetics are similar between copper, zinc and nickel and can be described through the same mathematical relationship (Tokuda et al. 2008).

3.3.3 Formation of the larger precipitates

The relationships above describe the formation of metal sulfide nanoparticles. The precipitation, where these nanoparticles create larger clusters, occurs subsequently to the chemical reaction. This process starts with nucleation formation of the particles followed by growth and agglomeration. This results in clusters of metal sulfides in the precipitation tank that can be separated from the fluid (Al-Tarazi et al., 2004).

The rate of nucleation and crystal growth is dependent on the amount of formed metal sulfide particles through the chemical reaction. The chemical reaction forms solids and when enough solids have been formed, there is a supersaturation of metal sulfides in the solution which initiates the nucleation, which is the most dominating part of the precipitation (Al-Tarazi et al., 2004). After nucleation, there is a crystal growth stage where more metal sulfide particles attach to the surface of the previously formed nuclei (Choi et al., 2006). The crystals agglomerate and create larger systems where the crystals attach to each other. The result of the precipitation is metal sulfide crystals with a specific particle size distribution (Al-Tarazi et al., 2004).

3.3.4 Metal removal efficiency

Metal ions and hydrogen sulfide form metal sulfides as stated earlier in this report. That is the basic principle for the metal recovery process simulated in this project. The metal sulfides are less soluble than for example metal hydroxides, which is an advantage using hydrogen sulfide as a precipitation agent when recovering metals (Kaksonen et al., 2004). The metal sulfides are formed according to following formulas presented in Equation (3.26) and (3.27), also the solubility constant are present in the equations (Touze et al., 2008).

$$Cu^{2+} + S^{2-} \rightarrow CuS \quad \mathrm{pK_{sp}} = -34.6 \quad (3.26)$$

$$Zn^{2+} + S^{2-} \rightarrow ZnS \quad \mathrm{pK_{sp}} = -8.7 - 11.5 \quad (3.27)$$

The metal removal efficiency is high, between 80 and 100% when using hydrogen sulfide with a variety of other process variables, the pH is however important for the removal efficiency (Kaksonen et al, (2004), Touze et al., (2008) and Tokuda et al., (2008)).

3.4 The importance of the process parameters

3.4.1 Temperature

This section will describe the temperature dependence of the bioreactor and the precipitation respectively.

3.4.1.1 Temperature dependence in the bioreactor

Several researchers have tested the optimal temperature for SRB growth. The temperature interval in which most research has been made is between 10-40°C. Not all research has been done with ethanol as an electron donor, but the temperature optimum should reasonably not be significantly substrate dependent. Nevatalo et al. (2010) found that the sulfidogenic activity on H_2 was the highest at a temperature between 30-35 °C and lower at temperatures between 9 °C and 15 °C. It seems like higher temperature results in higher sulfidogenic activity. Moosa et al. (2005) reports that the optimal temperature for SRB growth, giving the highest sulfate reduction rate, was 35°C. Here the bacterial yield and maximum specific growth rate were not affected by the temperature. It was reported that the SRB growth rate increased when increasing the reaction temperature from 20 to 35°C. Increasing the temperature to 40 °C led to inactivity of the bacteria. Al-Zuhair et al. (2008) also found that the optimal temperature was 35 °C. Here the fastest drop in sulfate concentration occurred at 35 °C. A temperature around 30 °C seems reasonable according to these sources.

3.4.1.2 Temperature dependence of precipitation

The spontaneity of metal sulfide formation depends on the thermodynamics of the reaction. The enthalpy and Gibbs free energy parameters are useful when describing the thermodynamics of a reaction. The equilibrium constant of the precipitation is the amount of precipitated metal ions compared to the dissolved ion concentration. The equilibrium constant of a reaction is dependent on Gibbs free energy as seen in Equation (3.28). This equation shows the temperature dependence of Gibbs free energy. The equilibrium constant K increases with temperature when Gibbs free energy decreases (Choi et al 2006).

$$\Delta G^0 = - RT\ln(K) \quad (3.28)$$

Gibbs free energy is also the difference between the enthalpy and the temperature times the entropy, see Equation (3.29).

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \text{ [18]} \quad (3.29)$$

The precipitation of copper sulfide was proven to be spontaneous and endothermic by Choi et al (2006) because of the negative ΔG^0 and the positive ΔH^0 and ΔS^0. The temperature dependence is especially important when a reaction is rate limited by the kinetics of the reaction, which is where Gibbs free energy affects the equilibrium constant of the reaction. This is however not the case for the metal precipitation according to Tokuda et al., (2008).

3.4.2 pH

Both the bioreactor and the precipitation tank are dependent on pH. To model the precipitation of metal sulfide and the bioreactor, the mole fraction of S^{2-} for example, is important. The dissociation of H_2S is dependent on pH. The mole fraction of S^{2-} is hence dependent on the solubility constants of H_2S and HS^- according to Equation (3.30) and (3.31).

$$H_2S \leftrightarrow H^+ + HS^-, K_{H_2S} = \frac{[H^+][HS^-]}{[H_2S]} \Longrightarrow pK = (-logK) = 7.1 \quad (3.30)$$

$$HS^- \leftrightarrow H^+ + S^{2-}, K_{HS^-} = \frac{[H^+][S^{2-}]}{[HS^-]} \Longrightarrow pK = 14 \quad (3.31)$$

The carbon dioxide produced in the bioreactor can be used to increase pH in the precipitation tank when dissolved as carbonates (Sahinkaya et al., 2007). When the dissolved carbonates from the bioreactor with pH 7 come in contact with the leachate in precipitation tank 1, the carbonates become protonated resulting in a decreased proton concentration, which means a higher pH. This phenomenon is dependent on the solubility constants for carbonic acid and carbonates, see Equation (3.32) and (3.33) (Aylward, 2013).

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^-, K_{H_2CO_3} = \frac{[HCO_3^-][H^+]}{[H_2CO_3]} \Longrightarrow pK = 6.3 \quad (3.32)$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}, K_{HCO_3^-} = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} \Longrightarrow pK = 10.3 \quad (3.33)$$

The formed CO_3^{2-} instantly reacts with water and forms CO_2 in an equilibrium reaction.

3.4.2.1 pH dependence in the bioreactor

Research has been done on how the pH affects the SRB growth and sulfate reduction rate. When sulfate is reduced to sulfide, the pH plays an important role. The sulfide can be present in different forms such as H_2S, HS^- and S^{2-} as mentioned earlier. The form of the sulfide depends on the pH of the environment. At a pH of 7 most of the hydrogen sulfide will be in the dissociated HS^- form (Perry and Green, 1984). At lower pH, the produced hydrogen sulfide will instead mostly be in its un-dissociated form, H_2S, and when the pH increases it dissociates into HS^- and S^{2-}. The pH inhibition will therefore be a larger problem at lower pH since inhibition only can occur from un-dissociated H_2S. According to Villa-Gomez et al. (2015) several studies have shown that low pH values causes a notable decrease of the sulfate reducing activity. Al-Zuhair et al. (2008) found that the optimal pH was 7, the fastest drop in sulfate concentration was observed at this pH.

It has been shown that at pH less than 7.0, un-dissociated H_2S is the dominant inhibitor. Whereas, at pH above 7 the total sulfide concentration is responsible for the inhibitory effect (O'Flaherty et al., 1998). In the comparison of different articles performed by Nevatalo et al. (2010) were all tests with ethanol as an electron donor performed in the pH range of 6.5-8.4. It is reasonable to assume that the optimal pH should be in this range. It can be argued that the pH should be kept around 7 to promote optimal cell growth in the bioreactor.

The reaction rate for ion dissociation can be calculated according to Equation (3.34). (Rosén and Jeppsson, 2005)

$$\rho_{A,i} = k_{A,Hi}(S_{i^-} * (S_{H^+} + K_{a,Hi}) - K_{a,Hi} * S_i) \quad (3.34)$$

3.4.2.2 pH dependence of precipitation

The pH dependence of precipitation efficiency is both affected by the dissociation of hydrogen sulfide and the pH dependent metal sulfide formation.

The metals will not only be present in the ion form in water. There is an interaction between the ions and the water molecules. Copper ions for example are proton donors interacting with the negatively charged hydroxide forming soluble metal hydrates. The total copper concentration will be the sum of the copper ions in the different hydrated forms. The precipitation is affected by this giving an additional pH dependence of precipitation.

The pH dependence of the precipitation results in different metal ions reacting with sulfide at different pH. This can be used to make the selective precipitation possible. Copper for example precipitates at a low pH, under 1 and the Zn^{2+} ions starts to precipitatate at pH 2 and at pH 5.7 only a soluble metal concentration of 0.001 mg L^{-1} remains (Huisman et al., 2006). The formed metal sulfides have very low solubility, see Table 2. Both CdS, cadmium sulfide and PdS, lead sulfide precipitates between copper and zinc (Huisman et al., 2006).

3.4.3 Sulfate reduction rates

The sulfate reduction rate is important for the metal recovery process and this rate varies with for example temperature, pH, incubation time and bacterial strain (Robador et al. 2009). Optimum temperature and pH spans are defined in the parameter section 3.4.1-3.4.2. The sulfate removal rate was found to be 1.8, 4.7, 6.3 and 9.9 g S L^{-1} d^{-1} for a temperature between 30 and 35^0C, a pH around 7 with ethanol as substrate for different tanks with other variables varying (Moosa et al., 2005, Vallero et al., 2005, (Nagpal et al., 2000b) and de Smul el al., 1997).

3.5 Environmental ethical aspects

3.5.1 Waste management

One problem in this process is the precipitation of toxic metals like, lead, cadmium, arsenic and antimony. These metals contaminate the metal sulfide products because the purity will be decreased and the prize will be lowered because the metal contaminants are hard to handle. Therefore, extra precipitation steps could be added to the process where these metals are precipitated. Cadmium and lead precipitates between copper and zinc. An extra tank could be placed there to avoid contamination in the zinc precipitator. Cd precipitates at pH between 1 and 3.8 and Pb precipitates between 1 and 4.6. Copper should therefore be precipitated under pH 1 to avoid impurities, zinc precipitated completely at pH ~5.8 but some of it precipitates earlier. The pH in the zinc tank should therefore be adjusted to meet the purity requirements at the same time as avoiding zinc precipitation in the tank where Cd and Pb are removed. (Huisman et al., 2006).

There is a risk of anaerobic corrosion in pipes etc when having sulfate reducing bacteria present. The bacteria should not be released because it kills animals, plants and microorganisms (Willey et al., 2008).

3.5.2 Safety aspects

When there is more than 10% hydrogen sulfide in the gas phase then it is very harmful to inhale the toxic gas, it is also an extremely flammable and very toxic to aquatic organisms if released to the environment (Aylward, 2013). The construction material for this process should therefore be carefully chosen. Plastic tanks are corrosion resistant and therefore an alternative to consider. With non-corrosive materials, the risk of leakage is decreased and the process gets safer (Huisman et al., 2006). Hydrogen sulfide gets ionized when dissolved in water. The ionized forms of hydrogen sulfide are not toxic and a liquid leakage would not be as dangerous as a gas leakage (Aylward, 2013).

Sulfuric acid is highly corrosive and can cause severe burns to the people working with the substance. Sodium hydroxide causes irritation at low concentrations and severe burns at high. It is also a corrosive substance. Ethanol is a highly flammable liquid and this compound should be kept away from ignition and held in closed containers. Acetic acid is a weak acid and can cause severe burns and it is also flammable (Aylward, 2013).

Copper or zinc are not considered harmful substances, however its bound state can be harmful and dangerous to the environment when bound to for example chloride or sulfate respectively (Aylward, 2013).

4 Material and Method

4.1 Literature study

The literature study presented in the Theory was conducted in the beginning of the project to gather information of the process that would be investigated. The literature search was based on published sources and books. A pre-project had already been carried out as a basis for this project where a more general process chart was designed for the entire metal recovery process using biologically produced hydrogen sulfide. Therefore, the authors of this report had some basic understanding of the process in the beginning and started the literature search by evaluating old sources, the supervisors also supplied some articles about metal recovery and sulfate reducing bacteria. *Lubsearch* and *Google scholar* were the two main search drives used for the literature search. *Lubsearch* is the search engine officially provided by Lund university for scientific articles. Words used for the search were for example *Sulfate reducing bacteria*, *Metal recovery, Ethanol SRB, Metal sulfides, Hydrogen sulfide production from SRB, Metal precipitation using hydrogen sulfide* etc. From the relevant articles found it was possible to use references from these articles to extend the literature search. To secure a high credibility of the articles used, the cited rate was evaluated. High citing rate could often indicate more credibility, since this is considered as concluded science. When interesting and useful articles were found in the literature search, the original source for this information was investigated as far as possible. Some original articles were not accessible online since they were written in the early 50s.

Lecture notes and books were used in addition to the literature search from *Lubsearch* and *Google scholar* to collect information necessary for the understanding of the process. The lecture notes were of course of debatable credibility because these are not published and therefore not reviewed, but these were still a useful complement to facilitate the understanding and readability of the sometimes complicated articles.

4.2 Building the mathematical model

In this part the mathematical model will be presented, which will further be implemented in the two simulation programs MATLAB and Aspen Plus.

4.2.1 Rate equation matrix, mass transfer and acid-base dissociation

In the ADM1 model by Batstone et al. (2002) a rate equation matrix is presented, which includes process rates and stoichiometry matrix for biochemical reactions. The same structure has been used to create the rate equation matrix for the reaction in the SRB process, see Table 5. The rates follow the Monod kinetics and are extended with terms for inhibition by pH and H_2S.

Table 5: Developed rate equation matrix for the SRB growth on Ethanol and Acetate respectively, substrate uptake, product formation, rates and bacterial decay.

	S_{EtOH}	S_{Ac}	$S_{SO_4^{2-}}$	S_{Sred}	S_{IC}	X_{eSRB}	X_{aSRB}	ρ_i rate
Uptake of ethanol	-1	1-Y_{EeSRB}	-(1-Y_{EeSRB})*$Y_{E.SO4}$	(1-Y_{EeSRB})*$Y_{E.SO4}$		Y_{EeSRB}		$\frac{\mu_{maxEt}}{Y_{EeSRB}} * \frac{S_{Et}}{K_S+S_{Et}} * \frac{S_{SO_4^{2-}}}{K_{SO_4^{2-}}+S_{SO_4^{2-}}} * X * I_{pH} * I_{sulfide}$
Uptake of Acetate		-1	-(1-$Y_{A.aSRB}$)*$Y_{A,SO4}$	(1-$Y_{A.aSRB}$)*Y_{ASO4}	1-Y_{AaSRB}		Y_{AaSRB}	$\frac{\mu_{maxAc}}{Y_{AaSRB}} * \frac{S_{Ac}}{K_S+S_{Ac}} * \frac{S_{SO_4^{2-}}}{K_{SO_4^{2-}}+S_{SO_4^{2-}}} * X * I_{pH} * I_{sulfide}$
Bacterial decay eSRB						-1		$k_{d,eSRB}X_{eSRB}$
Bacterial decay aSRB							-1	$k_{d,aSRB}X_{aSRB}$

From the general equation presented in the theory and the rate equation matrix it was possible to develop and rewrite the rates and dynamic mass balance equations for hydrogen sulfide production from SRB using ethanol and acetate as substrate. The different rates are presented in Equations (4.1) to (4.4). First for ethanol, then acetate and lastly the bacterial decay for ethanol-utilizing bacteria and acetate-utilizing bacteria respectively.

$$\rho_{EtOH} = \frac{\mu_{maxEt}}{Y_{EeSRB}} \frac{S_{EtOH}}{K_S+S_{EtOH}} * \frac{S_{SO_4^{2-}}}{K_{SO_4^{2-}}+S_{SO_4^{2-}}} X * I_{pH} * I_{sulfide} \quad (4.1)$$

$$\rho_{Ac} = \frac{\mu_{maxAc}}{Y_{AaSRB}} \frac{S_{Ac}}{K_S+S_{Ac}} * \frac{S_{SO_4^{2-}}}{K_{SO_4^{2-}}+S_{SO_4^{2-}}} X * I_{pH} * I_{sulfide} \quad (4.2)$$

$$\rho_{dec_{eSRB}} = k_{d_{eSRB}} * X_{eSRB} \quad (4.3)$$

$$\rho_{dec_{aSRB}} = k_{d_{aSRB}} * X_{aSRB} \quad (4.4)$$

The rates for the mass transfer of hydrogen sulfide and carbon dioxide from liquid to gas are presented in Equations (4.5) and (4.6) respectively.

$$\rho_{H2S}^t = k_L a\left(S_{H2S}^* - S_{H2S,(l)}\right) \quad (4.5)$$

$$\rho_{CO2}^t = k_L a(S_{CO2}^* - S_{CO2,(l)}) \quad (4.6)$$

Here is the S_i^* the saturation concentration of the compound and can as stated earlier in the theory be derived from Henry's law, see Equation (4.7).

$$S_i^* = p_i/H_i \quad (4.7)$$

The pressure can be calculated using the ideal gas law, see Equation (4.8).

$$p = nRT \quad (4.8)$$

The number of molecules present in the solution is a concentration, mol L^{-1}, which means that the volume is already taken into account in the ideal gas law. The volume difference between liquid and gas will be compensated in the dynamic mass balances for gas phase.

The acid-base equations and rates for the dissociation into ions for H_2S and CO_2 can be calculated according to Equations (4.9) to (4.12).

$$S_{H_2S} = S_{S_{red}} - S_{HS^-} \quad (4.9).$$

$$S_{CO_2} = S_{S_{IC}} - S_{HCO_3^-} \quad (4.10).$$

$$\rho_{A,HS} = k_{A,H_2S}(S_{HS^-} * \left(S_{H^+} + K_{a,H_2S}\right) - K_{a,H_2S} * S_{S_{red}}) \quad (4.11).$$

$$\rho_{A,HCO_3^-} = k_{A,CO_2}(S_{HCO_3^-} * \left(S_{H^+} + K_{a,HCO_3^-}\right) - K_{a,HCO_3^-} * S_{S_{IC}}) \quad (4.12).$$

These rates are considered when judging how much of every compound there is. The dissociation of HS^- to S^{2-} and HCO_3^- to CO_3^{2-} are not included here because the solubility constants for these substances to form is so low that they can be neglected, see Table 2.

4.2.2 Dynamic mass balances

The dynamic mass balances could be developed using the rate equation matrix relationships presented above in Table 5. The dynamic mass balances for biomass formation, substrate uptake and product formation are presented in Equations (4.13) to (4.21). Ethanol utilizing bacteria are denoted as eSRB and acetate utilizing bacteria are denoted aSRB.

$$\frac{dX_{aSRB}}{dt} = \frac{q_{in}}{V_{liq}} * \left(X_{aSRB_{in}} - X_{aSRB}\right) + Y_{AaSRB} * \rho_{Ac} - \rho_{dec_{aSRB}} \quad (4.13)$$

$$\frac{dX_{eSRB}}{dt} = \frac{q_{in}}{V_{liq}} * \left(X_{eSRB_{in}} - X_{eSRB}\right) + Y_{EeSRB} * \rho_{EtOH} - \rho_{dec_{eSRB}} \quad (4.14)$$

The dynamic mass balances equations for ethanol, sulfate and acetate respectively can be seen in Equations (4.15) and (4.16). Ethanol and sulfate is only taken up in the process, while acetate is both produced from ethanol and then taken up to produce carbon dioxide.

$$\frac{dS_{Ac}}{dt} = \frac{q_{in}}{V_{liq}} * \left(S_{Ac_{in}} - S_{Ac}\right) + (1 - Y_{EeSRB}) * \rho_{EtOH} - \rho_{Ac} \quad (4.15)$$

$$\frac{dS_{EtOH}}{dt} = \frac{q_{in}}{V_{liq}} * \left(S_{EtOH_{in}} - S_{EtOH}\right) - \rho_{EtOH} \quad (4.16)$$

$$\frac{dS_{SO_4}}{dt} = \frac{q_{in}}{V_{liq}} * \left(S_{SO_{4_{in}}} - S_{SO_4}\right) - (1 - Y_{EeSRB}) * Y_{eSRBSO_4} * \rho_{EtOH} - (1 - Y_{AaSRB}) * Y_{aSRBSO_4} * \rho_{Ac} \quad (4.17)$$

The product formation of hydrogen sulfide and its dissociated ions in liquid phase ($S_{red\text{-}liq}$) and carbon dioxide and its dissociated ions in liquid phase ($S_{IC\text{-}liq}$) are presented in Equations (4.18) and (4.19).

$$\frac{dS_{S_{red-liq}}}{dt} = \frac{q_{in}}{V_{liq}} * \left(S_{S_{red_{in}}} - S_{S_{red}}\right) + (1 - Y_{EeSRB}) * Y_{eSRBSO_4} * \rho_{EtOH} + (1 - Y_{AaSRB}) * Y_{aSRBSO_4} * \rho_{Ac} - \rho_{H_2S}^t \quad (4.18)$$

$$\frac{dS_{IC-liq}}{dt} = \frac{q_{in}}{V_{liq}} * \left(S_{\mathrm{IC}_{in}} - S_{IC}\right) + (1 - Y_{AaSRB}) * \rho_{Ac} - \rho_{CO_2}^t \quad (4.19)$$

The mass transfer rates are denoted as ρ_i^t and was explained in the section above, describing the mass transfer from liquid to gas of the compound *i*, here H_2S and CO_2.

The dynamic mass balances for describing the gas phase is presented below in Equations (4.20) and (4.21).

$$\frac{dC_{H_2S(g)}}{dt} = 0 - \frac{q_{gas}}{V_{gas}} * C_{H_2S(l)} + \rho_{H_2S}^t * \frac{V_{liq}}{V_{gas}} \tag{4.20}$$

$$\frac{dC_{CO_2(g)}}{dt} = 0 - \frac{q_{gas}}{V_{gas}} * C_{CO_2(l)} + \rho_{CO_2}^t * \frac{V_{liq}}{V_{gas}} \tag{4.21}$$

The mass transfer of reduced sulfur from liquid phase to gas phase is going to be dependent of how much H_2S is in gas phase and this will further be dependent of how much reduced sulfur is produced. The gas flow for the mass transfer equation can be calculated according to Equation (4.22) where the relation between the different gases present in the tank is presented. The tank will be sparged with N_2 gas to maintain anaerobic conditions. The gas flow of N_2 is fixed while the partial pressure of CO_2 and H_2S can be calculated using the ideal gas law and Henrys law.

$$q_{gas} = \frac{N_{2,gas}}{1-\left(\frac{p_{H_2S,gas}}{p_{atm}}\right)-\left(\frac{p_{CO_2,gas}}{p_{atm}}\right)} \tag{4.22}$$

The acid-base dynamic mass balances are presented in Equations (4.23) and (4.24).

$$\frac{dS_{HS^-}}{dt} = -\rho_{A,HS^-} \tag{4.23}$$

$$\frac{dS_{HCO_3^-}}{dt} = -\rho_{A,HCO_3^-} \tag{4.24}$$

4.2.3 Inhibition

It is possible to implement the expression for pH inhibition presented in the theory by adaptation to the given microorganisms. In this case, it would mean that two equations are used, one for ethanol utilizing SRB and one for acetate utilizing SRB, since the different species have different pH optimum, see Equations (4.25) and (4.26).

Ethanol utilizing SRB:

$$I_{pH,eSRB} = \frac{1+2*10^{0.5(pH_{LL,eSRB}-pH_{UL,eSRB})}}{1+10^{(pH-pH_{UL,eSRB})}+10^{(pH_{LL,eSRB}-pH)}} \tag{4.25}$$

Acetate utilizing SRB:

$$I_{pH,aSRB} = \frac{1+2*10^{0.5(pH_{LL,aSRB}-pH_{UL,aSRB})}}{1+10^{(pH-pH_{UL,aSRB})}+10^{(pH_{LL,aSRB}-pH)}} \tag{4.26}$$

If only low pH occurs another inhibition term can be used. The description of these inhibition terms is given in Equations (4.27) and (4.28).

Ethanol utilizing SRB:

$$I_{pH,eSRB} = \exp\left(-3\left(\frac{(pH-pH_{UL,eSRB})}{pH_{UL,eSRB}-pH_{LL,eSRB}}\right)^2\right)\Bigg|_{pH<pH_{UL,eSRB}} \tag{4.27}$$

Acetate utilizing SRB:

$$I_{pH,aSRB} = \exp\left(-3\left(\frac{(pH-pH_{UL,aSRB})}{pH_{UL,aSRB}-pH_{LL,aSRB}}\right)^2\right)\Bigg|_{pH<pH_{UL,aSRB}} \quad (4.28)$$

It is not known what kind of pH inhibition that occurs in the SRB process, therefore the equation that takes into account both low and high inhibition was implemented and evaluated first. It was later however very difficult to find literature values for the upper and lower limit and it could also be reasonable to assume that only low pH inhibition occurs in the bioreactor. This since the bacteria only should be sensitive to low pH when the amount of un-dissociated H_2S increases, causing inhibition. The equation for the low pH inhibition was therefore implemented and used instead.

Different expressions describing the product inhibition from hydrogen sulfide was presented in the theory. The chosen equations implemented in the model are presented in Equation (4.29) and (4.30).

$$I_{sulfide} = 1 - \frac{H_2S}{K_I} \quad (4.29)$$

$$I_{sulfide} = \frac{1}{1+\frac{S_I}{K_I}} \quad (4.30)$$

4.2.4 Precipitation tank model

The mass balance describing the precipitation can be built in the same manner as for the bioreactor. The most important mass balances are the metal sulfide formation and these are the only ones stated here, see Equation (4.31) and (4.33). The term that is different between the biological system and the purely chemical system in the precipitation tank is the equations describing the rate. As stated in the Theory, either the reaction rate or the mass transfer rate is limiting for the metal sulfide formation. In this model, the mass transfer is assumed to be the limiting factor used for describing the formation rate of the metal sulfides.

$$\frac{dX_{CuS}}{dt} = \frac{q_{in}}{V_{liq}} * \left(X_{CuS_{in}} - X_{CuS}\right) + \rho^t_{CuS} \quad (4.31)$$

$$\frac{dX_{ZnS}}{dt} = \frac{q_{in}}{V_{liq}} * \left(X_{ZnS_{in}} - X_{ZnS}\right) + \rho^t_{ZnS} \quad (4.32)$$

where the mass transfer rate is described as in the article by Tokuda et al., (2008), see Equation (4.33) and (4.34) and Table 1 for parameter description.

$$\rho^t_{CuS} = \frac{a}{V} k_L (S^t_{Cu^{2+}} + S^0_{H_2S}) \quad (4.33)$$

$$\rho^t_{ZnS} = \frac{a}{V} k_L (S^t_{Zn^{2+}} + S^0_{H_2S}) \quad (4.34)$$

The dissociation of H_2S and CO_2 are described in the same way as for the bioreactor. The precipitation tanks where not simulated in MATLAB and these mass balances where not used. The precipitation was only simulated in Aspen Plus and only the rate equations are used in that simulation.

4.3 MATLAB simulation

The kinetic modeling simulation of the bioreactor is performed in the computer software MATLAB R2014b. The program is developed and distributed by MathWorks Inc. and can be used for mathematical and technical calculations. The program code is built up by matrices and scripts are used to run the mathematical calculations. All known variables are defined and the unknowns stated. The program is based on matrix laboratory and was developed as a complement to the other programing languages like Fortran and Java. MATLAB is supposed to be able to interface with program languages like Fortran and Java in an relatively easy way, but the user should be able to use the MATLAB program without the knowledge of programming in the other programs. (MathWorks, 2017c), MathWorks, 2017d)

4.3.1 Ode solvers

The defined unknown variables in the used script in MATLAB can be solved using an ODE system for the ordinary differential equations (ODE). There are different ode solvers that can be used. The ode45 is the most generally used solver and often the first choice since it gives good results for most ODE problems. The ode23 and ode113 could sometimes be a better choice since it is more efficient for problems with tighter and looser accuracy requirements (MathWorks, 2017a). An ode23s can only solve problems with a mass matrix if the mass matrix is constant. ode15s and ode23t can be used to solve problems with singular mass matrices. This is called a differential-algebraic equation (DAE) (MathWorks, 2017b).

The ode solver chosen for simulating the developed model is an ode15s, which solves stiff differential equation. The system is stiff when it has a large range of time constants. One disadvantage with this solver is that it has a problem in handling dynamic inputs. The more random an input variable behaves, the more difficult it becomes to solve since the prediction of the future state becomes uncertain. Therefore the time for the simulation can be extensive (Rosén and Jeppsson, 2005). The ode15s solver has a low to medium accuracy and is recommended to use when an ode45 fails or takes too long time to solve and when it is suspected that the problem actually is stiff. An ode15s is also recommended to use when solving DAEs (MathWorks, 2017a).

4.3.2 Model design

The dynamic mass balances for all components in the reactions were defined and coded in MATLAB. The unknown state variables must be connected to specific differential equations which are stated in a dy-vector in which the differential equations are defined in the same order as the unknown are defined in the model. The unknown variables were solved using the ode15s, which gave model outputs in the same order as the unknown variables. An initial state must be given for the ode solver to start the calculation loops and this initial state vector (y0) should also be defined in the same order as the unknown variables.

The framework for the kinetic modeling in this project is as mentioned before the Anaerobic Digestion Model No. 1 (ADM1) developed by Batstone et al. (2002). The ADM1 is used as a template but altered to fit the given conditions to produce hydrogen sulfide using SRB. This means that almost all dynamic mass balances were altered and the methanogenic equations were removed. A simplification of the acid-base relation was also done. Total ion strength is used in

the ADM1 model, whereas in this model a set pH is stated and from that the dissociation of ions can be calculated.

4.3.3 Connections to the different function files

The kinetic model was designed in a model function file. All known parameter and variable values were defined in a separate parameter function file. A third function file was created to solve the model using an ode solver in which the model function file was called on as well as the parameter function file. This means that all three function files are connected, the solver file cannot be run without being connected in a proper way to the other two function files. The outputs from the model that were held from the ode solver was saved and plotted in the solver file. Figure (5) describes the connection between the different files.

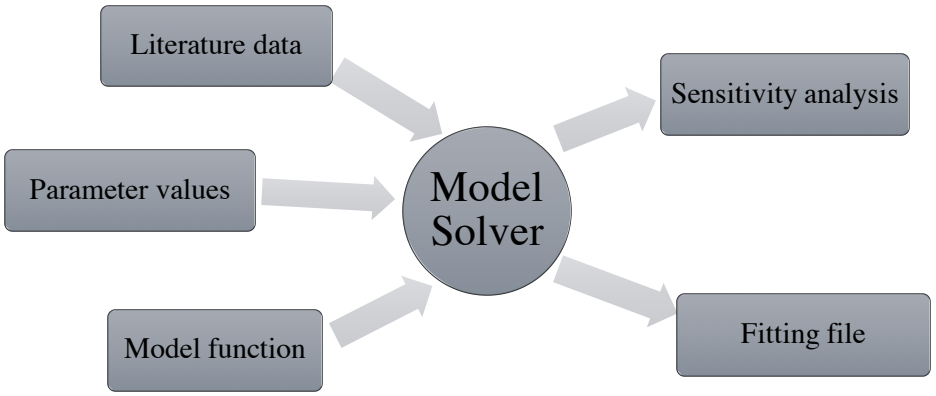

Figure 5: Overview of the connection between different MATLAB scripts, the model solver is the core and connected to the function file, parameter and literature values. The model solver is then used to construct a sensitivity analysis file and fitting file

4.3.4 Calibration of the model

The model simulation was compared to literature data. Data points from Nagpal et al. (2000) and Moosa et al. (2002) were used to compare to the model results. The data were saved as vectors in a separate data function file and called on in the model solver, since it was desirable to plot the output from the model in the same graphs as the data points. This gave the possibility for comparison of the model and literature data.

A sensitivity analysis was conducted to conclude which parameter or system variable that affects the model the most. This was done by altering selected parameter values by 1 % at a time and then normalize the value to see which parameter or variable that has the highest impact of the results. The analysis was carried out both manually and coded in MATLAB. The sensitivity analysis was performed on the model that was modified to fit the literature data from the first article Nagpal et al. (2000). The analysis was performed in a separate sensitivity function file, in which the model solver function file was used.

In addition to this, a fitting function was designed to make it possible to adapt one parameter value to fit the model to the literature data. The parameter can either be adapted to fit only one of the literature data or to find a best fit for many different data. Applied to this project it meant that the parameter could be adapted to fit only the H_2S liquid concentration or to find the best fit for both H_2S liquid production and ethanol consumption for instance. If the parameter is

adapted to several different data the fit will not be as good as for single data only. The fitting function can also adapt many parameters to an output, but has a risk in which the model parameters can become random. The fitting was design with the command *lsqcurvefit*, which uses a least square method to find the right parameter value for a nonlinear curve fitting. It needs a function, xdata and ydata in which data is given for the adaptation to the model, a guess of the parameter value as well as a lower and upper bound. The fitting was performed in a separate fitting function file, which used the model solver that was adapted to Nagpal et al. (2000). (MathWorks, 2017e)

Parameter values from the literature data used for the model evaluation for the MATLAB simulation are presented in Table 6.

Table 6: Parameter and variable values for the articles used for calibration of the model. Values with "" are not taken from literature, estimated from other literature sources, according to the given prerequisites. Boxes marked with "-" are parameters not used in the model.*

Parameter	Nagpal et al. (2000) value	Moosa et al. (2002) value
$\mu_{max\ EtOH}$	0.013 h^{-1}	-
Y_{eSO4}	0.5 $g_{protein} mol_{SO4}^{-1}$	-
Y_{EeSRB}	0.5 · Y_{eSO4} $g_{protein}$ mol_{SO4}^{-1}	-
Ks_{EtOH}	0.0045 mol L^{-1}	-
Ks_{SO4}	0.0085 mol L^{-1}	$7.39 \cdot 10^{-4}$ mol L^{-1}
$\mu_{max\ Ac}$	-	0.063 h^{-1}
Y_{AaSRB}	-	1.3913 mol mol^{-1}
Ks_{Ac}	-	$24 \cdot 10^{-3}$ mol L^{-1}
q_{in}	0 mol L^{-1} h^{-1}	-
$X_{eSRB\ in}$	0.018 mol L^{-1}	-
$X_{aSRB\ in}$	-	0.12189 mol L^{-1}
$S_{EtOH\ in}$	0.0615 mol L^{-1}	-
$S_{Ac\ in}$	-	0.2964 mol L^{-1}
S_{SO4_in}	0.0326 mol L^{-1}	0.05205 mol L^{-1}
Y_{aSO4}	-	2.21302 mol L^{-1}
k_{dec}	*0.002 h^{-1}	0.0035 h^{-1}
$k_L a_{H2S}$	10 h^{-1}	*10 h^{-1}
$k_L a_{CO2}$	-	*10 h^{-1}
H_{H2S}	10.70 h^{-1}	*10.70 h^{-1}
H_{CO2}	-	*25.88 h^{-1}
T	303 K	308 K
R	0.082057338 L atm K^{-1} mol^{-1}	0.082057338 L atm K^{-1} mol^{-1}
V_{liq}	*2.7 L	*0.9 L
V_{gas}	*0.3 L	*0.3 L
V_{tot}	3 L	1 L
P_{tot}	1 atm	1 atm
N_{2g}	6 L h^{-1}	6 L h^{-1}
$K_{ab\ H2S}$	10^{15}	*10^{15}
$K_{a\ H2S}$	$1.075 \cdot 10^{-7}$	*1.075 ··· 10^{-7}
K_{ab_CO2}	$4.97 \cdot 10^{-7}$	*$4.97 \cdot 10^{-7}$
K_{a_CO2}	10^{12}	*10^{12}
pH_{LL}	1.3	*1.3
pH_{UL}	*6.75	*6.75
pH	7.3	7.8
K_I	*$5.13 \cdot 10^{-3}$ mol L^{-1}	*$5.13 \cdot 10^{-3}$ mol L^{-1}

4.4 Aspen Plus simulation

Aspen Plus is a software used for flowsheet simulation where the whole process from raw material to purified product can be simulated. Aspen is built up of linear relationships and differential equations where the number of unknown variables equals the number of equations to solve the process problem (Al-Malah, 2016). There are several inputs needed for the process to run and resemble a real process.

The information stated in this section was taken from Aspen Plus help function, Aspen Tech support service and personal communications from employers at RISE. A description on how the process flows and the flow on information is to be implemented is schematically shown in Figure 6.

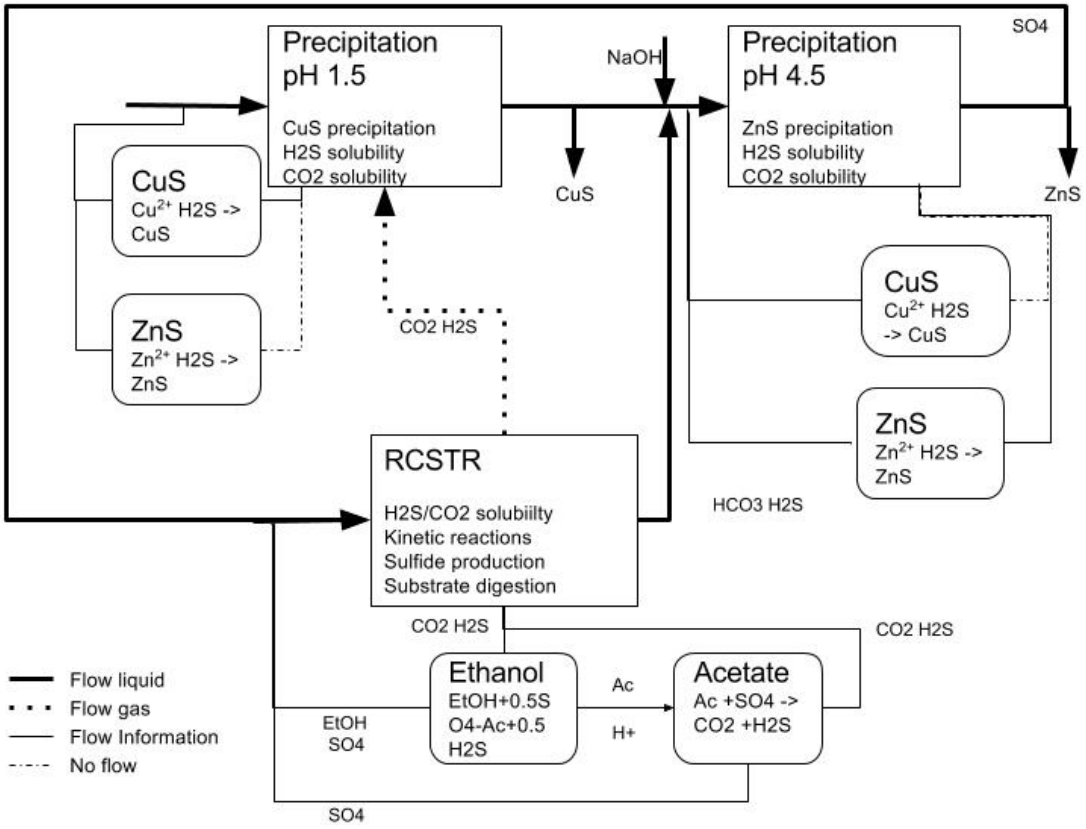

Figure 6: An overview of how the process is planned to be implemented into the simulation programme Aspen Plus.

Aspen Plus simulation set up

The basic steps for implementing the model in Aspen Plus V8.8 are (Al-Malah, 2016):

1. Specifying the components present in the model
2. Choosing a property method suitable for the system
3. Specifying the reactions that are present in the system
4. Building the flowchart

5. Specify parameters with calculation blocks to manually control the outcome for the process
6. Evaluating the process by comparing the outputs to experimental data

The precipitation and the bioreactor were initially simulated separately in Aspen. This separation was made to simplify the evaluation of the model and enable the use of different sources of experimental data to evaluate the two process sections. The description for the general model setup is true for both parts and the whole system was considered when choosing property method, specifying components etc.

4.4.1.1 Specifying the components present in the model

A blank simulation sheet with metric units was chosen and all the chemical components used as substrates, intermediates and products in the process were added under the "property mode", see Table 7. The metal sulfides were specified as conventional solids and these needs to be treated differently than the other components when simulating. These components are characterized with their molecular weights, vapor pressure and critical temperature. The metal sulfides were defined to be present in a substream suitable for solids and not the MIXED stream, as the other compounds. The solids can be treated as inert compounds after the reaction has occurred because of this substream.

Table 7: The compounds used for this simulation.

Component ID	Type	Component name	Alias
ZN++	Conventional	ZN++	ZN+2
ZNS	Solid	ZINC-SULFIDE(WURTZITE)	ZNS-2
CU++	Conventional	CU++	CU+2
CUS	Solid	COPPER-SULFIDE	CUS
S--	Conventional	S--	S-2
WATER	Conventional	WATER	H2O
H2S	Conventional	HYDROGEN-SULFIDE	H2S
HS-	Conventional	HS-	HS-
CO2	Conventional	CARBON-DIOXIDE	CO2
HCO3-	Conventional	HCO3-	HCO3-
OH-	Conventional	OH-	OH-
HSO4-	Conventional	HSO4-	HSO4-
SO4--	Conventional	SO4--	SO4-2
H3O+	Conventional	H3O+	H3O+
CO3--	Conventional	CO3--	CO3-2
N2	Conventional	NITROGEN	N2
H2SO4	Conventional	SULFURIC-ACID	H2SO4
NAOH	Conventional	SODIUM-HYDROXIDE	NAOH
NA+	Conventional	NA+	NA+
NA2SO4	Conventional	SODIUM-SULFATE	NA2SO4
ETHANOL	Conventional	ETHANOL	C2H6O-2
ACETICAC	Conventional	ACETIC-ACID	C2H4O2-1
ACETATE	Conventional	CH3COO-	CH3COO-

Most of the compound properties were retrieved from Aspen Plus databanks. The standard volume (stdv), $cm^3\ mol^{-1}$, were not present for all the compounds. These values were copied from the un-dissociated substances to its dissociated forms. For example, stdv for H_2O were used for OH^- and H_3O^+ and the stdv for H_2S were used for HS^- and S^{2-}. For the metal ions and the metal sulfides, the standard volume were instead calculated from the density and the molar mass at 25°C.

4.4.1.2 Choosing a property method suitable for the system

The property method was chosen according to Aspen Help function, "Guidelines for Choosing a Property Method". The choice of property method is important because it specifies what relationships Aspen used to calculate thermodynamic and transport properties. The property method has different approaches to calculate the equilibrium constants. The components in the bioreactor are polar for most part. There will be a low to medium pressure used for the process at close to ambient temperature. Therefore, an activity coefficient model should be used. There are both liquid and vapor phases present in the reactor and therefore a two phase system for liquid and vapor were specified. Alternative property methods that work for the above mentioned specifications are for example Wilson, NRTL and UNIQUAC. NRTL has been used by Rajendran et al. (2014) for simulation of the ADM1 model in Aspen and thereby been proven to be an alternative for this type of simulation. There is also the alternative of using an electrolyte method, which is beneficial when modelling dissociation reactions important for when acids are present in the system. In this process, sulfuric and acetic acid are present. The dissociation of compounds did not work properly with the NRTL method and therefore an electrolyte property method was chosen instead. ELECNRTL was the final choice for this simulation and it was set as the global property method used for all unit operations where nothing else is specified.

4.4.1.3 Specifying the reactions that are present in the system

The reactions relevant for the different unit operations was specified under the simulation mode. In short, the hydrogen sulfide formation and the metal sulfide precipitation that are the most important outputs resulting from these reactions, see Table 8. Power law kinetics were used for the reactions imported to the blocks representing bioreactor.

Table 8: The reactions added manually to the system that represent the model built for this project.

Reaction	Reactions added in Aspen	Stoichiometry
Precipitation 1	Block – PH1.5 – Reactions Rcn No. 1	$Cu^{2+} + H_2S + H_2O \rightarrow CuS + H_3O^+$
Precipitation 2	Block – PH4.5 – Reactions Rcn No. 1	$Zn^{2+} + H_2S + H_2O \rightarrow ZnS + H_3O^+$
Ethanol degradation	Reactions - R-1 – No. 1	$C_2H_5OH + 0.5SO_4^{2-} \rightarrow CH_3COO^- + 0{,}5S^{2-} + H_3O^+$
Acetate degradation	Reactions - R-2 – No. 1	$CH_3COO^- + SO_4^{2-} \rightarrow 2CO_2 + S^{2-} + H_2O + OH^-$

To achieve a realistic simulation, acid-base dissociation reactions should also be included. This can be done in two ways, either manually by adding the reactions in every block or automatically by using the built in reaction tool for electrolytes, the electrolyte wizard. By activating this feature, Aspen can find the possible equilibriums, dissociations and salt formations for the compounds present in the system. The electrolyte wizard was the method of choice for this project. The reactions that the system takes into consideration are presented in Table 9, no salt formations are taken into consideration for this project. This should be a reasonable assumption because of the low amounts of ions that could fall out as solid salts. Oxonium ions were specified as the species resulting from water dissociation.

Table 9: The equilibrium and dissociation reactions specified by the electrolyte wizard and used by the system automatically in every stream.

Reaction	Type	Stoichiometry
1	Equilibrium	ACETICAC + WATER <--> ACETATE + H3O+
2	Equilibrium	WATER + HSO4- <--> H3O+ + SO4--
3	Equilibrium	H2SO4 + WATER <--> H3O+ + HSO4-
4	Equilibrium	WATER + HCO3- <--> CO3-- + H3O+
5	Equilibrium	2 WATER + CO2 <--> HCO3- + H3O+
6	Equilibrium	WATER + HS- <--> H3O+ + S--
7	Equilibrium	WATER + H2S <--> H3O+ + HS-
8	Equilibrium	2 WATER <--> OH- + H3O+
NAOH	Dissociation	NAOH --> OH- + NA+
NA2SO4	Dissociation	NA2SO4 --> SO4-- + 2 NA+

4.4.1.4 Building the flowchart

The precipitation tanks in Aspen Plus were simulated with equilibrium reactors (REquil). This reactor calculates the chemical equilibrium and the phase equilibrium for the chemical reactions entered in the reactor block. To use an equilibrium reactor in Aspen, stoichiometry must be known for the reactions and the reaction rate is decided either by using temperature approach, letting Gibbs free energy decide the reaction rate, or restrictions can be entered manually by choosing to specify the molar extent of the reaction. Specifying molar extent enables the possibility to set the reaction extent based on imported data from a calculation block and then the mass transfer rate instead of reaction kinetics can be used to regulate the reaction extent, as desired for this project.

One REquil block was used for each pH stage in the process. This type of reactor was also chosen to enable the possibility of modelling solids in the system. Other tanks that work with solids are blocks based on reaction yield and Gibbs free energy (RYield and RGibbs).

Both the precipitation of Cu and Zn should be considered in each reactor and a pH restriction should be entered to the calculation block to regulate the output. This was done for the first reactor “PH1.5” but because of errors occurring due to the low amount of copper entering the second precipitation no CuS calculation block was specified for the second reactor, “PH4,5”. A solid separator blocks were added after each reactor block to simulate the metal sulfide removal.

The bioreactor was simulated using both a CSTR and a Batch block in Aspen Plus. These unit operations are more similar to a "real life" system than the equilibrium based unit operation. No solids are allowed in these unit operations in Aspen and therefore the solid metal sulfides present in a substream need to be separated before the stream is entered into the simulated bioreactor.

Mixers and splitters were added when needed. These are needed both to simulate an actual process split, mix or to simulate a part of a unit. The Mixer block was used to mix the different inflows before the reactors and these blocks does not necessarily represent real unit operations, depending on how the real process would be designed. Simple Sep blocks were used to mimic the gas-liquid separation that occur in the bioreactor and this block does not represent a real unit operation. Sep blocks were also used to separate water after the bioreactor and in this case the block mimics a real unit operation. The Sep block separates compounds dependent on for example flow or fraction. In some parts of the process, the whole stream was separated, in these cases a FSplit block was used. The recirculation in the process were simulated using these types of blocks. The substream was separated in a substream split block, SSplit. This separation is done before the bioreactor to avoid solids in these blocks. Due to time limitations in this project, no pumps or compressors were added to regulate flows or alter the process pressure.

4.4.1.5 Specifying parameters and kinetics manually to control the process output

The specifications described in this section were done to enable the implementation of the model developed in this project. The whole model will not be used because Aspen Plus already calculates mass balances. The reaction rates however will be the part of the developed model and this is the part that ties the Aspen and MATLAB simulation together.

The mass transfer rate was the only expression used to describe the precipitation of metal sulfides for this simulation because the reaction rate is assumed to be instantaneous (Tokuda et al., 2008). The only part of the bioreactor model used for the Aspen Plus simulation was the reaction rate (the ρ -value) from the ethanol/acetic acid degradation. The equations used to control the reactions in each unit operator resembling a reactor can be seen in Table 10.

The reaction extent for the reactions used in the precipitation units and the pre-exponential factor used to specify the extent of the reactions in the bioreactor can be manually manipulated by using calculator blocks. The values entered in the reactor block or under the reactions tab were specified to be overwritten by the exported variable calculated by the calculator blocks. The calculation blocks can be modeled using either an imported Excel file or by manually entering the code in the calculation block using Fortran language. The latter is used in this case. The imported variables are stated in Table 10 together with the implemented equations and the parameters to be defined. The import variables are imported from one of the streams entering the block where the kinetic is used. The exported variable is the reaction rate in mole per hour for the REquil blocks and the pre-exponential factor in per second for the Batch/CSTR reactor where the R-1/R-2 reactions were used. Detailed description of the code entered into the calculation blocks are displayed in Appendix C.

Table 10: The equations implemented in the different calculator blocks and the import/export variables.

Calculation block	Expressions used	Origin of values
Copper sulfide formation block (CUS1)	$\rho_{CuS} = A_b * \mathrm{k_L}\left(\mathrm{S^t_{Cu^{2+}}} + \mathrm{S^0_{H_2S}}\right)$ $\mathrm{S^0_{H_2S}} = \frac{S^t_{H_2S} g^{*R*T}}{H_{H_2S}}$ $pH = -\log\left[H_3O^+\right]$	$Import\ variables$: $\mathrm{S^t_{H_2S}}, \mathrm{S^t_{Cu^{2+}}}, \mathrm{T}, \mathrm{H_3O^+}$ $Export\ variable$: ρ_{CuS} $Defined\ parameters$: A_b, k_L, R, H_{H_2S}
Zinc sulfide formation block (ZNS2)	$\rho_{ZnS} = A_b * \mathrm{k_L}\left(\mathrm{S^t_{Zn^{2+}}} + \mathrm{S^0_{H_2S}}\right)$ $\mathrm{S^0_{H_2S}} = \frac{S^t_{H_2S} g^{*R*T}}{H_{H_2S}}$ $pH = -\log\left[H_3O^+\right]$	$Import\ variables$ $\mathrm{S^t_{H_2S}}, \mathrm{S^t_{Zn^{2+}}}, \mathrm{T}, \mathrm{H_3O^+}$ $Export\ variable$ ρ_{ZnS} $Defined\ parameters$: A_b, k_L, R, H_{H_2S}
Ethanol degradation calculator block (BETH)	$\rho_{EtOH} = \frac{\mu_{maxEt}}{Y_{EeSRB}} \frac{S_{Et}}{K_{S,Et}+S_{Et}} * \frac{S_{SO_4^{2-}}}{K_{SO_4^{2-}}+S_{SO_4^{2-}}} * I_{pH,eSRB}$ $I_{pH,eSRB} = \exp\left(-3\left(\frac{(pH-pH_{UL,eSRB})}{pH_{UL,eSRB}-pH_{LL,eSRB}}\right)^2\right)\Big\vert_{pH<pH_{UL,eSRB}}$ $pH = -\log\left[H_3O^+\right]$	$Import\ variables$: $S_{Et}, S_{SO_4^{2-}}, \mathrm{T}, \mathrm{H_3O^+}$ $Export\ variables$: ρ_{EtOH} $Defined\ parameters$: $\mu_{mEt}, Y_{EeSRB}, K_{S,et}, K_{SO_4}$, pH_{UL}, pH_{LL}
Acetate degradation calculator block (BACE)	$\rho_{Ac} = \frac{\mu_{maxAc}}{Y_{AaSRB}} \frac{S_{Ac}}{K_{S,Ac}+S_{Ac}} * \frac{S_{SO_4^{2-}}}{K_{SO_4^{2-}}+S_{SO_4^{2-}}} * I_{pH,aSRB}$ $I_{pH,aSRB} = \exp\left(-3\left(\frac{(pH-pH_{UL,aSRB})}{pH_{UL,aSRB}-pH_{LL,aSRB}}\right)^2\right)\Big\vert_{pH<pH_{UL,aSRB}}$ $pH = -\log\left[H_3O^+\right]$	$Import\ variable$: $S_{Ac}, S_{SO_4^{2-}}, \mathrm{T}, \mathrm{H_3O^+}$ $Export\ variable$: ρ_{Ac} $Defined\ parameters$: $\mu_{mAc}, Y_{AaSRB}, K_{S,Ac}, K_{SO_4}$, pH_{UL}, pH_{LL}

The pH was used to regulate the calculation blocks by importing the oxonium ion flow. Therefore, having the correct pH in the system is important to get a realistic simulation. The pH dependence was considered in the precipitation part of the process by adding "if" statements in the calculation blocks. The interval for Cu precipitation is between pH 0-2 and for Zn precipitation it is between 2-6. The pH is also important in the bioreactor because of the inhibitory effects of pH on the biological system. The pH was used to change the output in the calculation blocks exporting the pre-exponential factor by adding the inhibition term I_{pH}. The pH adjustments were done by adjusting H_2SO_4 in the inflow and by adding 0.01M NaOH in different parts of the system.

To avoid a trial and error approach for the pH adjustment, design specifications were added. These controls the inflow of base in the process, the base streams in the flowsheet is called "NAOH0,1" and stream "2NAOH0,1". One specification was defined to control the input of "NAOH0,1" which was added before the precipitation reactor with pH 4.5±0.2 and one design specification was used to control the inflow of stream "2NAOH0,1" which was added before

the bioreactor where the required pH is 7±0.2. The intervals were to 0.01-0.1 L min^{-1} and 0.0001-0.01 L min^{-1}, respectively.

The kinetic parameters describing this reaction rate are dependent on the system and will be different for different systems.

4.4.2 Evaluation by comparing the output to experimental data

The parameters specified in the general simulation were adjusted to fit specific experiments obtained from literature to test how well the model and simulation works. The evaluation of the precipitation part and the bioreactor were, as mentioned before, done separately because no well described literature data was found for the whole system. The method for these evaluations is described below. The inputs when evaluating the process are specified exactly as in the articles and therefore pH adjustments and design specifications are removed from the simulation.

4.4.2.1 Evaluating the Precipitation tank

In a study by Tokuda et al., (2008) metal precipitation of zinc, copper and nickel with hydrogen sulfide was examined. This study was used as a case study to evaluate the precipitation process simulation in Aspen Plus. A base case was implemented with the exact same inputs as in the literature experiments. The results were compared with the results from the simulation. There was also an investigation of how the scale up of the simulated results will affect the metal sulfide output and the reaction rate of the reaction.

The results in the article by Tokuda et al., (2008) were based on a batch reactor with constant liquid volume with a continuous gas flow of H_2S and N_2. This reactor was run at two pH stages, first pH 1.5 for 30 minutes when precipitating Cu and then pH 4.5 for 30 minutes when precipitating Zn. The gas flow was held at a constant value of 350 ml min^{-1} during the whole run. The exact conditions and kinetic data present for this reactor can be seen in Table 11. Because of the continuous gas flow and the steady state precipitation process modelled in this project, the values from literature were compared with the steady state REquil reactor in Aspen Plus and not a batch reactor. The first precipitation reactor, "PH1,5" in Aspen was compared to the first stage of the batch run and the second precipitation tank in Aspen, "PH4,5" was compared to the second stage in the batch run. The volume of the tank was recalculated to a time dependent volume. The batch was run for around 30 min for each pH stage and the total volume was 1300 ml. Therefore, the volume per hour is 2600 ml for each stage of the process. The concentration of metals is set to 100 mg l^{-1} in the continuous inflow. Only zinc and copper are included in the Aspen simulation, however the data were still be taken from the mixed system in the article.

Table 11: Experimental data from Tokuda et al., (2008) used for the evaluation of the Aspen Plus simulation.

Data from Tokuda et al., (2008)		
Process variables for the leach stream	Concentrations: $S^{t0}_{Cu^{2+}} = 100\ mg\ l^{-1} \rightarrow 0.00157\ mol\ l^{-1}$ $S^{t0}_{Zn^{2+}} = 100\ mg\ l^{-1} \rightarrow 0.00153 mol\ l^{-1}$ $S^{t0}_{SO_4^{2-}} = 0.00310\ mol\ l^{-1} \rightarrow 298\ mg\ l^{-1}$ Volumetric flow: $V = 1.3\ L\ batch\ (total\ time\ 30\ min \cdot 30\ min\ ) \rightarrow 2.6\ L\ h^{-1}$ $v_f = 2.6\ L\ h^{-1}$ Compounds: $Cu^{2+}, Zn^{2+}, SO_4^{2-} and\ H_2O$	
Process variables for the gas stream	Concentration: $S^0_{H_2S} = 5000 ppn\ v/v$ Volume flow: $v_f = 0.0058\ L\ h^{-1}$ Compounds: $H_2S\ and\ N_2$	
Reactor settings	**Precipitation tank 1 (PH1,5)** pH: 1.5 Temperature: 25^0C Purpose: Copper sulfide formation	**Precipitation tank 2 (PH4,5)** pH: 4.5 Temperature: 25^0C Purpose: Zinc sulfide formation
Kinetic Parameters $\boldsymbol{r_{Me^{2+}} = A_b * k_L\left(S^t_{Me^{2+}} + S^0_{H_2S}\right)}$ $\boldsymbol{S^0_{H_2S} = \frac{S^t_{H_2S_g} * R * T}{H_{H_2S}}}$	$A_b = 0{,}00402\ m^2$ $V = 130 * 10^4 m^3$ $k = \frac{A_b}{V} k_L = 6.71 * 10^{-4}\ s^{-1} \rightarrow$ $k_L = 1.7 * 10^{-4}\ m\ s^{-1}$ $R = 0.08205734\ l\ atm\ K^{-1}\ mol^{-1}$ $H_{H_2S} = 10.7\ atm\ l\ mol^{-1}$ $H_{CO_2} = 25.88\ atm\ l\ mol^{-1}$	$A_b = 0.00488\ m^2$ $V = 130 * 10^4 m^3$ $k = \frac{A_b}{V} k_L = 8.18 * 10^{-4} s^{-1} \rightarrow$ $k_L = 2.17 * 10^{-4} m\ s^{-1}$ $R = 0.08205734\ l\ atm\ K^{-1}\ mol^{-1}$ $H_{H_2S} = 10.7\ atm\ l\ mol^{-1}$ $H_{CO_2} = 25.88\ atm\ l\ mol^{-1}$
Precipitation efficiency	96.9% removal Time: 30.4 min	96 % (100%) Time: 30.4 min

4.4.2.2 Evaluating the Bioreactor

The parameters for the bioreactor were adjusted according to Nagpal et al., (2000) as in the model evaluation for the MATLAB simulation. The experiment was run in batch mode with a reactor volume of 3L in 30°C for 105 h. The inlet concentrations of the substrates in water were 0.0615 mol L^{-1} for ethanol and 0.0326 mol L^{-1} for sulfate in a 3L reactor. Nagpal et al., (2000) only present the amount of dissolved H_2S and not the total amount of reduced sulfur, therefore the Aspen simulation will be compared to the total reduced sulfur retrieved from the MATLAB simulation where the same values are used as in Aspen.

The amount of produced sulfur is compared between the MATLAB and the Aspen simulation by calculating the molar flow per hour for the two simulations. In MATLAB this was calculated by removing the mass transfer term from the differential equation describing sulfide formation, see Equation (4.18). This change results in a graph representing the total reduced sulfur concentration against time. The value at 105 hours was recalculated to a mole per hour basis.

In Aspen the output is presented in mole per hour and a total value was calculated by adding the different forms of sulfides together.

The total amount of H_2S in the gas phase was calculated in the same way, by removing the transfer term from the differential equation describing the sulfide amount in gas phase, se Equation (4.20). This value was used to determine the percentage of H_2S that transfer to the gas phase. This value is given as an input to the separation block used in Aspen to simulate the gas/liquid mass transfer.

A CSTR reactor was also evaluated with these experimental data. The CSTR was set to conditions that make it converge towards a Batch reactor, the through-flow was specified to get a retention time of 105 h and a volume of 2.1 L. These values will be compared to the values retrieved from the simulated Batch reactor. See Table 12 for a summary of the parameters and variables used in the evaluation.

Table 12: Data from Nagpal et al., (2000) used for the evaluation of the bioreactor Aspen Plus simulation.

Data from Nagpal et al., (2000)	
Process variables for substrate process stream	Concentration: $S_{EtOH} = 0.0615\ mol\ L^{-1}$ $S_{SO_4^{2-}} = 0.0326\ mol\ L^{-1}$ $\rightarrow COD/SO_4^{2-}\ ratio = 0.5$ Volume flow: $v_f = 1\ L\ h^{-1}$ Compounds: $Ethanol, SO_4^{2-} and\ H_2O$
Reactor settings	Volume: 3 L Temperature: 30ºC Batch time: 105 h pH: 7
Kinetic parameters $\boldsymbol{\rho_{EtOH} = \frac{\mu_{mEt}}{Y_{EeSRB}} \frac{S_{EtOH}}{K_{S,EtOH}+S_{EtOH}} * \frac{S_{so_4^{2-}}}{K_{so_4^{2-}}+S_{so_4^{2-}}} *}$ $\boldsymbol{I_{pH,eSRB}}$ $\boldsymbol{I_{pH,eSRB} = \frac{1+2*10^{0.5(pH_{LL,Et}-pH_{UL,Et})}}{1+10^{(pH-pH_{UL,Et})}+10^{(pH_{LL,Et}-pH)}}}$	$\mu_{maxEt} = 0.013\ h^{-1}$ $Y_{EeSRB} = 0.05\ g\ g^{-1}$ $K_{S,Et} = 0.045$ mol/l $K_{S,SO_4^{2-}} = 0.085$ mol/l $pH_{LL,Ac} = 1.3$

4.4.3 Sensitivity analysis for the Aspen Plus simulation

A sensitivity analysis was performed on the separate simulation scripts by altering variables and observing output changes. The values were increased by 10% for the precipitation simulation and both 1 and 10% for the bioreactor simulation. The 1% change was done to be able to compare the results with the MATLAB sensitivity analysis for the bioreactor. Otherwise 10% was chosen to see how the simulation reacts to a larger change, since it is desirable to be able to scale up the process in the future.

The sensitivity analysis was both performed by manually increasing one variable at the time, keeping the other values constant and by using the built in sensitivity tool in Aspen Plus. Both versions were performed to test the Aspen plus sensitivity analysis function. The variables

tested were concentrations and flows. The kinetic parameters were also included in this analysis; however, these were collectively evaluated by changing the export variable manually. To be able to do this, the calculation blocks were erased and the values were manually entered to the reactor block and the reactions kinetics instead.

4.4.4 Full model simulation

When the two simulation parts had been evaluated separately, the whole process was simulated. To perform the process merge, the inputs and outputs from the two separate simulations needed to match. The precipitation part was kept constant while the H_2S output from the bioreactor was scaled to match the H_2S input to the precipitation from literature.

The substrate stream was changed to consist of 95% ethanol and 5% water. Extra sulfate was added in a separate stream to meet the hydrogen sulfide demand from the precipitation tanks. Separation steps was added to split the solid substream from the rest of the stream before it was circulated to the bioreactor. There were also separation steps added to separate water and to purge part of the liquid stream to enable recirculation of H_2S without getting a liquid accumulation.

One extra batch reactor was added for the degradation of acetate and together with this block an acetate degradation rate calculation block was added. The parameters used for this block were the same used in MATLAB.

The full simulation was evaluated with a case study with the same properties as the precipitation evaluation. This case study was only used to evaluate if the model was working or not.

4.4.5 Assumptions

Assumptions that were made during the Aspen simulation are that the biomass was assumed to work as a chemical catalyst and the biomass growth is not included in the simulation. The model also included only two metals and impurities are therefore not taken into consideration. It was further assumed that the precipitation occurs at the right pH, no precipitation will occur at other pH for each substance.

5 Results and discussion

In this part, the results will be presented and discussed. The results from the MATLAB simulation will be presented first, followed by the results from Aspen Plus.

5.1 MATLAB model

The MATLAB simulation results of the bioreactor will be presented in this part. The results include comparison with literature data, sensitivity analysis, a fitting function for parameter values and a discussion of inhibition terms that affect the model.

5.1.1 General model results

The model simulation in MATLAB without any adaptation can be seen in Figure 7. The code for the simulation is presented in Appendix A. Some parameter values that were found in the articles Nagpal et al. (2000) and Moosa et al. (2002) were used and other values were estimated to obtain a working model simulation. The model in the figure is simulated in batch mode, which means that the inflow, q_{in}, is set to zero. The output result is behaving as expected, the amount of reduced sulfur is constantly increasing over time. Ethanol and sulfate concentration are decreasing, while biomass on both ethanol and acetate is increasing. The acetate concentration is increasing fast in the beginning and then slows down due to the formation of carbon dioxide. The H_2S gas is constantly increasing as well as the formation of CO_2 in gas phase. The number of dissolved ions is also increasing over time. In the graph in the lower right corner the relationship between reduced sulfur and H_2S gas can be seen. It can be observed that more of the reduced sulfur is in the liquid phase and that not all of this is transferred into the gas phase.

The figure show that the model simulation works and that the model has been correctly formulated in MATLAB. It is however important to calibrate the model to experimental values to investigate the reliability of the model. The calibration is presented in the next section.

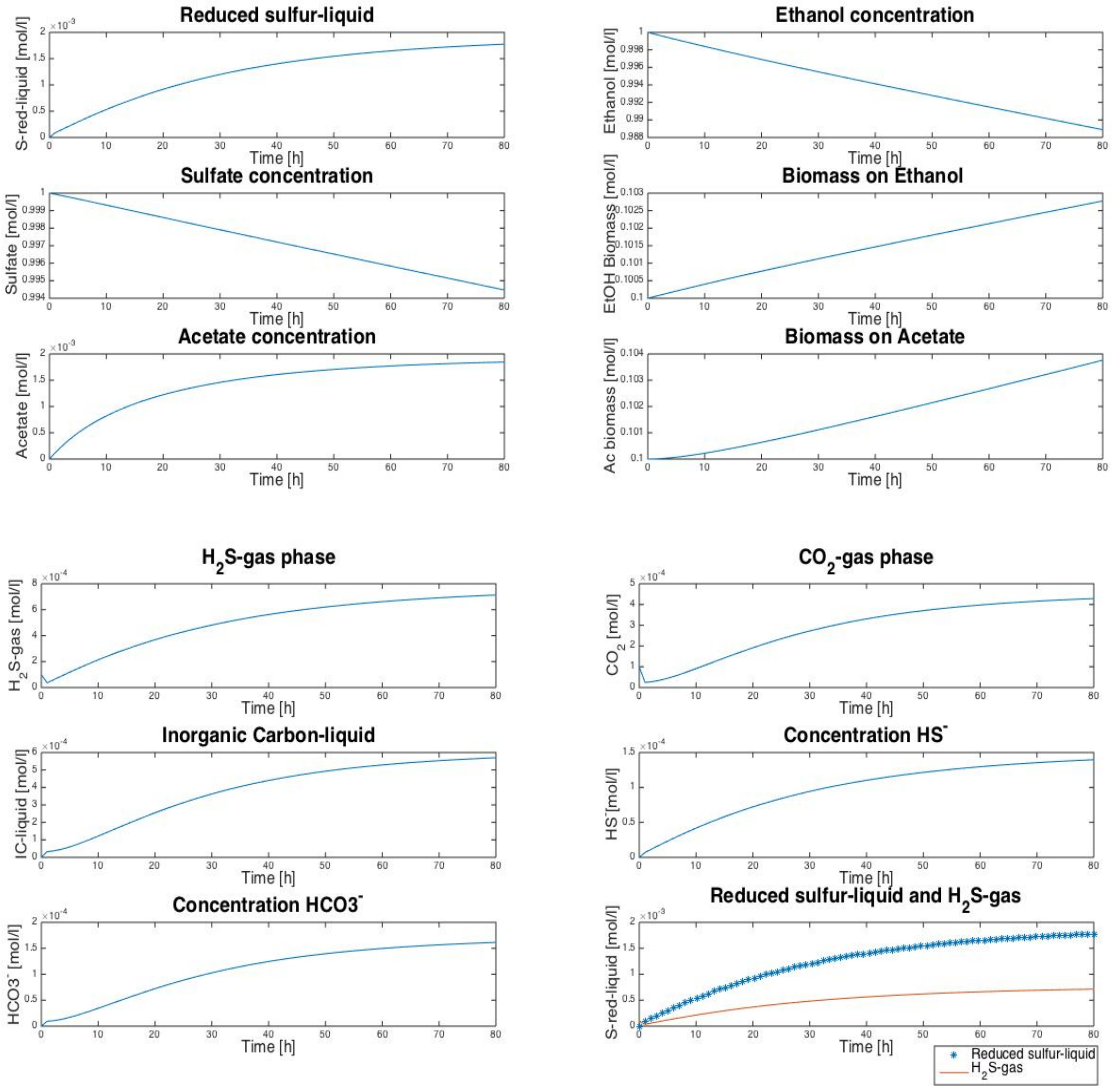

Figure 7: General model describing ethanol and sulfate uptake, production of biomass on both acetate and ethanol, acetate formation and uptake, production of hydrogen sulfide and carbon dioxide and their ion states. The graph also present the relation between reduced sulfur in liquid phase and H_2S in gas phase.

5.1.2 Comparison to literature data

Literature data was used to compare the model simulation results, since no experimental values, within the METGROW+ project were yet available. Two different articles were used. It was not possible to find articles that used both ethanol utilizing SRB and acetate utilizing SRB in the same experiment. Therefore, the article by Nagpal et al. (2000) was applied that used ethanol and the model was adapted to these data values. This will be referred to as literature data 1. When this was done, another article Moosa et al. (2002) was found that used acetate and the model was instead adapted to this separately. The second adaptation will be referred to as literature data 2. This means that an optimal fit for the entire model was not possible to conduct and the model was instead calibrated in two different steps.

5.1.2.1 Literature data 1

The adaptation to ethanol SRB with data from Nagpal et al. (2000) can be seen in Figure 8. The model fits the data points quite well. The parameter for the bacterial decay was adjusted manually to fit the data points. All parameter values are otherwise taken from the experiments done in the articles. The only thing that was not stated in the article was the liquid-gas ratio used, only the total volume of the system was given. This meant that the ratio had to be estimated in the model, which can result in a slightly different result than the actual outcome.

When investigating the outputs from the model it corresponds very well with the data points and the result is also expected. Ethanol and sulfate are consumed to produce acetate, biomass and hydrogen sulfide. No formation of carbon dioxide occurs because there is no utilization of acetate and it is therefore not included in the model. The article does not measure the amount of H_2S in gas phase and therefore this is not presented in these graphs.

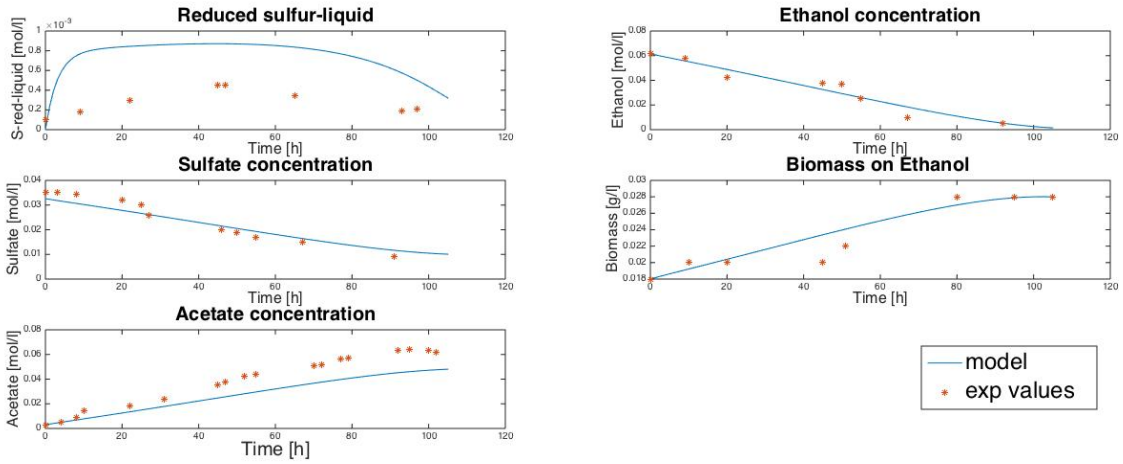

Figure 8: Model adaptation to literature data from Nagpal et al. (2000) showing the reduced sulfur in liquid phase, ethanol and sulfate uptake, biomass formation and acetate production.

The simulated values for the product formation of acetate is slightly lower than the data points from literature. A reason for this could be that the literature data uses yeast extract to build the biomass, while the model uses ethanol for biomass formation. The actetate formed in the model will be lower since some of the ethanol has already been used for biomass formation. The model gives instead higher values than the data points for the production of H_2S in liquid phase. The model seems to overestimate or underestimate the results when it comes to the modelling of the different product formations, since both acetate and H_2S in liquid are products. The modelling of the uptake of ethanol and sulfate however works well, and correspond well to the literature data. A possible explanation for the high values of the H_2S in liquid form given by the model could be the mass transfer. Comparison between the literature data and the model indicate that the model gives a too low mass transfer from liquid to gas phase. This means that too much of the produced H_2S is in the liquid phase and does not transfer into the gas phase. An explanation for this could be that measured experimental values according to the articles are a bit uncertain. The article explains the reason as a difficulty in measuring the volatile H_2S in liquid phase because a lot of the substance evidently went into gas phase. This implies that the mass transfer values held from the articles that was used in the model is not completely correct and that the

mass transfer from liquid to gas is larger than expected. It would be desirable to do experiments on the mass transfer to conclude the different rates. Another reason for the overestimation of the reduced sulfur in liquid from the model could be that the upper limit in the pH inhibition term is not correct. If the limit would be higher, it would give an active inhibition term and therefore decrease the amount of reduced sulfur in liquid.

It could be suggested that the difference between the model and the literature data is a combination between the too low mass transfer in the model and the problem in measuring the H_2S in liquid form that was encountered in the article. In the model, the mass transfer parameters given in the article are used, so it would reasonably not be a too large difference even if the simulated results differ from the results in the article. When the k_La value is changed in the model a somewhat better result is given, but the model still gives a too high result.

5.1.2.2 Literature data 2

The second article used for the comparison of the model was Moosa et al. (2002). The article used complicated and not fully presented data, where the experiments were performed as a mix between batch and continuous at different dilution rates. The article tested different dilution rates and let each of the tests reach steady state before changing to the next dilution rate. The model needed to be adapted according to this process set up. The change in dilution rates were implemented in the model by adding several ode solvers in the solver function file, as presented in the method. The parameters given in Moosa et al. (2002) were also adapted in the parameter script, but mass transfer parameters were taken from the Nagpal et al. (2000) since this was not given in Moosa et al. (2002). The liquid-gas ratio was also estimated in this adaptation, since it was not given in the article. All units were recalculated to fit the model. The results can be seen in Figure 9.

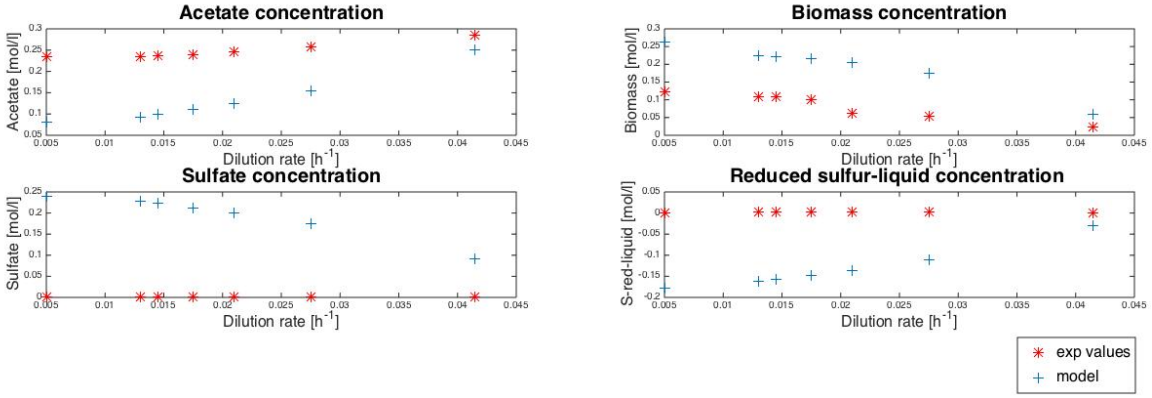

Figure 9: Model adaptation to literature data given in Moosa et al. (2002). The model does not correspond well to the data points, acetate concentration, biomass concentration, sulfate concentration and reduced sulfur in liquid phase.

The model does not correspond well to the literature data. Several alterations to the model were tested to try improving the fit, without success. There are several possible explanations to the misfit of the model and data from the Moosa et al. (2002) article. There could be miscalculations of the units, both when interpreting the data points from the article, but also when recalculating the data points into units used in the model. Another reason could be incorrect data in the article.

The fact that the mass transfer parameters were taken from another article could affect the model, but no improvements were held when taking away the mass transfer rates or changing the values. The mass transfer has no impact on the biomass production and this graph does still not correspond to the literature data. The different inhibition equations could also influence the model, but when trying both different expressions for the sulfide inhibition as well as silencing both the sulfide inhibition and pH inhibition, no improvements in the model were held.

The most probable explanation for the misfit between the model and the literature data is an inaccuracy in the model which results in an over- or underestimation of the results. This difference between model results and data points could be caused by the dynamic modelling at different dilution rates. Even if a new y0 vector is created in every new ode solver, which gives a new starting point for the solver, the same model function file with the same parameters is used in the solver function file. The shape of the biomass graph is also very dependent on the inlet concentration of biomass. First, the value was set to the first value given in the article. This is however at steady state which does not correspond to the initial concentration of biomass. The initial concentration of biomass is not given in the article and the value was therefore changed to a guessed lower value. It is reasonable to assume that it should be a lower value because the bioreactor is inoculated with bacterial culture and then run to obtain bacterial growth. It reaches a steady state level after a certain amount of time, which is the value given in the literature. The shape became better, but still changed a lot when altering the initial concentration at different low values.

To obtain a better fit from this article additional data would be needed, like the actual initial concentration of biomass. It would also be necessary to evolve the model function file and create different model function files for each dilution rate. All ode solvers would have to be connected to different model function files with given initial concentration for each compound at different dilution rates. Even if the dynamic modelling does not work, the first point of the model and the data should actually correspond. This because these initial values are given in the article and the modelling should be accurate for the first loop in the solver. It can be seen that this is not the case, so there have to be an additional error in either the data or the model formulation.

5.1.3 Sensitivity analysis

A manual sensitivity analysis as well as a MATLAB sensitivity analysis was conducted by changing one parameter or variable at the time by 1 %. The parameters are describing the system like the kinetic parameter K_s, while variables are set by the experimental set up design like volume, pH and temperature. The change in maximum production of reduced sulfur in liquid phase and H_2S gas respectively was analyzed. The adapted version of the model where parameter values from Nagpal et al. (2000) had been implemented were used. The values were normalized by Equation (5.1), which gave a percentage value change.

$$\frac{start\ value - new\ value}{start\ value} \tag{5.1}$$

In Figure 10 the pH has a large impact on the production of reduced sulfur. This is reasonable since the equation for low pH inhibition is exponential, which means that a small change in this variable value will result in a large change in the output value. Figure 10 also shows that other

parameters affecting the model are the maximum specific growth rate (μ_{max}) and ethanol yield on biomass (Y_{EeSRB}). Variables that can be manually chosen that have a large impact on the system are the temperature, the liquid volume and the gas flow of stripping gas, N_2. This seems reasonable since all these parameters and variables affect the system and are linked to production of the product reduced sulfur.

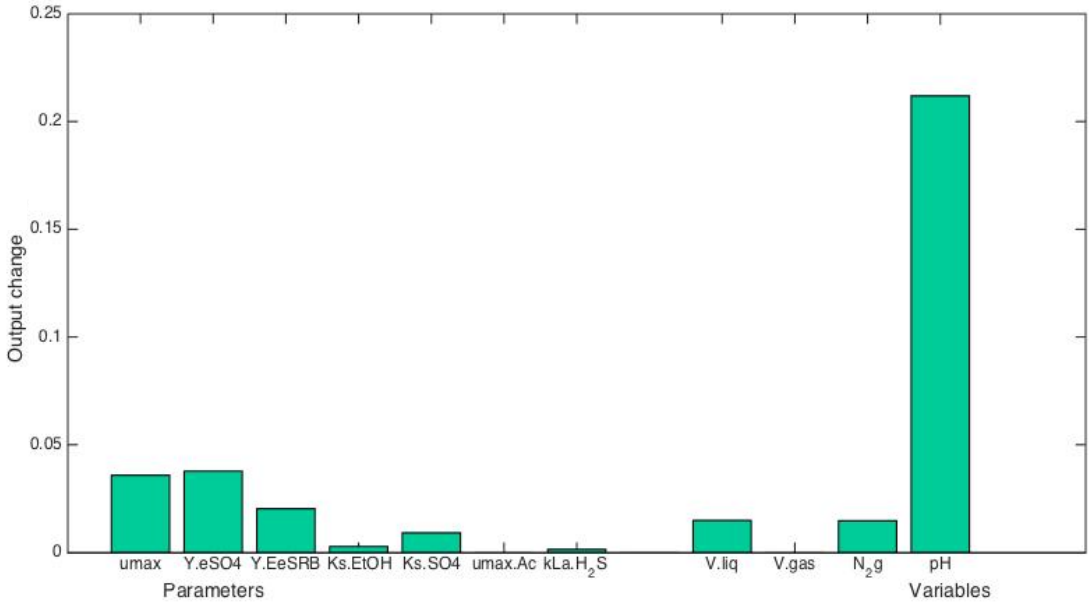

Figure 10: MATLAB sensitivity analysis for reduced sulfur-liquid, 1 % value change of chosen parameters (left) and variables (right).

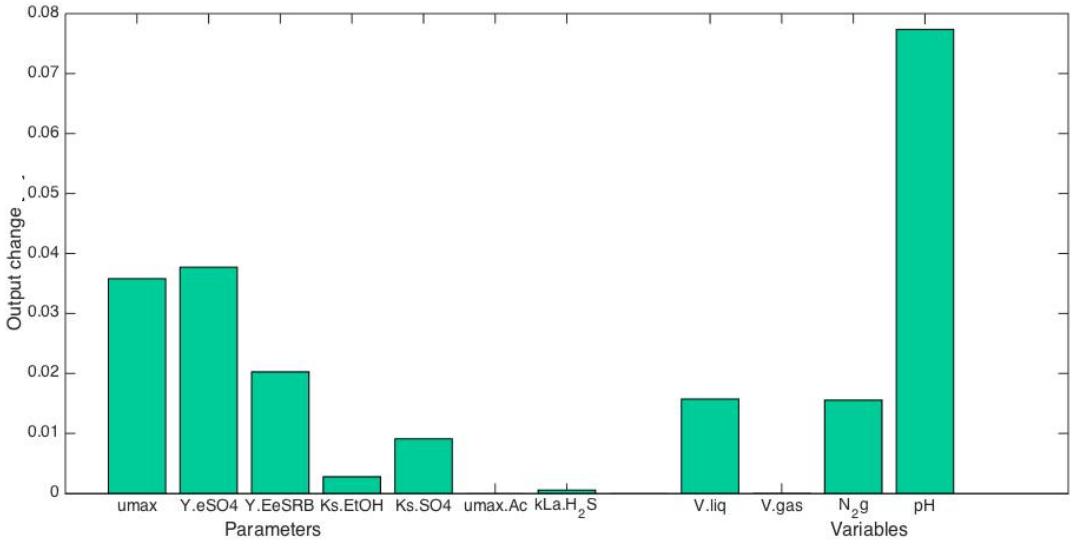

Figure 11: MATLAB sensitivity analysis for H_2S gas, 1 % value change of chosen parameters (left) and variables (right).

Comparing the sensitivity analysis for the reduced sulfur in liquid phase with the sensitivity analysis for the H_2S gas production, many differences can be seen in Figure 11. Here, the pH is still the variable that affects the system the most, but not as dominant as for the reduced sulfur in liquid phase. An explanation for this could be that the gas production is dependent on the

mass transfer rate and the production rate of reduced sulfur. This means that there are more parameters that together affects the production of H_2S gas then there is to produce reduced sulfur and therefore will the effect of pH decrease. The parameters that have a large effect on the H_2S gas differs slightly from the production of reduced sulfur. The maximum specific growth rate, μ_{max}, and ethanol yield on biomass are still two parameters that have a large impact. The variable temperature has however not as much impact anymore, probably due to the same reason as for the impact from pH. The liquid volume and the gas flow of the stripping gas N_2 still have a large impact on the system.

One parameter that was supposed to have no impact on the system was tested to verify that this actually was the case. The parameter chosen for this was the maximum specific growth rate for aSRB, $\mu_{max,Ac}$. Since there will be no biomass growing on acetate, this parameter should reasonably not affect the system at all, when using the model that has been adapted to literature values.

5.1.3.1 Testing the sensitivity analysis results

When analyzing the result held from the adaptation to the Nagpal et al. (2000) article it can be seen that the amount of reduced sulfur in liquid phase is decreasing at the end of the simulation. The reason for the decrease of hydrogen sulfide in the end should be the mass transfer from liquid to gas. If the mass transfer rate is removed from the model, the H_2S in liquid phase is constantly increasing, which seems reasonable because it would mean that no reduced sulfur is moving into the gaseous phase and everything is staying in the liquid phase. The mass transfer rate was only removed from the model dynamic mass balances according to Equation (4.18) to ensure that it was defined correctly and then added back to the model.

A reason for the high model results of the reduced sulfur in liquid phase could be the inhibition terms. The hydrogen sulfide inhibition equation should decrease the amount of produced sulfide.

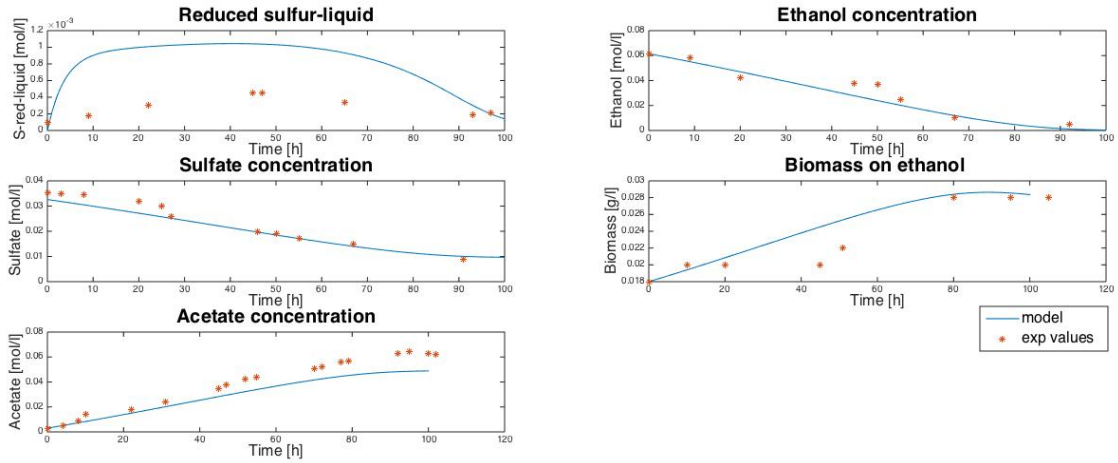

Figure 12 Model adaptation to Nagpal et al. (2000) with removed Hydrogen sulfide inhibition equation, giving higher model result of reduced sulfur in liquid phase and better fit to acetate production.

When the sulfide inhibition equation is removed from the model the results changes and can be seen in Figure 12 above. The model gives a better fit to the acetate concentration. The inhibition equation is included in the rate and will affect the product formation and when this is deleted it will result in a larger amount of formed product. The model also gives an even higher H_2S liquid

concentration as expected. This indicate that the equation for the inhibition from hydrogen sulfide is not completely describing reality. The model would require a better adapted inhibition equation in the future to obtain a better fit to the data points. It would be desirable to perform experiments in which the inhibition is tested on the exact experimental set up. It would also be necessary to perform experiments to determine the mass transfer parameters.

The effect from the pH could also be examined. The modelling of the pH is not completely accurate since a fixed pH is used. It is however possible to manually change the pH to see what effect this have on the model results. The low pH inhibition expression will not have any effect on the model if the pH is higher than the upper limit, which here is set to be 6.75. In the Nagpal et al. (2000) article a pH of 7.3 is used and this means that no pH inhibition occurs. When manually changing the pH the effect from the pH equation can be seen and is presented in Figure 13 where the pH is changed to 5.

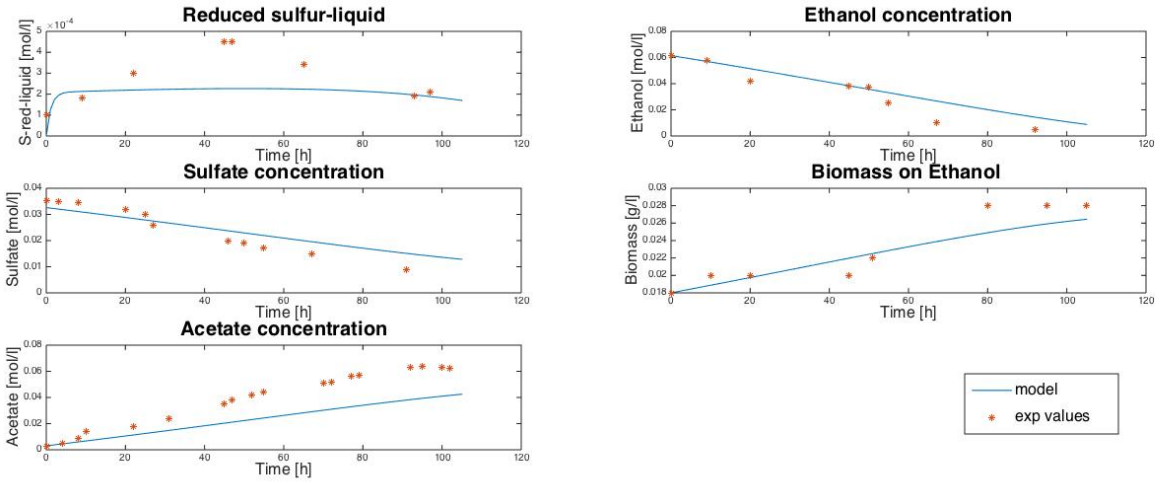

Figure 13: Manually change of pH value in the model to pH 5. This gives model with lower amount of produced reduced sulfur and biomass.

It is clear from Figure 13 that the pH has a large impact on the system. The produced reduced sulfur in liquid phase is decreased drastically and is now even lower than the literature values. The model for the biomass production decreases as well as the acetate production. This result is expected since a decreased pH should have an effect on the system in that sense that the growth of the bacteria should decrease as well as the production of product. This since the pH decrease results in a higher amount of un-dissociated H_2S that can cross the cell membrane and lower the pH inside the cell. As explained in the theory this will mean that the cell will have to actively transport the H_2S out of the cell and this requires energy that otherwise could have been spent on growth and product formation.

To investigate the model further, the pH is also set to a lower value than the lower limit. The lower limit is where the bacteria is completely inhibited by the pH. The result from setting the pH value to 1, which is lower than the lower limit 1.3 can be seen in Figure 14.

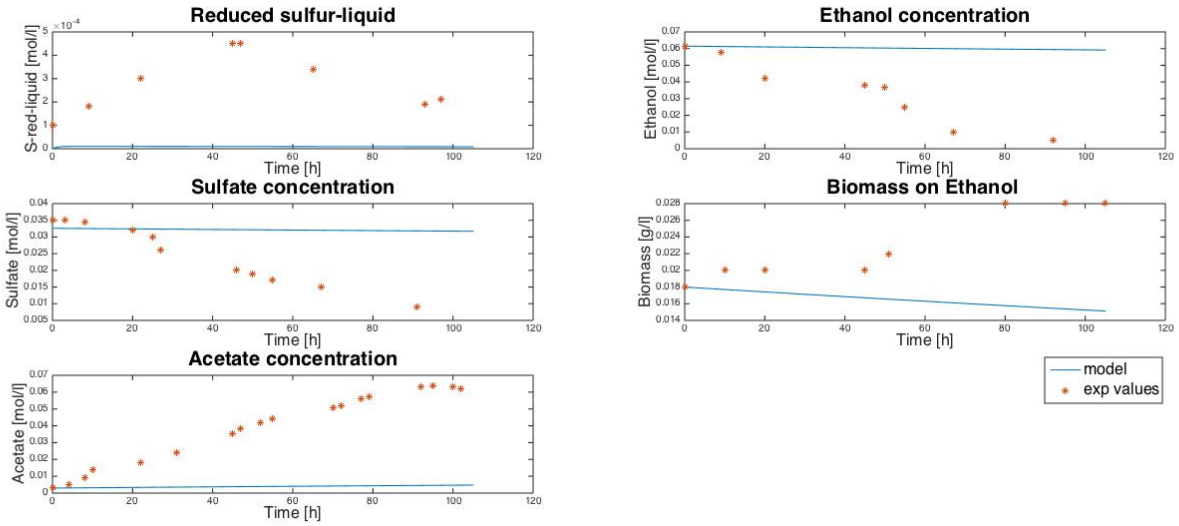

Figure 14: Complete pH inhibition when setting the pH below the lower limit for the pH equation.

Here, basically nothing happens in the model and this is an expected result. The biomass decreases with the decay rate, no ethanol or sulfate is utilized, the values are kept at the initial values. No product formation for reduced sulfur in liquid phase or acetate occurs which is also expected. This shows that the equation for the pH inhibition works in the model and describes what is expected to take place.

5.1.4 Parameter fitting

The fitting analysis was conducted on the literature data from Nagpal et al. (2000). The model already corresponded relatively well to the data, since almost all kinetic parameters were given in the article because the article also had modeled the experimental results. The modeling in the article was not exactly the same as this model so therefore it was interesting to compare the data with the developed model in this report. The fitting was performed on different outputs and with different parameters altered. One example is shown in Figure 15 where the parameter K_s for ethanol was altered to fit the model to the data points of reduced sulfur in liquid phase. The *lsqcurvefit* command is providing a new parameter value, which here became 0.02. This should be compared with the given parameter value in the article which was 0.0045. It can be seen that the values differ a lot. In the figure, it can also be seen that when changing the parameter value to fit the model to the data points for reduced sulfur in liquid, the model for the biomass growth does not correspond well anymore. Systematically testing of different parameter alterations and output fittings indicated that a relatively good estimation of the parameter value is needed, otherwise the new parameter value will not correspond to the correct value at all and have a large confidence interval. It is further difficult to fit more than one parameter at a time to outputs. The correlation between the parameters seems to act random and takes the best value, without it being a reasonable value. An example of a clear false result is a negative value of the decay coefficient, which should not be able to become negative. It is further difficult to adapt a parameter to several different outputs, it did not give a better result. The new parameter value differed a lot from the already given value from literature when adapting it to several outputs.

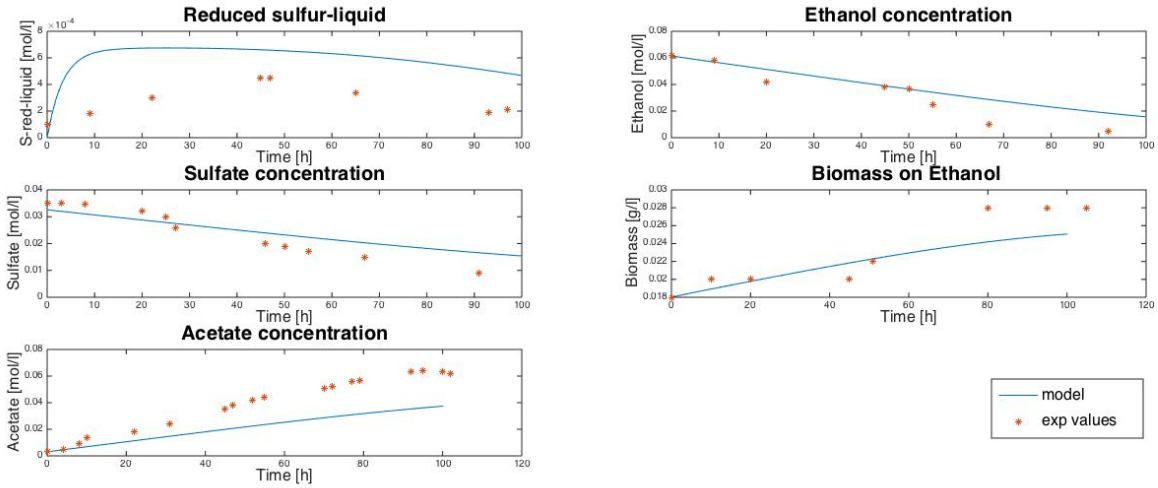

Figure 15: Parameter fitting of model to literature data in Nagpal et al. (2000). Ks for Ethanol fitted to reduced sulfur in liquid phase.

Since the difference between the model and literature data for Moosa et al. (2002) was large, it is not reasonable to try a fitting file for adaptation of parameter values. From the fitting file for the Nagpal et al. (2000) article it is concluded that the fitting works fine only when the model and data points are close and when the estimated parameter value is close to the correct value. Therefore, no parameter fitting was performed on the Moosa et al. (2002) article.

5.1.5 Inhibition terms

5.1.5.1 pH

The two equations for high/low pH inhibition and low pH inhibition were tested in the model. It was difficult to find parameter values for upper and lower limits. The article by Sharma et al. (2014) used the low pH inhibition equation and had values for sulfate reducing bacteria. This article was used even if it used sludge and not ethanol or acetate as carbon source. This meant that only the low pH inhibition equation could be used in the end, since the definitions of upper and lower limits differs from the two equations. It is assumed that the SRB are not significantly affected by a high pH, because the H_2S should be in dissociated form at high pH values. The dissociated form, HS^- and S^{2-} cannot cross the cell membrane and cause inhibition to the bacterial growth. The lower limit was set to the same value for ethanol and acetate respectively and the same was the case for the upper limit. This because no specific value was found for the different substrates, even if the different bacteria presumably have a slightly different pH optimum. This is something that can be investigated in future works.

5.1.5.2 Hydrogen sulfide

Different equations for hydrogen sulfide inhibition was tested in the model. It was however difficult to find a working equation. Many equations cannot handle high hydrogen sulfide concentrations, which is the case in this model. The equation that worked best was the non-competitive inhibition equation. The inhibition seems to work relatively well in the comparison of the model and Nagpal et al. (2000) article. Model values for biomass, ethanol and sulfate consumption as well as the production of reduced sulfur are dependent of the inhibition term. If the term is deleted from the model would these model values increase and not match the

literature data in the same extent anymore. It would however be desirable to perform experimental tests to find a more suitable equation describing the hydrogen sulfide inhibition for this process that does not only correspond to the literature data used and instead describes how the hydrogen sulfide affects the ethanol utilizing bacteria and the acetate utilizing bacteria. The different bacteria are probably affected by the hydrogen sulfide differently; some can be more sensitive than others.

5.1.5.3 Other inhibition factors

Substrate inhibition and metal/metal sulfide inhibition were not included in this model due to a lack of time. It is possible that the model would fit the data even better if this was implemented. The process of metal sulfide precipitation includes recirculation of liquids into the bioreactor. It is assumed that all metal ions have precipitated into metal sulfides and then been separated from the stream. If there is an error in the process in which not all metals can precipitate this would lead to recirculation of metal ions to the bioreactor. Here there will be a large amount of hydrogen sulfide produced by the SRB accessible and the metal ions will precipitate. These metal sulfides can inhibit the SRB and create problems in the process. It would therefore be interesting to investigate a possible inhibition term that can handle and model the issue. This could be added in future works. Another thing that has not been examined in this report is the impact from oxygen on the anaerobic SRB, ideal conditions with complete anaerobic environment for the bacteria was assumed.

5.2 Aspen Plus simulation results and discussion

This section will start by separately evaluating the precipitation tank and the bioreactor. There will be case studies with data from literature performed on each part together with sensitivity analyses for some of the variables and parameters similar to the ones made to the MATLAB simulations. All the blocks in the simulation is run at 1 bar and 25°C except for the bioreactor where 30°C was used.

The model developed in this project is used to determine the rate of the reactions in the reactor blocks. The reactions and the equations for these rates are shown in the previous section. The kinetic parameters used for the precipitation tank are based on the data from Tukuda et al,. (2008) and the kinetic data for the bioreactor is based on Nagpal el a., (2000) and the optimal parameters found in MATLAB.

5.2.1 Results from the precipitation simulation from Aspen Plus

The chosen block for the solid metal sulfide formation was an equilibrium reactor block (REquil). The separation of the solid metal sulfides with the liquid stream was done in a centrifuge adjusted with fraction “solids in solid outlet” of 0.9999 and a fraction “liquid in solid outlet” of 0.00001. This gave a high separation of the solid metal sulfides from the liquid stream. The data for the calculation blocks are imported from the reactor inlet streams. Both reactors have two inlet streams, one with the metal ions and one containing hydrogen sulfide and to accurately import data to the calculator blocks, mixer blocks are added before the unit blocks representing the second reactor.

The reaction specified in these blocks are dependent on a mole rate. The limiting reactant decide the extent of the reaction and the reaction rate in mol h^{-1} from the calculator blocks determine

the rate. The reactions are chosen to be fixed extent for this to work, otherwise Aspen Plus calculates the reaction extent based on temperature and Gibbs free energy of the reaction.

5.2.1.1 Evaluation of precipitation simulation based on literature data

The evaluation of the precipitation simulation is, as mentioned in the Method, based on a study by Tokuda et al. (2008). The variables and parameters chosen was entirely based on the inlet data from the study and therefore no pH adjustments were made and the gas from the first reactor block was transferred to the second block. The flowchart for the process in Aspen Plus is shown in Figure 16.

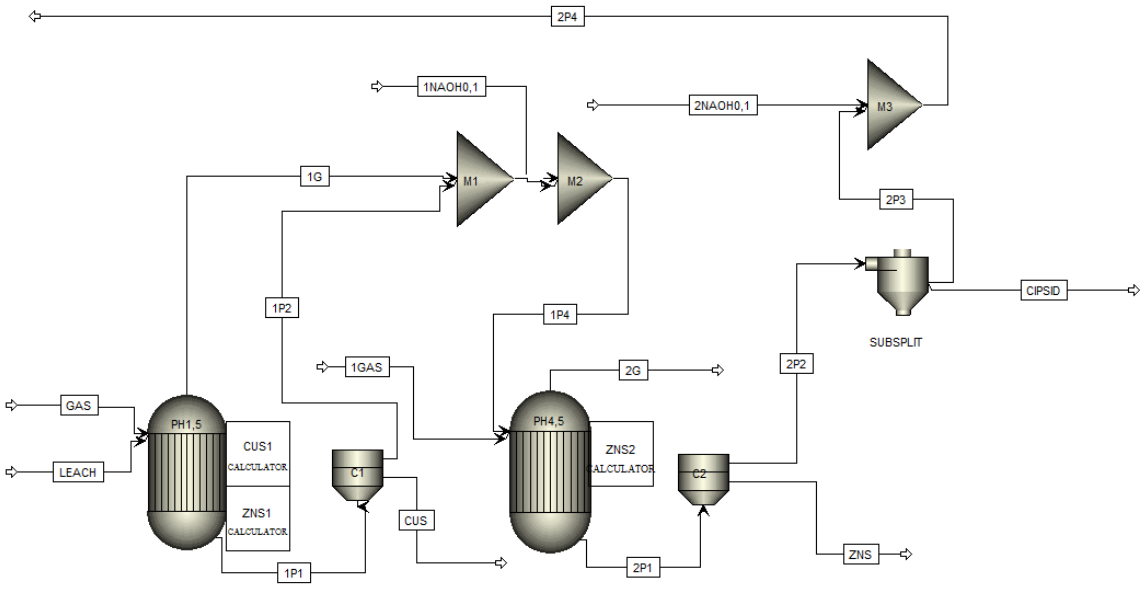

Figure 16: The process flowsheet used for the case study with data from Tokuda et al., (2008).

The results from the Aspen simulation compared with the experimental results from the article can be seen in Figure 17. Note that the removal rate is obtained from the literature results and the formation rate is obtained from the Aspen results. These results were changed to a molar basis to become directly comparable.

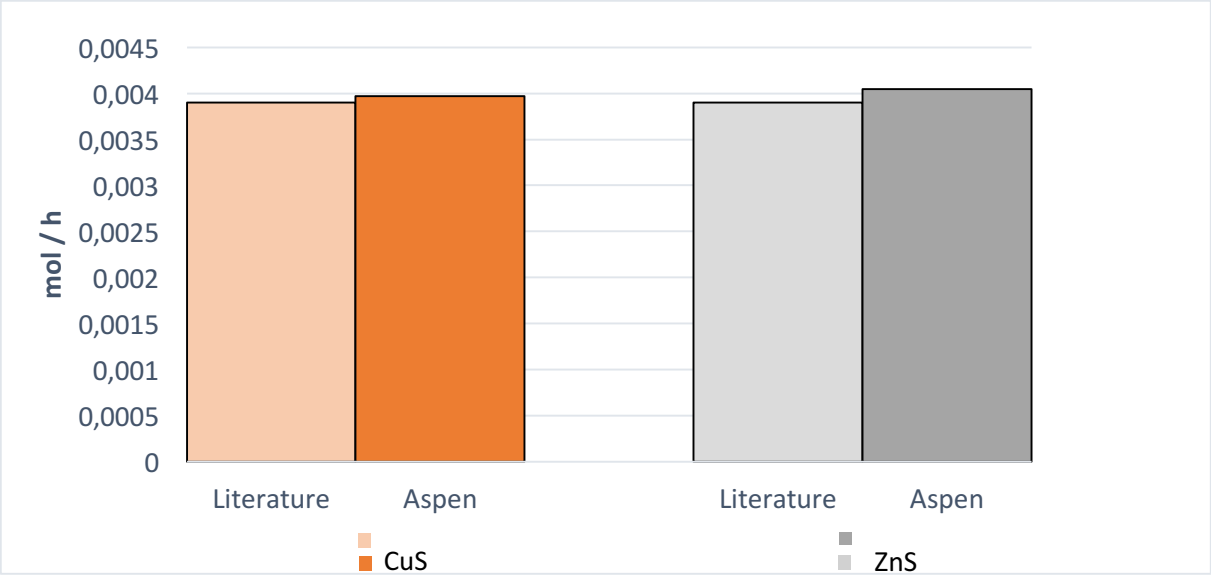

Figure 17: Comparison of the literature and Aspen Plus results with the same process variables.

The results from this simulation is close but slightly higher than the experimental results from literature. The difference when comparing the molar formation rate for the metal sulfides are 3% for CuS and 4% for ZnS. The removal efficiency in the Aspen simulation is 99% for both metal ions while the removal rates were around 96% in the literature experiments. These numbers indicate a well working simulation and a correctly implemented model. The reaction rate for the zinc sulfide formation is due to a higher concentration of reactants as an inlet to the zinc calculator block. The gas stream entering the blocks have the same characteristics. A small amount of the liquid gets separated together with the CuS. Therefore, the concentration of Zn^{2+} is slightly increased, leading to a higher reaction rate.

The model implementation can only be said to work with this exact system with certainty. The mass transfer rate is dependent on the mass transfer coefficient k_L and the gas-liquid interface area, a. These values are fixed in this model, which leads to an inflexible simulation. To be able to use this simulation for other volumetric flows in Aspen Plus an upscale of the process is needed.

5.2.1.2 Scaling up the precipitation tanks

As mentioned in the previous paragraph, the fact that k_L and a are fixed together with the fact that no volumes or retention times can be added to the REquil block is a drawback. This is shown when increasing the volumetric inflows for both the leach and the gas stream. There is no increase in product flow with this adjustment and the system is shown not to react to a scale up. This is because the mass-transfer rate, which is translated as the reaction rate, only depends on the concentration of reactants and not the volumetric flow. If a volumetric adjustment term is added to the mass transfer rate, then a scale up is possible.

Equation (5.2) shows the case where the rate is in molar flow per hour and in Equation (5.3) the rate is in molar concentration per hour, the second equation is the one presented in literature. Equation (5.2) can only be used if the volumes are specified as in the study by Tokuda et al., (2008). Equation (5.3) considers the concentration instead of the molar flow but the units do

not correspond to those describing the reaction rate in Aspen Plus and this equation can therefore not be used.

$$r_{MeS} = -A_b * k_L\left(S^t_{Me^{2+}} + S^0_{H_2S}\right) \qquad \frac{mole}{hr} \qquad (5.2)$$

$$r_{MeS} = -\frac{A_b}{V_{from\ article}} * k_L\left(S^t_{Me^{2+}} + S^0_{H_2S}\right) \qquad \frac{\frac{mole}{lL}}{hr} \qquad (5.3)$$

A mathematical relationship with the correct unit for describing the reaction rate in Aspen Plus is possible by adding a volumetric relationship to the reaction rate from Equation (5.3). This results in a linear scale up. Because there are no volumes specified in the REquil block used in Aspen Plus, volumetric flows are imported to the calculation blocks instead, see Equation (5.4).

$$r_{MeS} = -\frac{A_b}{\boldsymbol{v_{from\ article}}} * k_L\left(S^t_{Me^{2+}} + S^0_{H_2S}\right) * \boldsymbol{v_{new}} \qquad \frac{mole}{hr} \qquad (5.4)$$

The results from when Equation (5.4) is implemented in the calculator blocks and different flows are used in the leach and gas stream is shown in Figure 18.

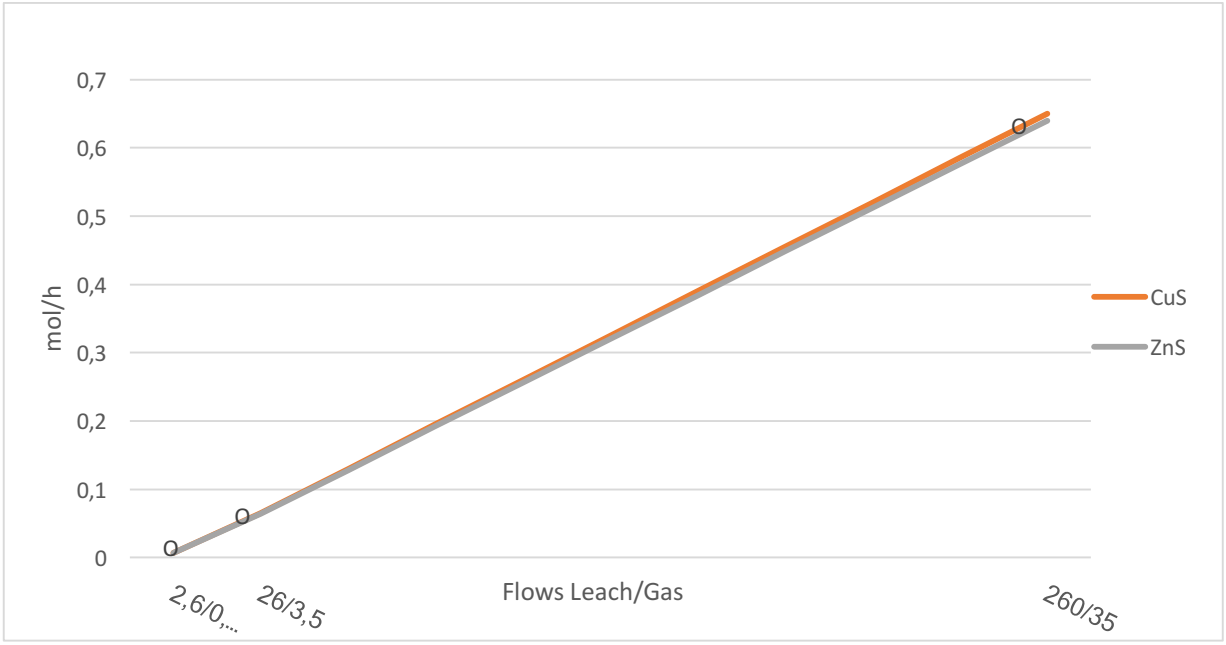

Figure 18: The output from the scale up adjustments.

When observing the results from Figure 18 it can be seen that the linear scale up worked for the precipitation simulation. The scale up only works if both the leach flow and gas flow is increased with the same factor.

In reality however, a scale up is not necessarily linear. Experiments would be needed to investigate how a scale up would look for this system. A better prediction could be done if more information was known about the tank. The mass transfer coefficient, k_L can be estimated using impeller type, height to width ratio of the tank, number of impellers etc. In the experiment by Tokuda et al., (2008) the reaction rate was used to calculate the k_L value but experiments are needed to do this calculation. Because of the novelty of this model development and lack of

experimental results, the linear scale up is considered satisfactory. The model with the scale-up adjustment is the one used for the complete model.

5.2.1.3 Sensitivity analysis on the precipitation simulation

The results from the sensitivity analysis are shown in Figure 19. The outputs tested in this sensitivity analysis are the concentrations of CuS and ZnS on the simulation where the scale-up term was added. When parameters and variables concerning copper are changed, CuS is the output and the same principle goes for ZnS. The change in copper is marked by orange and the changes in zinc is marked by grey in Figure 19.

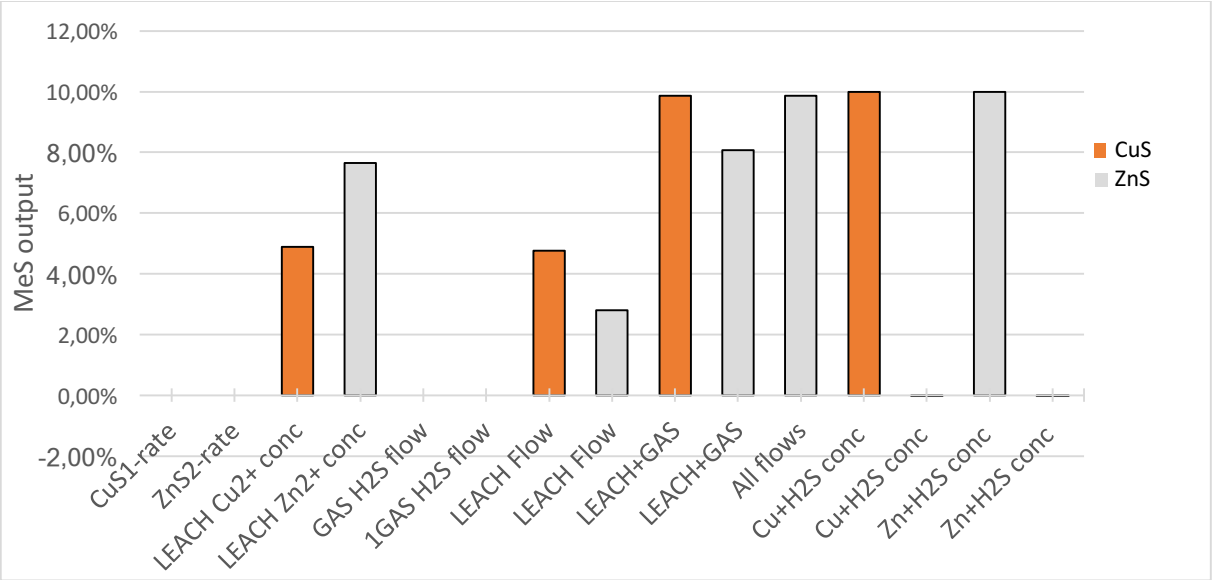

Figure 19: Sensitivity analysis for the precipitation tank with both Cu (orange) and Zn (grey) as outputs.

It can be seen in Figure 19 that the reaction rate, which collectively investigate how the kinetic parameters affect the system, does not change the output at all. This is reasonable because the metal ion concentration is the limiting parameter for this system. This is observed because the reaction rate in mole per hour is larger than the metal ion concentration in mole per hour. The reaction rate would however, most likely impact the MeS output if the latter is decreased to a lower value than the metal ion concentration.

The concentrations have an impact on the metal sulfide output. This is logical because the concentration is the limiting factor for this reaction when the reaction rate is higher than the concentration. The increase of copper ion concentration only increases linearly to a certain molar flow and then the CuS output is constant. The same can be observed for the increase of the zinc ion concentration. This results are explained by the fact that both reactants, the metal ions and the hydrogen sulfide, are important for the reaction rate. If only one of them is increased, the other will become limiting and the hydrogen sulfide concentration should also be increased to achieve a linear scale up. This is confirmed by the sensitivity analysis where both the metal ion concentration and the hydrogen sulfide concentration were increased. Then there is a 10% increase in output with a 10% increase of reactants and no change in the output when observing the zinc output when changing the copper ion input and vice versa.

The output of metal sulfide does not seem to depend on the gas flow at first, this is because only the leach flow was used for the scale up. Also, the concentration of H_2S is the same with an increased flow and the concentration is what affects the reaction rate. However only increasing the leach flow does not result in a high change in output. The change in both the gas flows and the leach flow does result in a 10% increase in output. This shows that the gas flow also has an impact on the output. This is probably because the amount of hydrogen sulfide becomes limited if the flow of gas is too low.

The concentrations and the flows is shown to work in a similar way during a 10% increase. This sensitivity analysis shows the importance of adjusting the concentration and flow of both reactants to get the predicted output for an upscale.

5.2.2 Results from the bioreactor simulation in Aspen Plus

The bioreactor is simulated both as an RCSTR and a RBatch reactor block, representing a more "close to reality" simulation compared to the REquil used for the precipitation simulation. In reality two outlet streams will be present, one gas and one liquid stream. In Aspen a simple separator block, RSep, is used to simulate the gas liquid separation and the MATLAB model is used to calculate the relationship between the phases. Separate unit blocks were used to simulate the ethanol and acetate degradation.

5.2.2.1 Evaluation of the bioreactor from the MATLAB model

The flowchart for the bioreactor evaluation can be seen in Figure 20.

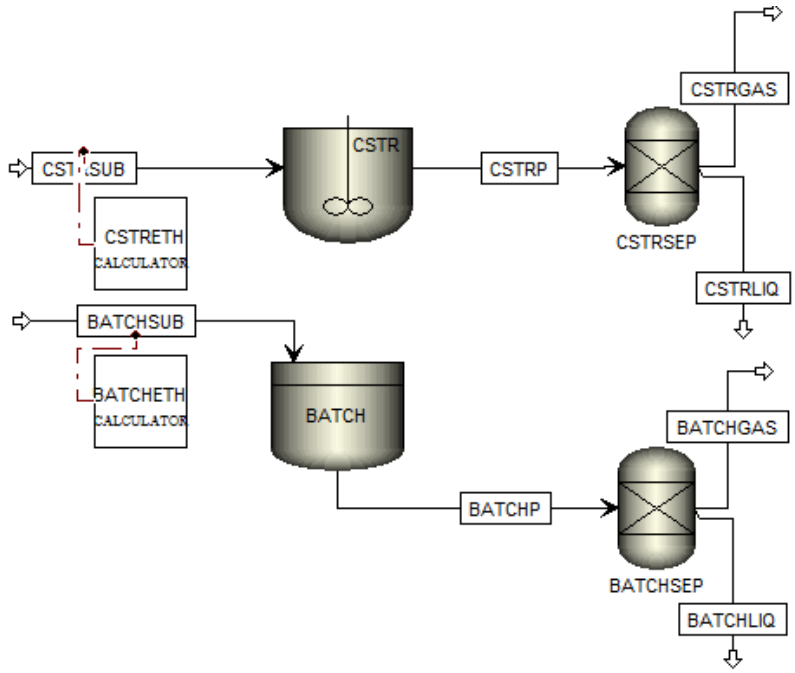

Figure 20: The process set up for a CSTR and a Batch reactor in Aspen Plus.

The produced sulfide was obtained from Aspen Plus according to Equation (5.5) and the molar flow of hydrogen sulfide from the batch reactor was 0.9 mmol h^{-1} and 4.7 mmol h^{-1} for the CSTR. When specifying the CSTR as a "liquid only" unit, the output of hydrogen sulfide was instead 0.88 mmol h^{-1}. The CSTR unit is set to conditions that are similar to a batch reactor and therefore this comparison is considered interesting as well.

Aspen: $n_{f,S_{red}} = S_{H_2S(l)} + S_{HS^-} + S_{S^{2-}}$ (5.5)

The data obtained from the experiments from literature and the evaluation for the reduced sulfur and a more specific evaluation of these experimental data with the model developed in this report can be seen in the section on the results from the MATLAB simulation. The total reduced sulfur concentration over time from the MATLAB model is shown in Figure 21.

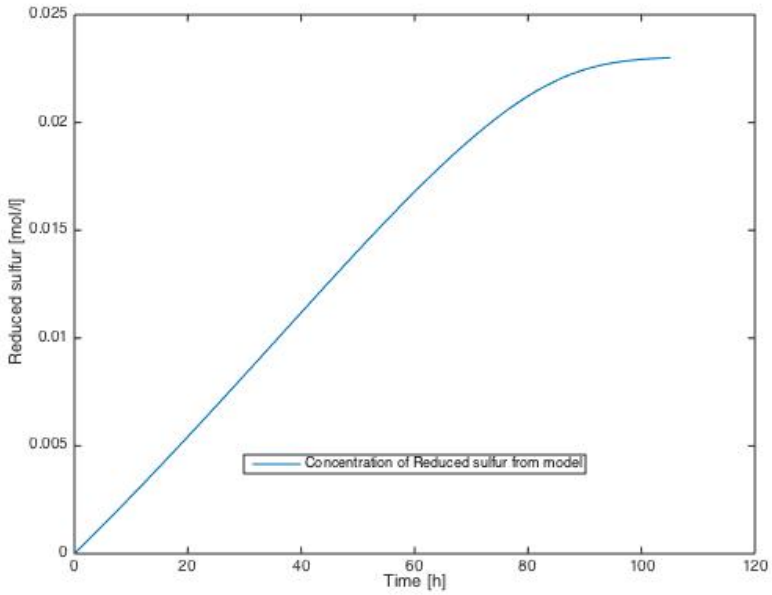

Figure 21: The results for the total reduced sulfur over time obtained from the MATLAB simulation.

The final concentration of 0.023 mol L^{-1} at time 105h can be seen in Figure 21 and this represent the total concentration of reduced sulfur and was obtained by removing the liquid-gas mass transfer term from the sulfide production differential equation, see Equation (4.18). The total reduced sulfur obtained from the MATLAB simulation was calculated to be in total 0.069 mole which is 6.6 10^{-4} mol h^{-1}. A comparison between the results for the molar flow per hour can be seen in Figure 22.

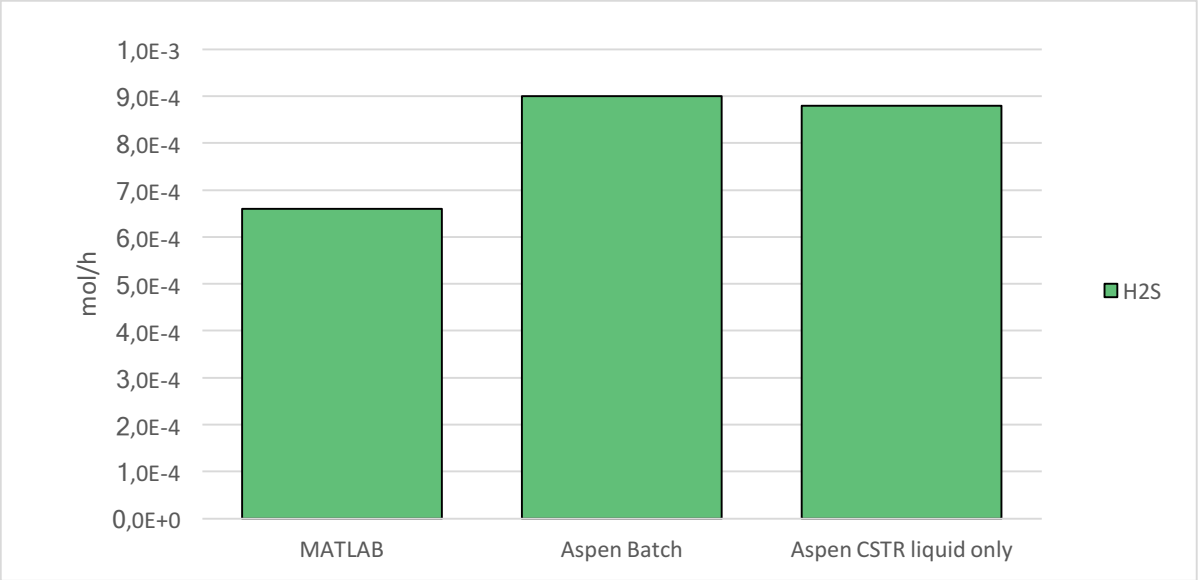

Figure 22: The outputs from the MATLAB simulation, Aspen batch simulation and Aspen CSTR simulation where only liquid phase was allowed with variables and parameters from Nagpal et al., (2000).

The MATLAB and the Aspen Batch runs differ by 36%, these are not optimal results yet the results are in the same order of magnitude. The CSTR however does not correspond to the other results at all if both a vapor phase and liquid phase are allowed. The reason for this is the change in outlet volumetric flow that increases because of the increase in vapor phase. Therefore, it would be more accurate to compare concentrations in the outlet stream instead. When only a liquid phase is allowed, the CSTR differs by 33%, which is about the same as the Batch reactor. The comparison for the bioreactor outlet concentrations can be seen in Figure 23.

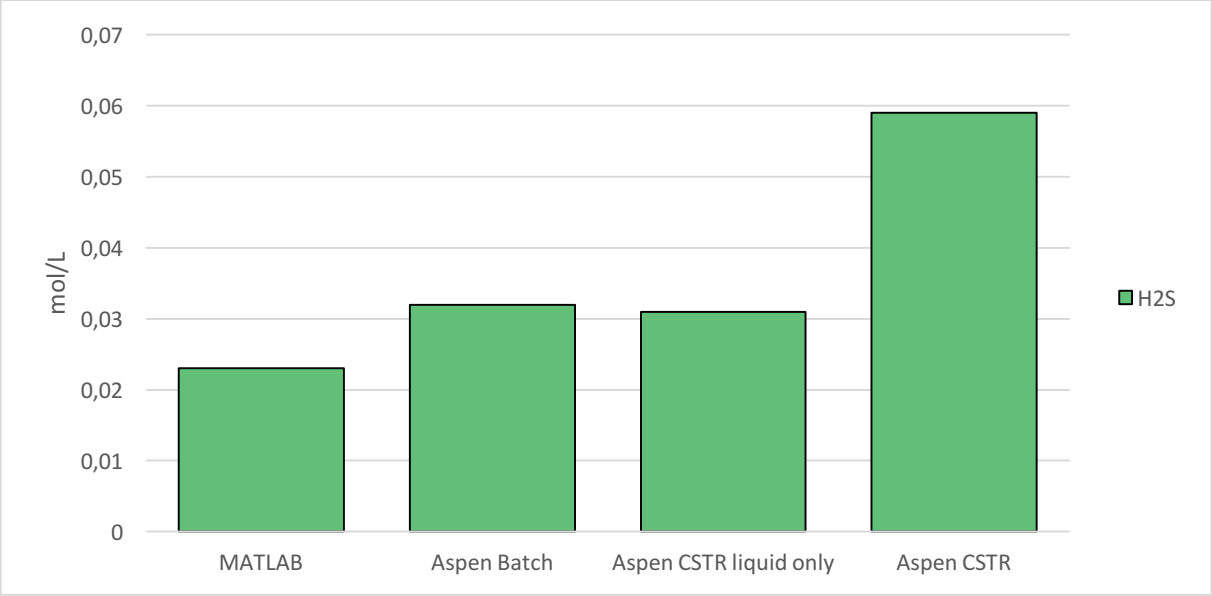

Figure 23: A comparison between MATLAB and Aspen Plus outputs where variables and kinetic parameters from Nagpal et al., (2000) was used.

The comparison between the concentrations of hydrogen sulfide shows that the CSTR where all phases are allowed is still furthest from the MATLAB results. The other outputs follow the same profile as in the mole flow comparison. A batch reactor was chosen for further simulation

due to the inconsistent results in the CSTR unit. It is also not certain that the CSTR works with the kinetic data if alterations to the flows are made to make the unit converge from the simulated "close to Batch run".

The amount of H_2S in gas phase is 0.0026 mol L^{-1} in total after 105 h, this amount was calculated without any transport of gas out from the tank. This means 10% of the reduced sulfur will be transferred to the gas phase if the conditions correspond to Nagpal et al. (2000) with N_2 as stripping gas. The amount of H_2S to be present in the gas phase may increase when an outflow of gas is added to the model due to a higher concentration difference between liquid and gas phase. This was however not used in this case and the value of 10% is the value implemented in the separation blocks in Aspen Plus.

No acetate degradation is used in this evaluation, a unit block for this purpose is however present in the simulation for the whole process. The bioreactor simulation reacts to a change in variables and no scale up alterations are therefore performed in this case.

5.2.2.2 Sensitivity analysis for the bioreactor

The impact that the variables and parameters have on the output hydrogen sulfide was tested by performing a sensitivity analysis. The kinetic parameters were tested collectively by changing the pre-exponential factor for the power law expression. To be able to compare with the MATLAB script, a 1% increase in the parameters were used for this analysis, see Figure 24.

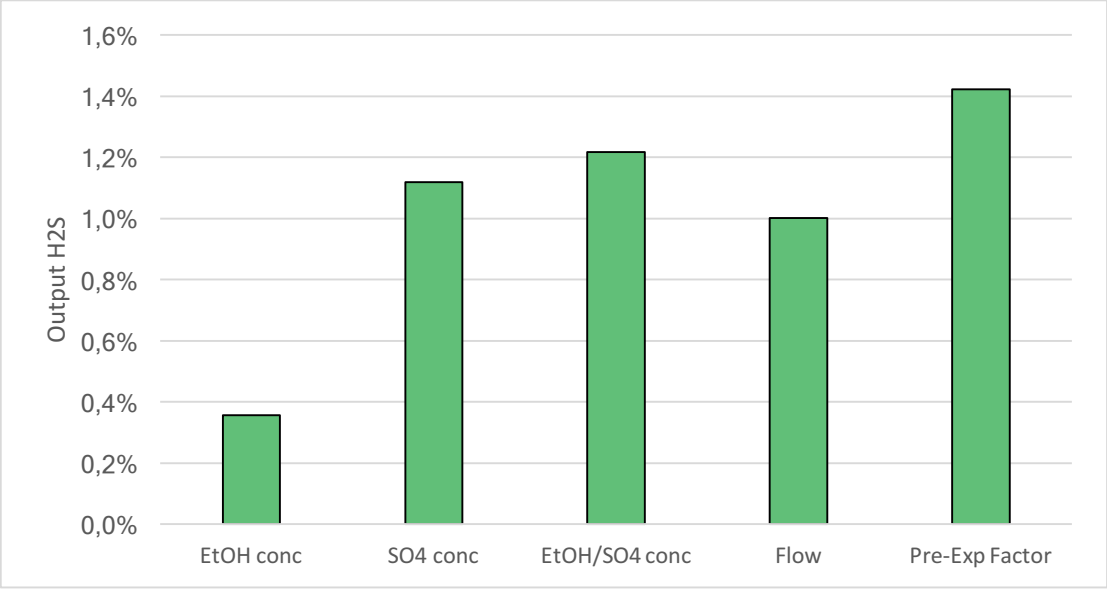

Figure 24: Sensitivity analysis with a 1% change of the variables and parameter presented on the x-axis and the output of H_2S on the y-axis.

The pre-exponential factor, representing the reaction rate, had the largest impact on the hydrogen sulfide production and a 1% increase gave a 1.4% increase. This shows the impact of the kinetic parameters on the system. Therefore, finding a well working biological system with a high productivity is important to get an efficient process.

The change in both reactants gave the highest impact among the changed variables. This is logical because two values are changed, these variables are also dependent on each other in the stoichiometric relationship used by the reactor. In this analysis, the sulfate concentration seems to have a larger impact than the ethanol concentration. This could be since only half of the sulfate is needed compared to the ethanol needed. An equal change should therefore result in twice the output change. It is however more than double in this analysis, this could be due to other limiting factors in the batch unit.

When increasing the variables and parameters with 10%, errors occurred and a negative change was observed for the output when changing the pre-exponential factor. A 7% increase was the limit for how much the kinetic factor could be altered and therefore a sensitivity analysis was performed with this increase instead, this analysis can be seen in Figure 25.

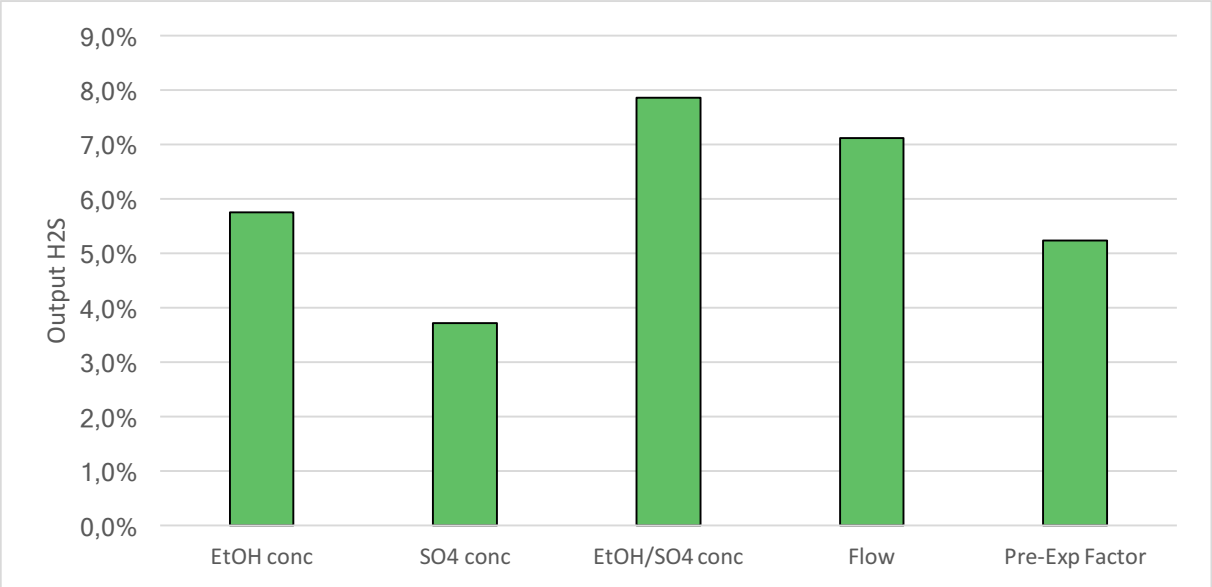

Figure 25: Sensitivity analysis with a 7% change of the variables and parameter presented on the x-axis and the output of H_2S on the y-axis.

The results for a 7% increase do not correspond to the 1% change. A reason for this could be that limiting factors impact the results. Also, the system might not be very robust towards changes, especially considering the kinetic factors. There is a non-linear effect on the output of the pre-exponential factor.

In this analysis, the ethanol concentration seems to have a larger impact than the sulfate concentration, contradictory to the analysis with 1% change. This is probably because ethanol becomes limiting when the sulfate concentration is changed to this large extent. The change in the ratio of both reactants and the change in flow were the two parameters that gave the same change during the analysis.

5.2.3 Results from the full process simulation

When connecting the precipitation and bioreactor part, alterations had to be done. The same unit operations were used as in the separate scripts but units were added to get the whole process to work. The full model also includes recirculation of the hydrogen sulfide rich streams from the bioreactor to the precipitation and the sulfate rich leach water from the precipitation to the

bioreactor, see Figure 26 for the process flowchart, for larger picture see Appendix D. There were also pH adjustments added to accurately simulate the pH dependent precipitation and the bioreactor kinetics including pH inhibition. All the calculation blocks are used by the system adjusting the reaction rate for the precipitation tanks and the pre-exponential factor for the bioreactor according to the model developed for this project.

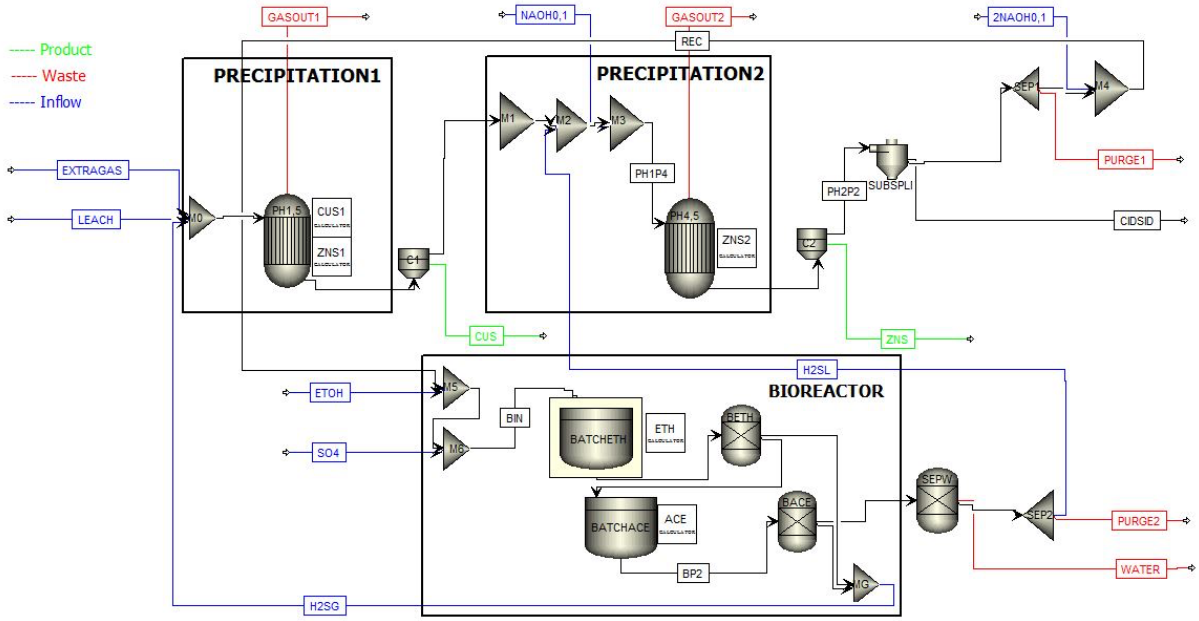

Figure 26: The process flowchart for the full process where the prodcts are shown with green lines, the inflows with blue and the waste streams with red lines. The different process parts are shown with squares.

The bioreactor output was adjusted to work with the precipitation system used by Tokuda et al., (2008). The "GAS" stream is the one used in the precipitation evaluation and "H2SG" is the hydrogen sulfide is the gas phase from the bioreactor and "H2SL" is the hydrogen sulfide dissolved in liquid. These streams are compared and adjusted to get a suitable input to the precipitation tank, see Table 13.

Table 13:The hydrogen sulfide gas flow in different process streams.

	GAS [mol h^{-1}]	**H2SG [mol h^{-1}]**	**H2SL [mol h^{-1}]**
H_2S	0.8402	1.0144	0.0535
HS^-	0	0	0.2627

Here it is shown that enough hydrogen sulfide is produced in the bioreactor and that a separation step can be added for the "H2SL" stream and still have a sufficient amount of H_2S. The bioreactor settings for when this hydrogen sulfide output was retrieved is shown in Table 14.

Table 14: The running conditions for the batch reactors.

Ethanol digestion batch "BETH"	
Variables	30^0C and 1atm
Times	20 h
Stop criterion	90% ethanol conversion or 20 h
Acetate degradation batch "BACE"	
Variables	30^0C and 1atm
Times	20 h
Stop criterion	85% acetate conversion or 20 h

Due to recirculation, the model simulation becomes more complicated. An equal amount of flow must be present in the inflow as the outflow to avoid accumulation in the process. This was solved by controlling the recirculation and adding purge streams to compensate for the recirculation streams.

5.2.3.1 Results from the full model study

The variables presented in Table 15 is one example of values that the full process can be run at. The recirculation and separation steps are chosen to match and to ensure a process where no accumulation occurs.

Table 15: Inputs, recirculations and separations for the full process simulation. The variables for the bioreactor are adapted to the precipitation evaluation.

Inputs	
EXTRAGAS	0.001 L min^{-1} extra gas (5000ppm H_2S)
LEACH	2.6 L h^{-1} leach (0.1 g L^{-1} of Zn^{2+} and Cu^{2+})
ETOH	0.459 L h^{-1} (95% Ethanol)
SO4	0.6 L h^{-1} (70% Na_2SO_4)
Recirculation	
H2SG	0.7 L min^{-1} H_2Sgas
H2SL	0.006 L min^{-1} H_2Sleach
Separation steps	
PURGE1	Purge liquid 0.006 L min^{-1} to match the recirculation from H_2Sleach
P1G/P2G	Purge gas automatically calculated from every precipitation tank.

The complete process simulation were run successfully with the specifications that can be seen in Table 15. The results from the simulation can be seen in Table 16. These results are focused on metal sulfide output and hydrogen sulfide flows. The streams can be located in the process flowchart in Figure 26. A complete set of results can be seen in Appendix B.

Table 16: Examples of what outputs a certain input results in.

Input	
LEACH	4.0 kmol h^{-1} (Cu^{2+}) 4.1 kmol h^{-1} (Zn^{2+}) 16.1 kmol h^{-1} (OH^-) 84.8 kmol h^{-1} (H_2SO_4)
BIN	0.0094 kmol h^{-1} (SO_4^{2-}) 0.0078 kmol h^{-1} (EtOH)
Outputs	
CUS	3.9 kmol h^{-1} (CuS)
ZNS	4.0 kmol h^{-1} (ZnS)
H2SG	770 kmol h^{-1} (H_2S)
H2SL	6.9 kmol h^{-1} ($H_2S+HS^-+S^{2-}$ after liquid separation)

The conversion of both copper and zinc ions was 99% and also 99% was separated in the solid separator blocks. The sulfate to sulfide conversion in the bioreactor were 66% and 90%, respectively of the ethanol that was consumed. These results should be examined by experimental results to confirm how realistic these outputs are.

If a 1:1 relationship between the metal ions and the hydrogen sulfide gas would be used, then the bioreactor should be down-scaled. The relationship that is present now is adapted according to Tokuda et al., (2008) and the over-dimensioning also gives a possibility of purging gas in the same way as the liquid.

5.2.3.2 pH adjustments

The pH at different stages of the process was adjusted by the design specifications added to the system where the flows of 1NAOH0,1 and 2NAOH0,1 were controlled. These flows were controlled by adding a lower and higher value and adjusted to pH 4.5±0.2 and pH 7.0±0.2 respectively. These adjustments are done for every run and are only changed if any input is changed. The output from these design specifications can be seen in Table 17.

Table 17: The pH adjustments are performed automatically with the design specification added to the simulation. The values presented here show the adjustments done for one simulation run. If the pH was already correct, no change in NaOH flow was made.

Adjustments to pH 4.5			
Variable	Initial value	Final value	Units
MANIPULATED	0.002658768	0.00354254	L/MIN
P1P4	4.233455345	4.50235539	
Adjustments to pH 7			
Variable	Initial value	Final value	Units
MANIPULATED	0.00731173	0.00731173	L/MIN
P2P4	6.99872147	6.99872147	

The resulting values for the pH are as desired. It can be seen that for PH7 the pH was already the correct one, the design specification is run either way. This control system for the model is convenient and makes simulation easier. A problem with adding this type of control system is that the simulation becomes more sensitive to large changes in input. If the inflow on NaOH

cannot be adjusted within the limit given to the system, errors will occur in the process and the streams will have the wrong pH. Therefore, the flow range for where the design specification iterates must be adjusted if large adjustments are to be done for the process.

The model overall is fairly adjustable to increase of flows and concentrations. The batch reactor is the hardest part to understand in this simulation. This is because Aspen uses interface holding tank before and after the system limit for the batch reactor. These holding tanks works by adjusting the flow into and out of the batch reactor to make it possible to model the dynamic batch reactor together with a steady-state system. Therefore, the output from the batch reactor gives a molar flow instead of a finished concentration as it would in reality. Simulating a CSTR would be easier, experimental and kinetic data for ethanol degradation would however be needed to do this.

6 Reflection

This part consists of a reflection regarding model improvements, model drawbacks and comparison between the software. It also includes a reflection of the process which the model is built upon, environmental aspects etc.

6.1 Improvements of the MATLAB simulation

There are many ways to improve the simulation in MATLAB. First of all, it is important to perform experiments with exact the right conditions as the model is designed for. This means that both ethanol and acetate utilizing SRB should be used in the same experiments. Then it will be possible to determine the kinetic parameters for the entire model. Right now, the model is calibrated in two parts and is not coupled. With experiments, it will be possible to compare other factors in the model such as CO_2 and H_2S formed in the gas phase.

The model is for now designed with a set value for pH. This will not be the case in reality and if the model should be more accurate it is necessary to implement an equation that can calculate the pH at each iteration step. This would improve the pH inhibition term in the model. This is especially important since the sensitivity analysis showed that the pH is the system variable affecting the model the most. The inhibition term will now only have relevance if the pH is manually switched to a lower value in which the inhibition then will be included. In this implementation of pH, correct values for the upper and lower limits for each kind of bacteria should be determined. Now the upper and lower limits are set to be the same for both ethanol SRB and acetate SRB. This is the case since only one article provided the upper and lower limits for SRB. The article by Sharma et al. (2013) used sewage as substrate and not ethanol or acetate.

One suggestion for future improvements to the process is to do experiments where the mass transfer for this exact set up is tested. Now the mass transfer parameters have been taken from other experiments and will not be accurate for the real set up and therefore makes the model less exact. The model was first developed as a CSTR, but then altered to be run as a batch to fit the features of the article by setting the inflow to zero. The model was also adapted to be run as a continuous system, but since the model does not provide accurate results from this, further improvements are needed. In the future, it would be desirable to calibrate the model to both CSTR and batch mode and compare the models with each other.

When the simulation is more developed and calibrated to experimental data it would be practical to create a graphical user interphase (GUI). This would facilitate usability for users that does not know MATLAB well because the user do not have to code the model, but only select parameter and variable values. Here it is possible to just click in a box and change the number and the model will adapt accordingly.

It would be interesting to create interval values for parameters in which the model is accurate and reliable to use. With these conditions, it is possible to get a prediction of how the process will look like and how much H_2S can be produced. As mentioned in the discussion it would also be desirable to add other inhibition terms to the model, like substrate, metal ions and metal sulfide terms. This could improve the model and create a more accurate result.

6.2 Drawbacks and improvements of the Aspen simulation

One major drawback of this simulation is the fact that the hydrogen sulfide gas is not completely recirculated. The vapor outlet streams from both of the unit block representing the precipitation tanks should be recirculated as well as the liquid outflow from the tanks. Difficulties in implementing this was due to the change of volume and accumulation of hydrogen gas in the system. A similar solution as in the liquid recirculation case could be performed here.

The simulation is performed on a laboratory scale and cannot be said to represent a full scale process. This is a drawback because at least a pilot scale process would be needed if this process simulation would to be used to predict full scale outputs.

The data for the evaluation and calibration of the model are taken from literature performed by external sources. This can be a drawback because the raw data is not present. There is also a risk of interpretation mistakes when using the parameters and values from these experiments. The two different experimental runs are also altered to make a connection possible, the accuracy of these results are therefore questionable.

There are quite large assumptions made on both parts of this process. For example, the precipitation is only assumed to be restricted to mass transfer and no nucleation rate or agglomeration is considered. In the bioreactor, no biomass degradation of bacteria is added, the system is basically assumed to work more like a chemical catalyst. This can lead to errors in the model that would be amplified when changing the simulation inputs. The fact that the bioreactor is compared to the MATLAB outputs and not the experimental data itself is also a source of error in this simulation.

Improvements to the Aspen Plus simulation could be done by adding a control system to regulate the purge streams from the process and connecting these to the recirculation streams. This would make a complete gas recirculation possible and an increase in recirculation during the process run could be made. The extra hydrogen sulfide gas that goes into the reactor would then only be needed in the first iteration and the gas from the bioreactor would completely be used afterwards.

If the model would be developed to include a hydrogen sulfide inhibition term, a self-control system could be used to control the hydrogen sulfide production by the bioreactor. When too much hydrogen sulfide is present in the system, the bacteria would slow down, producing less and when the hydrogen sulfide is used up, the production would increase. This would mean than the inlet of ethanol could be decreased and money could be saved.

There could also be improvements done to make the process look more like the actual process, pumps and compressors would be needed to make this happen. With this improvement, an energy evaluation could be performed on the system. However, a more specific flowchart would be needed and a more specific case study including the process set up. This evaluation would also need exact separation steps, including water separation, purge separation system, solid separators and realistic tanks to use for the system.

6.3 Comparing the software tools

Evaluating variables like flows, concentrations and process set up is beneficial to do in Aspen. It is harder to evaluate kinetic parameters on a detailed scale. Manual changes are needed in that case. Another advantage about Aspen is the user friendly set up. It is easy to understand and the mathematics are pre-programmed for systems with different pressure, temperature and phases. Also a lot of information about different chemical substances are present in Aspen Plus databases which makes it simple to compare the characteristics for reactants. Aspen also have pre-programmed interactive relationships between different compounds. There is also a possibility of changing the compounds characteristics manually and adding new compounds. By using the electrolyte wizard for example, Aspen Plus can calculate dissociation and salt formation automatically. This a big advantage, especially when desiring a well-working pH control in the system.

Compared to MATLAB, Aspen Plus is to prefer when complex and whole processes are to be examined while MATLAB is to prefer when specific systems or part of systems are to be evaluated. The kinetic data can be very well evaluated in MATLAB but not in Aspen Plus.

6.4 Environmental aspects

The process simulated in this project is beneficial from an environmental perspective. This is because recycling in general is a more sustainable method than for example mining. The fact that the metals are released into the environment today is another reason for why this process should be further developed.

The biological part of the process is run at ambient temperature, atmospheric pressure and a pH around neutral. This makes the process safe for the operators. The inhibitory characteristics for the hydrogen sulfide for the bacteria regulates the process because the production stops when the hydrogen sulfide concentration gets too high.

To ensure an efficient precipitation, a higher hydrogen sulfide to metal ion ratio is desired. To be able to have this but still avoid discharge of hydrogen sulfide gas, a recycle stream should be used in the system. The hydrogen sulfide gas is recycled into the bioreactor, here it controls the production of new hydrogen sulfide gas by inhibiting the SRB. The H_2S gas does not kill the bacteria and therefore production will start again when the H_2S is transferred away from the bioreactor and consumed in the precipitation tank. This would therefore work as an internal controller of the system.

Carbon dioxide is not harmful to the people that come in contact with the substance, it is however a well-known greenhouse gas that is harmful to the environment.

7 Conclusion

The model developed in this project describes the dynamic mass balances for a bioreactor where sulfate reducing bacteria uses dissimilatory sulfate reduction to produce hydrogen sulfide. This part of the model is built on kinetic parameters describing the rate of ethanol and acetate degradation with sulfate uptake. There are two inhibition terms included in this model, pH inhibition and sulfide inhibition. The model describes a dynamic CSTR but evaluations are made on a batch reactor. A model has also been defined for the precipitation of metal sulfides with H_2S. This model is based on mass transfer rates. No experimental data is used for the evaluation of this model, but only literature data.

The model describing the dynamic mass balances in the bioreactor has been implemented. The evaluation of the MATLAB simulation has been successful for the dynamic batch reactor and unsuccessful for the static CSTR. Further improvement to the MATLAB scripts are needed.

The whole process, bioreactor and precipitation tanks has been simulated in Aspen Plus. The parts implemented from the model are rate of ethanol/acetate degradation and the mass-transfer rate in the precipitation tanks. A successful evaluation has been performed on both parts of the process.

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Appendix A – MATLAB Simulation Code

Model function file for the SRB process

```
function dy = SRBmodel (t,y,par)
%=========================================================================
% Unknown
%=========================================================================
S_Sred  = y(1);             %Reduced sulfur in liquid phase
S_EtOH  = y(2);             %Ethanol
S_SO4   = y(3);             %Sulfate
X_eSRB  = y(4);             %Ethanol biomass
S_Ac    = y(5);             %Acetate
X_aSRB  = y(6);             %Acetate biomass
S_HS    = y(7);             %Dissolved H2S in HS form
S_IC    = y(8);             %Inorganic carbon in liquid phase
S_HCO3  = y(9);             %Dissolved CO2 in HCO3 form
S_H2S_g = y(10);            %H2S in gas phase
S_CO2_g = y(11);            %CO2 in gas phase

%=========================================================================
%Inhibition terms
%=========================================================================
S_H = 10^-(par.pH);

% .........................................................................
% Low pH inhibition
%.........................................................................

%Inhibition term for eSRB
if(par.pH < par.pH_UL_eSRB)
I_pH_eSRB = exp(- 3 * ((par.pH - par.pH_UL_eSRB)/
(par.pH_UL_eSRB - par.pH_LL_eSRB))^2);
else
I_pH_eSRB = 1;
end

%Inhibition term for aSRB
if(par.pH < par.pH_UL_aSRB)
I_pH_aSRB = exp(-3 * ((par.pH - par.pH_UL_aSRB)/(par.pH_UL_aSRB
- par.pH_LL_aSRB))^2);
else
I_pH_aSRB = 1;
end

%=========================================================================
%H2S inhibition
%=========================================================================

% H2S inhibition (First order)
% if (S_Sred > par.KI)
%     I_H2S = 1;
% else
% I_H2S = 1 - (S_Sred/par.KI);
% Inhibition term from H2S (if H2S > KI, IH2S = 0)
% %end
```

```
%Non-competitive inhibition
I_H2S = 1/(1 + (S_Sred/par.KI));

%Inhibition for high H2S concentration
%I_H2S = exp(-(S_Sred/0.60056 * par.KI)^2); %

%=========================================================================
% Rates for eSRB and aSRB
%=========================================================================

%Rate for eSRB
r_EtOH = (par.umax_EtOH/par.Y_EeSRB) * S_EtOH/(par.Ks_EtOH + S_EtOH)
* S_SO4/(par.Ks_SO4 + S_SO4) * X_eSRB * I_pH_eSRB * I_H2S;

%Rate for aSRB
r_Ac = (par.umax_Ac/par.Y_AaSRB) * S_Ac/(par.Ks_Ac + S_Ac)
* S_SO4/(par.Ks_SO4 + S_SO4) * X_aSRB * I_pH_aSRB * I_H2S;

%Rate of decay of eSRB
r_dec_eSRB = par.k_dec_eSRB * X_eSRB;

%Rate of decay of aSRB
r_dec_aSRB = par.k_dec_aSRB * X_aSRB;

%=========================================================================
% Acid base rates
%=========================================================================
S_H2S = S_Sred - S_HS;
S_CO2 = S_IC - S_HCO3;

% Hydrogen sulfide dissociation
rho_A_HS = par.K_ab_H2S * (S_HS * (S_H + par.K_a_H2S)
- par.K_a_H2S * S_Sred);

% Carbon dioxide dissociation
rho_A_HCO3 = par.K_ab_CO2 * (S_HCO3 * (S_H + par.K_a_CO2)
- par.K_a_CO2 * S_IC);

%=========================================================================
% Mass transfer for gas phase
%=========================================================================
p_H2S_gas = S_H2S_g * par.R * par.T ;   %Partial pressure of H2S [atm]
p_CO2_gas = S_CO2_g * par.R * par.T;    %Partial pressure of CO2 [atm]

q_gas = par.N2g/(1 - (p_H2S_gas/1) - (p_CO2_gas/1));

%Henry's law, maximum solubility of H2S in liquid
S_prim_H2S = p_H2S_gas/par.H_H2S;

%Henry's law, maximum solubiliy of CO2 in liquid
S_prim_CO2 = p_CO2_gas/par.H_CO2;

%Mass transfer for H2S gas from liquid to gas
r_H2St = par.kLa_H2S * (S_H2S - S_prim_H2S);


%Mass transfer for CO2 gas from liquid to gas
r_CO2t = par.kLa_CO2 * (S_CO2 - S_prim_CO2);

%=========================================================================
% Dynamic mass balances
```

```
%=========================================================================

%.........................................................................
%Biomass
%.........................................................................

%EtOH biomass change
dX_eSRB_dt = par.q_in/par.V_liq * (par.X_eSRB_in - X_eSRB) + par.Y_EeSRB
* r_EtOH - r_dec_eSRB;

%Acetate biomass change
dX_aSRB_dt = par.q_in/par.V_liq * (par.X_aSRB_in - X_aSRB) + par.Y_AaSRB
* r_Ac - r_dec_aSRB;

%.........................................................................
%Uptake and production
%.........................................................................

%Ethanol concentration
dS_EtOH_dt = par.q_in/par.V_liq * (par.S_EtOH_in - S_EtOH) - r_EtOH;

%Acetate concentration
dS_Ac_dt = par.q_in/par.V_liq * (par.S_Ac_in - S_Ac) + (1 - par.Y_EeSRB)
* r_EtOH - r_Ac;

%Sulfate concentration
dS_SO4_dt = par.q_in/par.V_liq * (par.S_SO4_in - S_SO4) - (1 - par.Y_EeSRB)
* par.Y_eSO4 * r_EtOH - (1 - par.Y_AaSRB)*par.Y_aSO4*r_Ac;

%Reduced sulfur in liquid phase
dS_S_red_dt = par.q_in/par.V_liq * (par.S_red_in-S_Sred) + (1-par.Y_EeSRB)
* par.Y_eSO4 * r_EtOH + (1 - par.Y_AaSRB) * par.Y_aSO4 * r_Ac - r_H2St;

%Inorganic carbon in liquid phase
dS_IC_dt = par.q_in/par.V_liq * (par.S_IC_in - S_IC) + (1 - par.Y_AaSRB)
* r_Ac - r_CO2t;

%.........................................................................
%Acid-base
%.........................................................................
d_S_HS_dt   = -rho_A_HS;        %Dissociation of H2S to HS-
d_S_HCO3_dt = -rho_A_HCO3;      %Dissociation of CO2 to HCO3-

%.........................................................................
%Gas phase
%.........................................................................
%Gas phase for H2S with compensation for volume difference
dS_H2S_g_dt = 0 - (q_gas/par.V_gas) * S_H2S_g + r_H2St *
(par.V_liq/par.V_gas);

%Gas phase for CO2 with compensation for volume difference
dS_CO2_g_dt = 0 - (q_gas/par.V_gas) * S_CO2_g + r_CO2t *
(par.V_liq/par.V_gas);

%.........................................................................
%Vector for odesolver
%.........................................................................
dy = [dS_S_red_dt;dS_EtOH_dt;dS_SO4_dt;dX_eSRB_dt;dS_Ac_dt;dX_aSRB_dt;
      d_S_HS_dt;dS_IC_dt;d_S_HCO3_dt;dS_H2S_g_dt;dS_CO2_g_dt];

end
```

SRB model parameters

```
function [par] = SRBparameters
%=========================================================================
% Ethanol and acetate utilizing SRB
%=========================================================================
par.umax_EtOH    = 0.013;         %Maximum specific growth rate of eSRB [h^1]
par.Y_eSO4       = 0.5;           %Yield sulfate/eSRB,[gprotein/molSO4]
par.Y_EeSRB      = 0.5*par.Y_eSO4;%Yield of eSRB biomass on ethanol [g/g]
par.Ks_EtOH      = 0.0045;        %Ks for EtOH [mol/l]
par.Ks_SO4       = 0.0085;        %Ks for SO4 [mol/l]
par.umax_Ac      = 0.063;         %Maximum specific growth rate of aSRB[h^-1]
par.Y_AaSRB      = 0.58;          %Yield Acetate/aSRB[g bacteria/g acetate]
par.Ks_Ac        = 0.0035;        %Ks for Acetate
par.q_in         = 0;             %Flow rate in bioreactor [mol/l h]
par.X_eSRB_in    = 0.1;           %Inflow of eSRB biomass [mol/l]
par.X_aSRB_in    = 0.1;           %Inflow of aSRB biomass [mol/l]
par.S_EtOH_in    = 1;             %EtOH inflow [mol/l]
par.S_Ac_in      = 0.1;           %Acetate inflow [mol/l]
par.S_SO4_in     = 1;             %Sulfate inflow [mol/l]
par.Y_aSO4       = 0.5;           %Yield sulfate/aSRB [gprotein/molSO4]
par.S_red_in     = 0.01;          %Reduced sulfur-liquid inflow [mol/l]
par.S_IC_in      = 0.01;          %Inorganic carbon-liquid inflow [mol/l]
par.k_dec_eSRB   = 0.00;          %Decay coefficient for eSRB [h^-1]
par.k_dec_aSRB   = 0.00;          %Decay coefficient for aSRB [h^-1]

%=========================================================================
% Mass transfer gas-liquid parameters
%=========================================================================
par.kLa_H2S      = 10;            %kLa mass transfer coefficient H2S[h^-1]
par.kLa_CO2      = 10;            %kLa mass transfer coefficient CO2 [h^-1]
par.H_H2S        = 10.70;         %Henrys constant for H2S [atmL/mol]
par.H_CO2        = 25.88;         %Henrys constant for CO2 [atmL/mol]
par.T            = 298;           %Temperature [K]
par.R            = 0.082057338;   %Gas constant [L atm K^-1 mol^-1]
par.V_liq        = 70;            %Liquid volume [l]
par.V_gas        = 30;            %Gas volume [l]
par.P_tot        = 1;             %Total pressure from all gases [atm]
par.N2g          = 6;             %Stripping gas, flow of N2 [l/h]

%=========================================================================
% Acid-base
%=========================================================================
par.K_ab_H2S     = 10^15;         %Acid base kinetic parameter for H2S
par.K_a_H2S      = 1.075 * 10^-7;%Acid-base equilibrium coefficient for H2S

par.K_a_CO2      = 4.97 * 10^-7; %Acid-base equilibrium coefficient for HCO3
par.K_ab_CO2     = 10^12;         %Acid base kinetic parameter for HCO3

%=========================================================================
% Inhibition parameters
%=========================================================================
par.pH_LL_eSRB   = 1.3;           %Lower limit: Completely inhibited eSRB
par.pH_UL_eSRB   = 6.75;          %Upper limit: Not inhibited at all eSRB
par.pH_LL_aSRB   = 1.3;           %Lower limit: Completely inhibited aSRB
par.pH_UL_aSRB   = 6.75;          %Upper limit: Not inhibited at all aSRB
par.pH           = 5;             %Set pH

par.KI           = 5.13*10^-3;    %KI for the H2S inhibition [mol/l]

save('par','par')                 %save par as par in a .mat file
end
```

SRB solver and plot function for Ethanol and Acetate utilizing SRB

```
% ODE solver, outputs and subplots for the output

function [R] = SRBsolver

Data = SRBparameters;          %Load indata from parameter file
load par;

Data = SRBpardata;             %Load data from literature
load D;

%.....................................................................
% Time
%.....................................................................
tspan = linspace(0, 80, 80); % [h]

%=====================================================================
% Start values
%=====================================================================
S_Sred0 = 0;           %H2S liquid concentration
S_EtOH0 = 1;           %EtOH concentration
S_SO40 = 1;            %Acetate concentration
X_eSRB0 = 0.1;         %EtOH biomass
S_Ac0 = 0;             %Acetate concentration
X_aSRB0 = 0.1;         %Acetate biomass
S_HS0 = 0;             %Dissovled H2S in HS form
S_IC0 = 0;             %Inorganic carbon in liquid phase
S_HCO3 = 0;            %Ion state of CO2 and HCO3
S_H2S_g0 = 0.0001;     %H2S concentration gas phase
S_CO2_g0 = 0.0001;     %CO2 in gas phase

y0 = [S_Sred0 S_EtOH0 S_SO40 X_eSRB0 S_Ac0 X_aSRB0 S_HS0 S_IC0 S_HCO3
      S_H2S_g0 S_CO2_g0];

[t,y] = ode15s(@SRBmodel,tspan,y0,[],par);

%=====================================================================
% Outputs
%=====================================================================
R.Reducedsulfur = y(:,1);        %Total amount of reduced sulfur out
R.Ethanol = y(:,2);              %EtOH concentration
R.Sulfate = y(:,3);              %SO4 concentration
R.Ebiomass = y(:,4);             %EtOH biomass
R.Acetate = y(:,5);              %Acetate concentration
R.Abiomass = y(:,6);             %Acetate biomass
R.DisSulfide = y(:,7);           %Dissolved H2S
R.ICarbonliquid = y(:,8);        %Inorganic carbon in liquid phase
R.Carbonate = y(:,9);            %Dissociated CO2
R.Sulfidegas = y(:,10);          %H2S gas phase
R.Carbondioxidegas = y(:,11);    %CO2 gas phase

R.tspan = linspace(0, 80, 80);  %Time [h]
R.t=t;
save ('R','R')


%=====================================================================
% Plots
%=====================================================================
```

```
subplot(3,2,1)
plot(R.tspan,R.Reducedsulfur)
xlabel('Time [h]')
ylabel('Reduced sulfur-liquid [mol/l]')
title('Reduced sulfur-liquid')

subplot(3,2,2)
plot(R.tspan,R.Ethanol)
xlabel('Time [h]')
ylabel('Ethanol [mol/l]')
title('Ethanol concentration')

subplot(3,2,3)
plot(R.tspan,R.Sulfate)
xlabel('Time [h]')
ylabel('Sulfate [mol/l]')
title('Sulfate concentration')

subplot(3,2,4)
plot(R.tspan,R.Ebiomass)
xlabel('Time [h]')
ylabel('Ethanol Biomass [mol/l]')
title('Biomass on Ethanol ')

subplot(3,2,5)
plot(R.tspan,R.Acetate)
xlabel('Time [h]')
ylabel('Acetate [mol/l]')
title('Acetate concentration')

subplot(3,2,6)
plot(R.tspan,R.Abiomass)
xlabel('Time [h]')
ylabel('Acetate biomass')
title('Biomass on Acetate')


figure(2)

subplot(3,2,1)
plot(R.tspan,R.Sulfidegas)
xlabel('Time [h]')
ylabel('H_2S-gas [mol/l]')
title('H_2S-gas phase')

subplot(3,2,2)
plot(R.tspan,R.Carbondioxidegas)
xlabel('Time [h]')
ylabel('CO_2 [mol/l]')
title('CO_2-gas phase')


subplot(3,2,3)
plot(R.tspan,R.ICarbonliquid)
xlabel('Time [h]')
ylabel('Inorganic Carbon-liquid [mol/l]')
title('Inorganic Carbon-liquid')

subplot(3,2,4)
plot(R.tspan,R.DisSulfide)
xlabel('Time [h]')
ylabel('HS^-[mol/l]')
```

```
title('Concentration HS^-')

subplot(3,2,5)
plot(R.tspan,R.Carbonate)
xlabel('Time [h]')
ylabel('HCO3^- [mol/l]')
title('Concentration HCO3^-')

subplot(3,2,6)
plot(R.tspan,R.Reducedsulfur,'*')
hold on
plot(R.tspan,R.Sulfidegas)
xlabel('Time [h]')
ylabel('Concentration [mol/l]')
title('Reduced sulfur-liquid and H_2S-gas')
legend('Reduced sulfur-liquid','H_2S-gas')

end
```

SRB literature data

```
function [D] = SRBpardata

%=========================================================================
% Data from Nagpal (2000)
% Batch, uses only Ethanol. No CO2 production, only Acetate.
% Very low amount of dissolved H2S
%=========================================================================
D.t_1   = [0 9 22 45 47 65 93 97]; % Time at specific data points [h]
%H2S production in liquid phase             [mol/l]
D.H2S_1 = [0.0001 0.00018 0.0003 0.00045 0.00045 0.00034 0.00019 0.00021];

D.t_2   = [0 9 20 45 50 55 67 92]; %Time    [h]
%EtOH consumption                           [mol/l]
D.EtOH_1 = [0.0615 0.058 0.042 0.038 0.037 0.025 0.01 0.005];

D.t_3   = [0 3 8 20 25 27 46 50 55 67 91]; %Time [h]
%Sulfate consumption                        [mol/l]
D.SO4_1 = [0.0351 0.035 0.0345 0.032 0.030 0.026 0.02 0.019 0.017
           0.015 0.009];

D.t_4   = [0 10 20 45 51 80 95 105]; %Time  [h]
%Biomass concentration                      [g protein/l]
D.X_1   = [0.018 0.02 0.02 0.02 0.022 0.028 0.028 0.028];

D.t_5   = [0 4 8 10 22 31 45 47 52 55 70 72 77 79 92 95 100 102]; %Time [h]
%Acetate concentration                      [mol/l]
D.Ac_1  = [0.003 0.005 0.009 0.014 0.018 0.024 0.035 0.038 0.042 0.044
           0.051 0.052 0.056 0.057 0.063 0.064 0.063 0.062];

%=========================================================================
% Data from Moosa (2002)
%=========================================================================
% Steady state continuous reactor using Acetate.
% Sulfate conversion at different dilution rates.
% No given time, no presented production of H2S-gas or CO2.

D.D_1       = [0.005 0.013 0.0145 0.0175 0.021 0.0275 0.0415]; %[h^-1]

%Literature data in units from article

% D.X_2     = [3.0 2.7 2.65 2.45 1.55 1.3 0.6];         %[g/l]
% D.SO4_2   = [0.027 0.06 0.07 0.08 0.105 0.135 0.21];  %[kg/m3/h]
% D.Ac_2    = [13.8 13.89 13.95 14.1 14.5 15.2 16.8];   %[kg/m3/h]
% D.H2S_2   = [0.027*0.9 0.06*0.87 0.07*0.865 0.08*0.85 0.105*0.7
%              0.135*0.54 0.21*0.1];                    %[kg/m3/h]

%.........................................................................
%Literature data in recalculated units to [mol/l] instead [kg/m3]
%.........................................................................
%D.X_2      = [3.0 2.7 2.65 2.45 1.55 1.3 0.6]; %[g/l]
D.M_X       = 24.611547;                        %[g/mol]
D.X_2       = [3.0/D.M_X 2.7/D.M_X 2.65/D.M_X 2.45/D.M_X 1.55/D.M_X
               1.3/D.M_X 0.6/D.M_X];            %[mol/l]
%D.SO4_2    = [2.8107*10^-4 6.246*10^-4 7.287*10^-4 8.3281*10^-4 0.001093
%              0.0014 0.0022];                  %[mol/l/h]
D.Ac_2      = [0.2337 0.2353 0.2363 0.2388 0.2456 0.2575 0.2846];%[mol/l/h]
D.H2S_2     = [0.000713 0.001532 0.001777 0.001995 0.002157 0.002139
               6.162*10^-4];                    %[mol/l/h]
D.t_6 = linspace(0, 240, 240);
D.SO4_2     = [(2.8107*10^-4/D.D_1(1))*(1-0.9)/100 (6.246*10^-4/D.D_1(2))*
```

```
                (1-0.87)/100 (7.287*10^-4/D.D_1(3))*(1-0.865)/100
                (8.3281*10^-4/D.D_1(4))*(1-0.85)/100 (0.001093/D.D_1(5))*
                (1-0.7)/100 (0.0014/D.D_1(6))*(1-0.54)/100 (0.0022/D.D_1(7))
                *(1-0.1)/100];                    %[mol/l]

save('D','D')                  %save par as pardata in a .mat file
end
```

Sensitivity test

```
%Script for testing sensitivity of the model. By changing a number of
%parameters one by one the models sensitivity is evaluated by finite
%difference.

%The parameters tested are
% umax_EtOH, Y_eSO4, Y_EeSRB, Ks_EtOH, Ks_SO4,umax_Ac, kLa_H2S, Ks_Ac,
% V_liq, V_gas, N2g and pH

%Vector to store results in
vec     = zeros(1,12);

%Create a reference model to measure shift
var     = ones(1,12);               %Input vector of changes
R       = SRBsolver(var);           %Do calculation
gas_ref = R.Sulfidegas;             %Save reference result

%Test change in parameters
for i   = 1:12
var     = ones(1,12);               %Reset input vector to model

var(i)  = 1.01;                     %Add change to correct element
R       = SRBsolver(var);           %Retrieve result
gas_101 = R.Sulfidegas;             %Calculate gas partial pressure

%vec(i) = gas_101(end)-(gas_ref(end)); %save difference for plotting
vec(i)  =((gas_ref(end))-gas_101(end))/(gas_ref(end)); %Normalized value
end

%% PLOT result in bar graph
bfigure = figure;
bar(abs(vec));
set(get(bfigure,'Child'), 'XTickLabel', ...
    {'umax', 'Y.eSO4','Y.EeSRB', 'Ks.EtOH', 'Ks.SO4','umax.Ac', 'kLa.H_2S',
     '', 'V.liq', 'V.gas', 'N_2g', 'pH'})
xlabel('Parameters and variables')
ylabel('Output change [%]')
```

Run file for SRB parameter fitting

```
function res = SRB_run_fitting (guess,t_data,data_y)

% ODE solver, outputs and subplots for the output.

close all

indata = SRBparameters_fitting;
load par

Data = SRBpardata;
load D;

%Parameter for fitting
par.Ks_EtOH  = guess(1,1);
%par.umax_Ac    = guess(1,2);

%.....................................................................
% Time
%.....................................................................
tspan = linspace(0, 100, 100); % [h]

%=====================================================================
%Start values
%=====================================================================
S_Sred0 = 0;                %H2S liquid concentration
S_EtOH0 = 0.0615;           %EtOH concentration
S_SO40 = 0.0326;            %Sulfate concentration
X_eSRB0 = 0.018;            %EtOH biomass
S_Ac0 = 0.003;              %Acetate concentration
%X_aSRB0 = 0.1;             %Acetate biomass
S_HS0 = 0;                  %Dissolved H2S in HS form
%S_HCO3 = 0;                %Relation between CO2 and HCO3
S_H2S_g0 = 0.000001;        %H2S concentration gas phase
%S_CO2_g0 = 0.0001;         %CO2 in gas phase
%S_IC0 = 0;                 %Inorganic carbon in liquid phase

y0 = [ S_Sred0 S_EtOH0 S_SO40 X_eSRB0  S_HS0 S_Ac0 S_H2S_g0 ];

 %Running the simulation
    options = odeset('abstol', 10^-6, 'reltol', 10^-6);
    [t,y] = ode15s(@SRBmodel, tspan, y0, options,par);
    k=size(t,1);
    save ('t','t')

%=====================================================================
%Outputs
%=====================================================================
R.Reducedsulfur     = y(:,1);           %Reduced sulfur-liquid
R.Ethanol           = y(:,2);           %EtOH
R.Sulfate           = y(:,3);           %Sulfate
R.Ebiomass          = y(:,4);           %EtOH biomass
%R.Abiomass         = y(:,6);           %Acetate biomass
R.DisSulfide        = y(:,5);           %Dissolved H2S
%R.Carbonate        = y(:,6);           %Dissociated CO2
R.Acetate           = y(:,6);           %Acetate
R.Sulfidegas        = y(:,7);           %H2S gas phase
%R.Carbondioxidegas = y(:,8);           %CO2 gas phase
%R.ICarbonliquid    = y(:,9);           %Inorganic carbon in liquid phase
R.tspan             = linspace(0, 100, 100); %Time [h]
```

```
save ('R','R')

%Model output for fitting
%Ethanol_1 = pchip(t,R.Ethanol,D.t_2);
%Acetate_1 = pchip(t,R.Acetate,D.t_5);
Reducedsulfur_1 = pchip(t,R.Reducedsulfur,D.t_1);

%Out = [Ethanol_1,Acetate_1];
Out = [Reducedsulfur_1];

res=(Out);

%=========================================================================
% Plots
%=========================================================================
subplot(3,2,1)
plot(R.tspan,R.Reducedsulfur)
xlabel('Time [h]')
ylabel('Reduced sulfur-liquid  [mol/l]')
title('Reduced sulfur-liquid')
hold on
plot(D.t_1,D.H2S_1,'*')
xlabel('Time [h]')
ylabel('Reduced sulfur-liquid [mol/l]')
legend('model','exp values','location','best')

subplot(3,2,2)
plot(R.tspan,R.Ethanol)
xlabel('Time [h]')
ylabel('Ethanol [mol/l]')
title('Ethanol concentration')
hold on
plot(D.t_2,D.EtOH_1,'*')
xlabel('Time [h]')
ylabel('Ethanol [mol/l]')
legend('model','exp values','location','best')

subplot(3,2,3)
plot(R.tspan,R.Sulfate)
xlabel('Time [h]')
ylabel('Sulfate [mol/l]')
title('Sulfate concentration')
hold on
plot(D.t_3,D.SO4_1,'*')
xlabel('Time [h]')
ylabel('Sulfate [mol/l]')
legend('model','exp values','location','best')



subplot(3,2,4)
plot(R.tspan,R.Ebiomass)
xlabel('Time [h]')
ylabel('Ethanol Biomass [g/l]')
title('Biomass on Ethanol ')
hold on
plot(D.t_4,D.X_1,'*')
xlabel('Time [h]')
ylabel('Biomass [g/l]')
legend('model','exp values','location','best')
```

```
subplot(3,2,5)
plot(R.tspan,R.Acetate)
xlabel('Time [h]')
ylabel('Acetate [mol/l]')
title('Acetate concentration')
hold on
plot(D.t_5,D.Ac_1,'*')
xlabel('Time [h]')
ylabel('Acetate [mol/l]')
legend('model','exp values','location','best')

end
```

SRB parameter fitting file

```
function SRB_fitting

%Fits simulated data to experimental data by varying different parameters

Data = SRBpardata;
load D;

%Fitting to different data points

% t_data = [D.t_2];
% data_y = [D.EtOH_1];

t_data = [D.t_1];
data_y = [D.H2S_1];

% t_data = [D.t_1];
% data_y = [D.H2S_1];

% t_data = [D.t_2,D.t_5];
% data_y = [D.EtOH_1,D.Ac_1];

%x_data = R.Ethanol;
%EtOH_data = D.EtOH_1;

lb=[0];          %Lower bound
ub=[10];         %Upper bound
guess=[0.004];   %Guessed parameter value

options = optimset('TolFun',1e-4,'TolX',1e-4); %Steps

[BETA,resnorm,residual,exitflag,output,lambda,jacobian] = lsqcurvefit
(@(guess,t_data) SRB_run_fitting(guess,t_data,data_y),guess,t_data,
data_y,lb,ub,options)

%Confidence interval
ci=nlparci(BETA,residual,'jacobian',jacobian)
```

SRB solver adapted to Moosa et al. (2002)

```
% ODE solver, outputs and subplots for the output.
function [R] = SRBsolverMoosa

%.....................................................................
%Indata values
%.....................................................................
Data = SRBparametersMoosa;          %Load indata from parameter file
load par;

Data = SRBpardata;                  %Load data from literature
load D;
%.....................................................................
% Time and Dilution rates
%.....................................................................
par.dilution_test = [0.005 0.013 0.0145 0.0175 0.021 0.0275 0.0415];%[h^-1]

tspan = linspace(0, 240, 240); %[h]

%=====================================================================
% Start values
%=====================================================================
S_Sred0     = 0;            %Reduced sulfur-liquid
S_SO40      = 0.05205;      %Acetate concentration
S_Ac0       = 0.2964;       %Acetate concentration
X_aSRB0     = 0.0001;       %Acetate biomass
S_HS0       = 0;            %Dissolved H2S in HS form
S_IC0       = 0;            %Inorganic carbon-liquid
S_HCO3      = 0;            %Ion state of CO2 and HCO3
S_H2S_g0    = 0.0001;       %H2S concentration gas phase
S_CO2_g0    = 0.0001;       %CO2 in gas phase

y0 = [S_Sred0 S_Ac0 S_SO40 X_aSRB0 S_HS0 S_IC0 S_HCO3 S_H2S_g0 S_CO2_g0 ];

%Run simulation nr 1 with initial y0 values
par.dilution = par.dilution_test(1);
[t,y] = ode15s(@SRBmodelMoosa,tspan,y0,[],par);

%=====================================================================
% Outputs
%=====================================================================
R.Reducedsulfur_1     = y(:,1);       %Reduced sulfur-liquid
R.Acetate_1           = y(:,2);       %Acetate concentration
R.Sulfate_1           = y(:,3);       %SO4 concentration
R.Abiomass_1          = y(:,4);       %Acetate biomass
R.DisSulfide_1        = y(:,5);       %Dissolved H2S
R.ICarbonliquid_1     = y(:,6);       %Inorganic carbon-liquid
R.Carbonate_1         = y(:,7);       %Dissociated CO2
R.Sulfidegas_1        = y(:,8);       %H2S gas phase
R.Carbondioxidegas_1  = y(:,9);       %CO2 gas phase
R.tspan = linspace(0, 240, 240);      %Time [h]
R.t=t;


%Save the last output value from the given dilution rate
R.Reducedsulfur1_1      = R.Reducedsulfur_1(end);
R.Acetate1_1            = R.Acetate_1(end);
R.Sulfate1_1            = R.Sulfate_1(end);
R.Abiomass1_1           = R.Abiomass_1(end);
R.DisSulfide1_1         = R.DisSulfide_1(end);
```

```
R.ICarbonliquid1_1      = R.ICarbonliquid_1(end);
R.Carbonate1_1          = R.Carbonate_1(end);
R.Sulfidegas1_1         = R.Sulfidegas_1(end);
R.Carbondioxidegas1_1   = R.Carbondioxidegas_1(end);

%Create new y0-vector from output results
y0_1 = [R.Reducedsulfur1_1 R.Acetate1_1 R.Sulfate1_1 R.Abiomass1_1
        R.DisSulfide1_1 R.ICarbonliquid1_1 R.Carbonate1_1 R.Sulfidegas1_1
        R.Carbondioxidegas1_1];

%Run simulation nr 2 with new y0-values from the first run
par.dilution = par.dilution_test(2);
[t,y] = ode15s(@SRBmodelMoosa,tspan,y0_1,[],par);

%New outputs saved for a new y0 vector
R.Reducedsulfur_2     = y(:,1);       %Reduced sulfur-liquid
R.Acetate_2           = y(:,2);       %Acetate concentration
R.Sulfate_2           = y(:,3);       %SO4 concentration
R.Abiomass_2          = y(:,4);       %Acetate biomass
R.DisSulfide_2        = y(:,5);       %Dissolved H2S
R.ICarbonliquid_2     = y(:,6);       %Inorganic carbon-liquid
R.Carbonate_2         = y(:,7);       %Dissociated CO2
R.Sulfidegas_2        = y(:,8);       %H2S gas phase
R.Carbondioxidegas_2  = y(:,9);       %CO2 gas phase
R.tspan = linspace(0, 240, 240);      %Time [h]

R.Reducedsulfur2_2      = R.Reducedsulfur_2(end);
R.Acetate2_2            = R.Acetate_2(end);
R.Sulfate2_2            = R.Sulfate_2(end);
R.Abiomass2_2           = R.Abiomass_2(end);
R.DisSulfide2_2         = R.DisSulfide_2(end);
R.ICarbonliquid2_2      = R.ICarbonliquid_2(end);
R.Carbonate2_2          = R.Carbonate_2(end);
R.Sulfidegas2_2         = R.Sulfidegas_2(end);
R.Carbondioxidegas2_2   = R.Carbondioxidegas_2(end);

y0_2 = [R.Reducedsulfur_2(end) R.Acetate_2(end) R.Sulfate_2(end)
        R.Abiomass_2(end) R.DisSulfide_2(end)  R.ICarbonliquid_2(end)
        R.Carbonate_2(end) R.Sulfidegas_2(end) R.Carbondioxidegas_2(end)];

%Run simulation nr 3 with y0_2
par.dilution = par.dilution_test(3);
[t,y] = ode15s(@SRBmodelMoosa,tspan,y0_2,[],par);

R.Reducedsulfur_3     = y(:,1);       %Reduced sulfur-liquid
R.Acetate_3           = y(:,2);       %Acetate concentration
R.Sulfate_3           = y(:,3);       %SO4 concentration
R.Abiomass_3          = y(:,4);       %Acetate biomass
R.DisSulfide_3        = y(:,5);       %Dissolved H2S
R.ICarbonliquid_3     = y(:,6);       %Inorganic carbon-liquid
R.Carbonate_3         = y(:,7);       %Dissociated CO2
R.Sulfidegas_3        = y(:,8);       %H2S gas phase
R.Carbondioxidegas_3  = y(:,9);       %CO2 gas phase

R.Reducedsulfur3_3      = R.Reducedsulfur_3(end);
R.Acetate3_3            = R.Acetate_3(end);
R.Sulfate3_3            = R.Sulfate_3(end);
R.Abiomass3_3           = R.Abiomass_3(end);
R.DisSulfide3_3         = R.DisSulfide_3(end);
R.ICarbonliquid3_3      = R.ICarbonliquid_3(end);
R.Carbonate3_3          = R.Carbonate_3(end);
R.Sulfidegas3_3         = R.Sulfidegas_3(end);
```

```
R.Carbondioxidegas3_3   = R.Carbondioxidegas_3(end);

y0_3= [R.Reducedsulfur_3(end) R.Acetate_3(end) R.Sulfate_3(end)
       R.Abiomass_3(end) R.DisSulfide_3(end) R.ICarbonliquid_3(end)
       R.Carbonate_3(end) R.Sulfidegas_3(end) R.Carbondioxidegas_3(end)];

%Run simulation nr 4 with y0_3
par.dilution = par.dilution_test(4);
[t,y] = ode15s(@SRBmodelMoosa,tspan,y0_3,[],par);

R.Reducedsulfur_4     = y(:,1);       %Reduced sulfur-liquid
R.Acetate_4           = y(:,2);       %Acetate concentration
R.Sulfate_4           = y(:,3);       %SO4 concentration
R.Abiomass_4          = y(:,4);       %Acetate biomass
R.DisSulfide_4        = y(:,5);       %Dissolved H2S
R.ICarbonliquid_4     = y(:,6);       %Inorganic carbon-liquid
R.Carbonate_4         = y(:,7);       %Dissociated CO2
R.Sulfidegas_4        = y(:,8);       %H2S gas phase
R.Carbondioxidegas_4  = y(:,9);       %CO2 gas phase

R.Reducedsulfur4_4      = R.Reducedsulfur_4(end);
R.Acetate4_4            = R.Acetate_4(end);
R.Sulfate4_4            = R.Sulfate_4(end);
R.Abiomass4_4           = R.Abiomass_4(end);
R.DisSulfide4_4         = R.DisSulfide_4(end);
R.ICarbonliquid4_4      = R.ICarbonliquid_4(end);
R.Carbonate4_4          = R.Carbonate_4(end);
R.Sulfidegas4_4         = R.Sulfidegas_4(end);
R.Carbondioxidegas4_4   = R.Carbondioxidegas_4(end);

y0_4 = [R.Reducedsulfur_4(end) R.Acetate_4(end) R.Sulfate_4(end)
        R.Abiomass_4(end) R.DisSulfide_4(end)  R.ICarbonliquid_4(end)
        R.Carbonate_4(end) R.Sulfidegas_4(end) R.Carbondioxidegas_4(end)];

%Run simulation nr 5 with y0_4
par.dilution = par.dilution_test(5);
[t,y] = ode15s(@SRBmodelMoosa,tspan,y0_4,[],par);

R.Reducedsulfur_5     = y(:,1);       %Reduced sulfur-liquid
R.Acetate_5           = y(:,2);       %Acetate concentration
R.Sulfate_5           = y(:,3);       %SO4 concentration
R.Abiomass_5          = y(:,4);       %Acetate biomass
R.DisSulfide_5        = y(:,5);       %Dissolved H2S
R.ICarbonliquid_5     = y(:,6);       %Inorganic carbon-liquid
R.Carbonate_5         = y(:,7);       %Dissociated CO2
R.Sulfidegas_5        = y(:,8);       %H2S gas phase
R.Carbondioxidegas_5  = y(:,9);       %CO2 gas phase

R.Reducedsulfur5_5      = R.Reducedsulfur_5(end);
R.Acetate5_5            = R.Acetate_5(end);
R.Sulfate5_5            = R.Sulfate_5(end);
R.Abiomass5_5           = R.Abiomass_5(end);
R.DisSulfide5_5         = R.DisSulfide_5(end);
R.ICarbonliquid5_5      = R.ICarbonliquid_5(end);
R.Carbonate5_5          = R.Carbonate_5(end);
R.Sulfidegas5_5         = R.Sulfidegas_5(end);
R.Carbondioxidegas5_5   = R.Carbondioxidegas_5(end);

y0_5 = [R.Reducedsulfur_5(end) R.Acetate_5(end) R.Sulfate_5(end)
        R.Abiomass_5(end) R.DisSulfide_5(end) R.ICarbonliquid_5(end)
        R.Carbonate_5(end) R.Sulfidegas_5(end) R.Carbondioxidegas_5(end)];
```

```
%Run simulation nr 6 with y0_5
par.dilution = par.dilution_test(6);
[t,y] = ode15s(@SRBmodelMoosa,tspan,y0_5,[],par);

R.Reducedsulfur_6     = y(:,1);       %Reduced sulfur-liquid
R.Acetate_6           = y(:,2);       %Acetate concentration
R.Sulfate_6           = y(:,3);       %SO4 concentration
R.Abiomass_6          = y(:,4);       %Acetate biomass
R.DisSulfide_6        = y(:,5);       %Dissolved H2S
R.ICarbonliquid_6     = y(:,6);       %Inorganic carbon-liquid
R.Carbonate_6         = y(:,7);       %Dissociated CO2
R.Sulfidegas_6        = y(:,8);       %H2S gas phase
R.Carbondioxidegas_6  = y(:,9);       %CO2 gas phase

R.Reducedsulfur6_6      = R.Reducedsulfur_6(end);
R.Acetate6_6            = R.Acetate_6(end);
R.Sulfate6_6            = R.Sulfate_6(end);
R.Abiomass6_6           = R.Abiomass_6(end);
R.DisSulfide6_6         = R.DisSulfide_6(end);
R.ICarbonliquid6_6      = R.ICarbonliquid_6(end);
R.Carbonate6_6          = R.Carbonate_6(end);
R.Sulfidegas6_6         = R.Sulfidegas_6(end);
R.Carbondioxidegas6_6   = R.Carbondioxidegas_6(end);

y0_6 = [R.Reducedsulfur_6(end) R.Acetate_6(end) R.Sulfate_6(end)
        R.Abiomass_6(end) R.DisSulfide_6(end) R.ICarbonliquid_6(end)
        R.Carbonate_6(end) R.Sulfidegas_6(end) R.Carbondioxidegas_6(end)];

%Run simulation nr 7 with y0_6
par.dilution = par.dilution_test(7);
[t,y] = ode15s(@SRBmodelMoosa,tspan,y0_6,[],par);

R.Reducedsulfur_7     = y(:,1);       %Reduced sulfur-liquid
R.Acetate_7           = y(:,2);       %Acetate concentration
R.Sulfate_7           = y(:,3);       %SO4 concentration
R.Abiomass_7          = y(:,4);       %Acetate biomass
R.DisSulfide_7        = y(:,5);       %Dissolved H2S
R.ICarbonliquid_7     = y(:,6);       %Inorganic carbon-liquid
R.Carbonate_7         = y(:,7);       %Dissociated CO2
R.Sulfidegas_7        = y(:,8);       %H2S gas phase
R.Carbondioxidegas_7  = y(:,9);       %CO2 gas phase

R.Reducedsulfur7_7      = R.Reducedsulfur_7(end);
R.Acetate7_7            = R.Acetate_7(end);
R.Sulfate7_7            = R.Sulfate_7(end);
R.Abiomass7_7           = R.Abiomass_7(end);
R.DisSulfide7_7         = R.DisSulfide_7(end);
R.ICarbonliquid7_7      = R.ICarbonliquid_7(end);
R.Carbonate7_7          = R.Carbonate_7(end);
R.Sulfidegas7_7         = R.Sulfidegas_7(end);
R.Carbondioxidegas7_7   = R.Carbondioxidegas_7(end);

R.Reducedsulfur = [R.Reducedsulfur1_1 R.Reducedsulfur2_2 R.Reducedsulfur3_3
                   R.Reducedsulfur4_4 R.Reducedsulfur5_5 R.Reducedsulfur6_6
                   R.Reducedsulfur7_7];
R.Acetate       = [R.Acetate1_1 R.Acetate2_2 R.Acetate3_3 R.Acetate4_4
                   R.Acetate5_5 R.Acetate6_6 R.Acetate7_7];
R.Sulfate       = [R.Sulfate1_1 R.Sulfate2_2 R.Sulfate3_3 R.Sulfate4_4
                   R.Sulfate5_5 R.Sulfate6_6 R.Sulfate7_7];
R.Abiomass      = [R.Abiomass1_1 R.Abiomass2_2 R.Abiomass3_3 R.Abiomass4_4
                   R.Abiomass5_5 R.Abiomass6_6 R.Abiomass7_7];
```

```
%=========================================================================
%Plots
%=========================================================================
subplot(3,2,1)
plot(D.D_1,D.Ac_2,'*')
xlabel('Dilution rate [h^-1]')
ylabel('Acetate  [mol/l]')
title('Acetate concentration')
hold on
plot(D.D_1,R.Acetate)
xlabel('Dilution rate [h^-1]')
ylabel('Acetate [mol/l]')
legend('lit values','model','location','best')

subplot(3,2,2)
plot(D.D_1,D.X_2,'*')
xlabel('Dilution rate [h^-1]')
ylabel('Acetate biomass [mol/l]')
title('Biomass concentration')
hold on
plot(D.D_1,R.Abiomass)
xlabel('Dilution rate [h^-1]')
ylabel('Acetate biomass [mol/l]')
legend('exp values','model','location','best')

subplot(3,2,3)
plot(D.D_1,D.SO4_2,'*')
xlabel('Dilution rate [h^-1]')
ylabel('Sulfate [mol/l]')
title('Sulfate concentration')
hold on
plot(D.D_1,R.Sulfate)
xlabel('Dilution rate [h^-1]')
ylabel('Sulfate [mol/l]')
legend('exp values','model','location','best')

subplot(3,2,4)
plot(D.D_1,D.H2S_2,'*')
xlabel('Dilution rate [h^-1]')
ylabel('Reduced sulfur-liquid [mol/l]')
title('Reduced sulfur-liquid concentration ')
hold on
plot(D.D_1,R.Reducedsulfur)
xlabel('Dilution rate [h^-1]')
ylabel('Reduced sulfur-liquid [mol/l]')
legend('exp values','model','location','best')

end
```

Appendix B – Aspen Plus Results

Table R: The result summary for the different blocks specified in Aspen Plus

Sep			
Name	BACE	BETH	SEPW
Property method	ELECNRTL	ELECNRTL	ELECNRTL
Henry's component list ID	GLOBAL	GLOBAL	GLOBAL
Electrolyte chemistry ID	GLOBAL	GLOBAL	GLOBAL
Use true species approach for electrolytes	YES	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA	STEAM-TA
Water solubility method	3	3	3
Inlet flash pressure [atm]	0	0	0
First outlet flash temperature [C]		25	
First outlet flash pressure [atm]		1	
First outlet flash temperature change [K]			
First outlet flash vapor fraction			
First outlet flash temperature estimate [K]			
First outlet flash pressure estimate [atm]			
Second outlet flash temperature			
Second outlet flash pressure			
Second outlet flash temperature change			
Second outlet flash vapor fraction			
Second outlet flash temperature estimate			
Second outlet flash pressure estimate			
EO Model components			
Heat duty [cal/sec]	0,081766794	-0,064415854	0,215016977
Total feed stream CO2e flow [kg/hr]	0,076700535	0,002512768	0,048436435
Total product stream CO2e flow [kg/hr]	0,086786702	0,002565669	0,052065555
Net stream CO2e production [kg/hr]	0,010086168	5,29014E-05	0,003629119
Utility CO2e production [kg/hr]	0	0	0
Total CO2e production [kg/hr]	0,010086168	5,29014E-05	0,003629119
Utility usage			
Utility cost			
Utility ID			

REquil		
Name	PH1,5	PH4,5
Property method	ELECNRTL	ELECNRTL
Henry's component list ID	GLOBAL	GLOBAL
Electrolyte chemistry ID	GLOBAL	GLOBAL
Use true species approach for electrolytes	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA
Water solubility method	3	3
Specified pressure [atm]	0,986923267	0,986923267
Specified temperature [K]	293,15	293,15

Specified vapor fraction		
Specified heat duty [cal/sec]		
Products generation: molar extent [mol/hr]	0,0000001	0,1
Temperature approach [K]	0	0
EO Model components		
Outlet temperature [K]	293,15	293,15
Outlet pressure [atm]	0,986923267	0,986923267
Calculated heat duty [cal/sec]	-0,013481138	-0,51576011
Net heat duty [cal/sec]	-0,013481138	-0,51576011
Calculated vapor fraction	0,018748487	6,69047E-06
Total feed stream CO2e flow [kg/hr]	0,039606627	0,002941899
Total product stream CO2e flow [kg/hr]	0,039606627	0,002941899
Net stream CO2e production [kg/hr]	0	0
Utility CO2e production [kg/hr]	0	0
Total CO2e production [kg/hr]	0	0
Utility usage		
Utility cost		
Utility ID		
RBatch		
Name	BATCHACE	BATCHETH
Property method	ELECNRTL	ELECNRTL
Henry's component list ID	GLOBAL	GLOBAL
Electrolyte chemistry ID	GLOBAL	GLOBAL
Use true species approach for electrolytes	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA
Water solubility method	3	3
Reactor pressure [bar]	1	1
Total cycle time [hr]	30,1237	30
Batch feed time [hr]	5	10
Down time [hr]	0,01	0,01
Stop criterion number	2	1
Reaction time [hr]	20	16,7658791
Heat load per cycle [cal/sec]	2,11909026	-22,987958
Reactor minimum temperature [K]	303,030091	302,87051
Reactor maximum temperature [K]	303,561643	312,06857
Maximum volume deviation		
Maximum volume deviation time		
Total feed stream CO2e flow [kg/hr]	0,001309285	0,00067589
Total product stream CO2e flow [kg/hr]	0,076700535	0,002512768
Net stream CO2e production [kg/hr]	0,075391249	0,001836878

Mixer								
Name	M0	M1	M2	M3	M4	M5	M6	MG
Property method	ELECNRTL	ELECNRTL	ELECNRTL	ELECNRTL	ELECNRTL	ELECNRTL	ELECNRTL	ELECNRTL

Henry's component list ID	GLOBAL	GLOBAL	GLOBAL	GLOBAL	GLOBAL	GLOBAL	GLOBAL	GLOBAL
Electrolyte chemistry ID	GLOBAL	GLOBAL	GLOBAL	GLOBAL	GLOBAL	GLOBAL	GLOBAL	GLOBAL
Use true species approach for electrolytes	YES	YES	YES	YES	YES	YES	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA	STEAM-TA
Water solubility method	3	3	3	3	3	3	3	3
Specified pressure [atm]	0	0	0	0	0	0	0	0
Temperature estimate [K]								
EO Model components								
Outlet temperature [K]	293,133596	293,147438	293,297186	293,683269	294,599857	295,130517	305,427284	303,146675
Calculated outlet pressure [atm]	0,986923267	0,986923267	0,986923267	0,986923267	0,986923267	0,986923267	0,986923267	0,986923267
Vapor fraction	0,018772377	0	0,000132455	9,02411E-06	0	0	0	1
First liquid /Total liquid	1	1	1	1	1	1	1	1
Total feed stream CO2e flow [kg/hr]	0,039606651	0,001342816	0,001630166	0,002986947	0,002612812	0,000671557	0,000689151	0,039606651
Total product stream CO2e flow [kg/hr]	0,039606627	0,001342817	0,002986947	0,002941899	0,000671557	0,000689151	0,000675689	0,039606651
Net stream CO2e production [kg/hr]	-2,40856E-08	1,45355E-09	0,001356781	-4,50473E-05	-0,001941254	1,75932E-05	-1,32611E-05	0
FSplit								
Name					01-sep	02-sep		
Property method					ELECNRTL	ELECNRTL		
Henry's component list ID					GLOBAL	GLOBAL		
Electrolyte chemistry ID					GLOBAL	GLOBAL		
Use true species approach for electrolytes					YES	YES		
Free-water phase properties method					STEAM-TA	STEAM-TA		
Water solubility method					3	3		
First outlet stream								
First specified split fraction								
First calculated split fraction					0,89703253	0,005518967		
First actual volume flow [l/min]								

First limit flow [kmol/hr]		
First volume limit flow [l/min]		0,006
First cum limit flow [kmol/hr]		
First cum volume limit flow [l/min]		
First residual fraction		
Second outlet stream		
Second specified split fraction		
EO Model components		
Second calculated split fraction	0,10296747	0,994481033
Second actual volume flow [l/min]		
Second limit flow [kmol/hr]		
Second volume limit flow [l/min]	0,006	
Second cum limit flow [kmol/hr]		
Second cum volume limit flow [l/min]		
Second residual fraction		
Total feed stream CO2e flow [kg/hr]	0,002912728	0,052065555
Total product stream CO2e flow [kg/hr]	0,002912728	0,052065555
Net stream CO2e production [kg/hr]	0	0

SSplit	
Name	SUBSPLIT
Property method	ELECNRTL
Henry's component list ID	GLOBAL
Electrolyte chemistry ID	GLOBAL
Use true species approach for electrolytes	YES
Free-water phase properties method	STEAM-TA
Water solubility method	3
First outlet stream	
First specified split fraction	
First flow [kmol/hr]	
First calculated split fraction	0
Second outlet stream	
Second specified split fraction	1
Second flow [kmol/hr]	
Second calculated split fraction	1
Total feed stream CO2e flow [kg/hr]	0,002912728
Total product stream CO2e flow [kg/hr]	0,002912728
Net stream CO2e production [kg/hr]	0

Name	C1	C2
Property method	ELECNRTL	ELECNRTL
Henry's component list ID	GLOBAL	GLOBAL
Electrolyte chemistry ID	GLOBAL	GLOBAL
Use true species approach for electrolytes	YES	YES
Free-water phase properties method	STEAM-TA	STEAM-TA
Water solubility method	3	3
Model	DECANTER	DECANTER

Fraction of solids to solid outlet	1	0,999
Fraction of liquid to liquid outlet	0,99	
liquid load of solid oulet stream	0,001	
Solid load of liquid outlet stream	0,01	0,01
Characteristic of separation	VELOCITY	VELOCITY
Separation sharpness	0	0
Offset of fines	0	0
Ratio of liquid surface to radius	0,738	0,738
Ratio of filter cake surface to radius	0,79	0,79
Ratio of height to radius	0,9545	0,9545
Decanter classification model	IDEAL-SEP	IDEAL-SEP
Disc classification model	IDEAL-SEP	IDEAL-SEP
Pusher classification model	IDEAL-SEP	IDEAL-SEP
Cut size [meter]		
Boundary particle size [meter]		
Consider concentration effect	NO	NO
Consider drag effect	NO	NO
Drag effect model	LANGELOH	LANGELOH
Shear gradient [m/sqsec]		
Laminar flow	NO	NO
Friction factor		
Critical particle size [meter]		
Separation sharpness		
Area ratio factor	0,85	0,85
Decanter deliquoring model	SPEC-RM	SPEC-RM
Disc deliquoring model	SPEC-RM	SPEC-RM
Pusher deliquoring model	RM	RM
Perforated basket deliquoring model	ESTIM-RM	ESTIM-RM
Residual moisture	0,1	0,1
Residual moisture at small throughput		
Critical throughput [kg/hr]		
Stahl f1 parameter [sqm/sqsec]		
Redeker correlation factor a		
Redeker correlation exponent b		
Stadager f2 parameter		
Schubert saturation coefficient	2,5	2,5
Residual cake saturation		
Filter cake specific resistance [meter/kg]		
Filter cake medium resistance [1/meter]		
Bulk flow resistance [1/sqm]		
Porosity	0,45	0,45
Average sphericity	0,75	0,75
Average diameter [meter]		
Drum diameter [meter]		
Cylindrical length [meter]		

Solids discharge diameter [meter]		
Cone angle		
Number of screw starts	1	1
Screw blade pitch [meter]		
Gap width [meter]		
Beach residence time [hr]		
Transport angle		
Screw blade angle		
Bulk angle		
Drum friction factor		
Screw friction factor		
Advancing screw	NO	NO
Solids feed on pond surface	NO	NO
Drum rotary speed [rpm]		
Differential rotary speed [rpm]		
Pond depth [meter]		
Outer disc radius [meter]		
Inner disc radius [meter]		
Number of discs	1	1
Height of channel [meter]		
Angle of disc		
Decanter drum rotary speed [rpm]		
Stroke length [meter]		
Sieve friction factor		
Product friction factor		
Pusher drum rotary speed [rpm]		
Push frequency [1/hr]		
Calculated fraction of solids to solid outlet		
Calculated fraction of liquid to liquid outlet		
Calculated Solid load of liquid outlet		
Calculated Liquid load of solid outlet		
Calcultaed D50 of separation curve		
Calculated residual moisture	0,1	0,1
Calculated dry substance content	0,9	0,9
Calculated liquid load	0,111111111	0,111111111
Calculated critical throughput		
Calculated drag out particle size		
Calculated shear gradient		
Calculated reduced clarifying length		
Calculated wall shear stress		
Calculated number of filtration		
Calculated cake height (1st stage)		
Calculated cake height (2nd stage)		
Calculated total separation grade	1	1
Calculated solid mass concentration (1st stage)	0	0

Calculated solid mass concentration (2nd stage)		
Calculated solid volume concentration (1st stage)	0	0
Calculated solid volume concentration (2nd stage)		
Calculated conveying efficiency		
Calculated residence time		
Calculated transport angle		
Calculated axial bulk flow		
Calculated bulk height at screw blade		
Calculated dimensionless residence time		
Calculated bulk flow resistance		
Calculated particle diameter [meter]	0,0001	0,0001
Calculated bowl radius		
Calculated revolution speed		
Calculated basket height		
Calculated moisture content		
Total feed stream CO2e flow [kg/hr]	0,001342838	0,002912764
Total product stream CO2e flow [kg/hr]	0,001342838	0,002912764
Net stream CO2e production [kg/hr]	0	0
Design Specs		
Name	PH	PH7
Specification	PH4	PH7
Specification target	4,5	7
Specification tolerance	0,2	0,8
Lower bound	0,001	0,0001
Upper bound	0,1	0,1

Table S: The results for all the streams connected to the precipitatoin part of the process.

Substream: ALL (MIXED AND CIDSD)									
Component Mass Flow									
	Units	PH1,5IN	PH1P1	CUS	PH2P1	ZNS	PH1P4	H2SG	H2SL
From		M0	PH1,5	C1	PH4,5	C2	M3	MG	02-sep
To		PH1,5	C1		C2		PH4,5	M0	M2
ZN++		0,00445638	0,00445638	7,17E-08	4,46E-05	5,54E-10	0,00445652	0	2,14E-07
ZNS		0	0	0,00E+00	6,58E-03	6,58E-03	0	0	0,00E+00
CU++	G/MIN	0,00420772	4,21E-05	6,77E-10	4,23E-05	5,25E-10	4,23E-05	0	2,03E-07
CUS	G/MIN	0	6,27E-03	6,27E-03	0,00E+00	0,00E+00	0,00E+00	0	0,00E+00
NI++	G/MIN	0	0	0	0	0	0	0	0
NIS	G/MIN	0	0	0	0	0	0	0	0
S--	G/MIN	5,93E-21	5,93E-21	9,54E-26	1,02E-14	1,27E-19	1,02E-14	0	4,17E-08
WATER	G/MIN	4,31E+01	4,31E+01	6,93E-04	5,85E+01	7,26E-04	5,85E+01	0	2,73E-01
H2S	G/MIN	0,440685	0,0421214	6,77E-07	0,059657	7,41E-07	0,0621058	0,4375034	0,00386882
HS-	G/MIN	1,48E-07	1,48E-07	2,37E-12	0,000224	2,79E-09	0,00022427	0	0,015864
CO2	G/MIN	6,60E-01	2,24E-02	3,60E-07	0,047824	5,94E-07	0,0481879	0,6603572	0,00486083
HCO3-	G/MIN	5,57E-07	5,57E-07	8,95E-12	0,001214	1,51E-08	0,00121394	0	0,0269745
H+	G/MIN	0,00E+00	0,00E+00	0,00E+00	0	0,00E+00	0	0	0
OH-	G/MIN	2,13E-13	2,13E-13	3,43E-18	3,17E-10	3,94E-15	3,17E-10	0	2,62E-08
HSO4-	G/MIN	8,18E-02	8,18E-02	1,32E-06	2,03E-04	2,52E-09	2,03E-04	0	8,52E-10
SO4--	G/MIN	0,0546537	0,0546537	8,79E-07	0,1531223	1,90E-06	0,1531223	0	1,77E-02
H3O+	G/MIN	0,0325617	0,0350558	5,64E-07	0,00260862	3,24E-08	4,16E-05	0	4,53E-11
CO3--	G/MIN	1,52E-15	1,52E-15	2,44E-20	3,65E-09	4,53E-14	3,65E-09	0	3,22E-03
N2	G/MIN	5,21E-01	3,36E-04	5,40E-09	2,38E-04	2,95E-09	3,36E-04	0,00021339	0
H2SO4	G/MIN	1,60E-12	1,60E-12	2,57E-17	4,25E-18	5,28E-23	4,25E-18	0	3,11E-27
NAOH	G/MIN	0,00E+00	0,00E+00	0,00E+00	0,00E+00	0,00E+00	0,00E+00	0	0,00E+00
NA+	G/MIN	0	0	0	0,0733969	9,12E-07	0,0733969	0	0,0387256
NA2SO4	G/MIN	0	0	0	0	0,00E+00	0	0	0
ETHANOL	G/MIN	0	0	0	0,00304119	3,78E-08	0,00304119	0	0,00304096
ACETIC AC	G/MIN	0	0	0	0,0102429	1,27E-07	0,0102429	0	3,25E-06
ACETATE	G/MIN	0	0	0	0,00683902	8,49E-08	0,00683902	0	1,69E-02
Solid Fraction		0	2,74E-05	0,6298564	2,07E-05	6,25E-01	0	0	0
Component Mole Flow									
ZN++	MOL/H	0,00408911	0,00408911	6,58E-08	4,09E-05	5,08E-10	0,00408924	0	1,96E-07
ZNS	MOL/H	0	0	0	0,00404835	0,00404835	0	0	0
CU++	MOL/H	0,00397299	3,97E-05	6,39E-10	3,99E-05	4,96E-10	3,99E-05	0	1,92E-07

CUS	MOL/H	0	0,00393326	0,00393326	0	0	0	0	0
NI++	MOL/H	0	0	0	0	0	0	0	0
NIS	MOL/H	0	0	0	0	0	0	0	0
S--	MOL/H	1,11E-20	1,11E-20	1,78E-25	1,92E-14	2,38E-19	1,92E-14	0	7,81E-08
WATER	MOL/H	143,508	143,435	0,00230653	194,7067	0,0024185	194,7148	0	0,9076925
H2S	MOL/H	0,7758111	0,0741533	1,19E-06	0,1050233	1,30E-06	0,1093352	0,77021	0,00681093
HS-	MOL/H	2,68E-07	2,68E-07	4,31E-12	0,00040684	5,05E-09	0,00040684	0	0,0287788
CO2	MOL/H	0,900286	0,0305162	4,91E-07	0,0652004	8,10E-07	0,0656962	0,9002866	0,00662692
HCO3-	MOL/H	5,47E-07	5,47E-07	8,80E-12	0,0011937	1,48E-08	0,0011937	0	0,0265246
H+	MOL/H	0	0	0	0	0	0	0	0
OH-	MOL/H	7,52E-13	7,52E-13	1,21E-17	1,12E-09	1,39E-14	1,12E-09	0	9,23E-08
HSO4-	MOL/H	0,0505563	0,0505563	8,13E-07	0,00012559	1,56E-09	0,00012559	0	5,27E-10
SO4--	MOL/H	0,0341355	0,0341355	5,49E-07	0,0956369	1,19E-06	0,0956369	0	0,0110717
H3O+	MOL/H	0,1027041	0,1105706	1,78E-06	0,00822794	1,02E-07	0,00013123	0	1,43E-10
CO3--	MOL/H	1,52E-15	1,52E-15	2,44E-20	3,65E-09	4,53E-14	3,65E-09	0	0,00322197
N2	MOL/H	1,115141	0,00071925	1,16E-08	0,00050906	6,32E-09	0,00071924	0,00045704	0
H2SO4	MOL/H	9,78E-13	9,78E-13	1,57E-17	2,60E-18	3,23E-23	2,60E-18	0	1,90E-27
NAOH	MOL/H	0	0	0	0	0	0	0	0
NA+	MOL/H	0	0	0	0,1915601	2,38E-06	0,1915601	0	0,1010709
NA2SO4	MOL/H	0	0	0	0	0	0	0	0
ETHANOL	MOL/H	0	0	0	0,00396082	4,92E-08	0,00396082	0	0,00396053
ACETIC AC	MOL/H	0	0	0	0,0102339	1,27E-07	0,0102339	0	3,25E-06
ACETATE	MOL/H	0	0	0	0,00694962	8,63E-08	0,00694962	0	0,0171805

Results for the streams concerning the bioreactor

Table T: The results for all the streams connected to the bioreactor part of the process.

	Units	**BP2**	**H2SG**	**H2SL**	**BIN**	**SO4**	**ETOH**
From		BATCHACE	MG	SEP2	M6		
To		BACE	M0	M2	BATCHETH	M6	M5
Substream: ALL							
Mole Flow_MOL/HR	MOL/HR	281,5391	1,670954	1,112943	269,4837	31,93503	8,163671

Mole Flow_KMOL/HR	KMOL/HR	0,2815391	0,00167095	0,00111294	0,2694837	0,031935	0,00816367
Component Mole Flow							
ZN++	MOL/HR	3,67141E-05	0	1,96353E-07	3,67141E-05	0	0
ZNS	MOL/HR	0	0	0	0	0	0
CU++	MOL/HR	3,58418E-05	0	1,91688E-07	3,58418E-05	0	0
CUS	MOL/HR	0	0	0	0	0	0
NI++	MOL/HR	0	0	0	0	0	0
NIS	MOL/HR	0	0	0	0	0	0
S--	MOL/HR	9,20599E-06	0	7,80677E-08	1,19243E-09	0	0
WATER	MOL/HR	242,0321	0	0,9076925	233,2558	3,991878	0,4081835
H2S	MOL/HR	1,713275	0,77021	0,00681093	0,0571355	0	0
HS-	MOL/HR	5,198309	0	0,0287788	0,0375218	0	0
CO2	MOL/HR	1,744144	0,9002866	0,00662692	0,0145201	0	0
HCO3-	MOL/HR	5,510634	0	0,0265246	0,0450382	0	0
H+	MOL/HR	0	0	0	0	0	0
OH-	MOL/HR	2,17278E-05	0	9,22526E-08	3,35536E-07	3,50602E-08	3,0807E-14
HSO4-	MOL/HR	1,66112E-07	0	5,2679E-10	5,56187E-05	3,49525E-08	0
SO4--	MOL/HR	2,070205	0	0,0110717	9,400304	9,314382	0
H3O+	MOL/HR	5,82061E-08	0	1,4288E-10	5,32787E-06	1,0777E-10	3,0807E-14
CO3--	MOL/HR	0,4184246	0	0,00322197	5,16353E-05	0	0
N2	MOL/HR	0	0,000457044	0	0,000457044	0	0
H2SO4	MOL/HR	0	0	1,8995E-27	3,0569E-20	4,368E-26	0
NAOH	MOL/HR	0	0	0	0	0	0
NA+	MOL/HR	18,89828	0	0,1010709	18,89828	18,62876	0
NA2SO4	MOL/HR	0	0	0	0	0	0
ETHANOL	MOL/HR	0,7405415	0	0,00396053	7,759043	0	7,755487
ACETICAC	MOL/HR	0,000843795	0	3,24555E-06	0,000325689	0	0
ACETATE	MOL/HR	3,212182	0	0,0171805	0,0151021	0	0
Substream: MIXED							
Phase: All							
Volume Flow	L/MIN	1,535674	0,694311	0,006	0,0827448	0,0112817	0,0077787
Solid Fraction		0	0	0	0	0	0
Vapor Fraction		0,0122848	1	0,0121061	0	0	0

Table U: The results for all the streams connected to the pH adjustments in the process.

PH	Units	PH1P4	NAOH0,1	PH2P4	2NAOH0,1
From		M3		01-sep	
To		PH4,5	M3	M4	M4
Substream: ALL					
Component Mass Flow					
ZN++	G/MIN	0,004457	0	4,00E-05	0
ZNS	G/MIN	0	0	0,00E+00	0
CU++	G/MIN	4,23E-05	0	3,80E-05	0
CUS	G/MIN	0,00E+00	0	0,00E+00	0
NI++	G/MIN	0	0	0	0
NIS	G/MIN	0	0	0	0
S--	G/MIN	1,02E-14	0	9,20E-15	0
WATER	G/MIN	5,85E+01	15,05626	5,25E+01	16,20869
H2S	G/MIN	0,062106	0	0,053561	0
HS-	G/MIN	0,000224	0	0,000201	0
CO2	G/MIN	4,82E-02	0	4,29E-02	0
HCO3-	G/MIN	0,001214	0	0,00109	0
H+	G/MIN	0,00E+00	0	0,00E+00	0
OH-	G/MIN	3,17E-10	0,02565	2,85E-10	0,027646
HSO4-	G/MIN	2,03E-04	0	1,82E-04	0
SO4--	G/MIN	1,53E-01	0	1,37E-01	0
H3O+	G/MIN	4,16E-05	3,80E-14	0,002342	6,01E-14
CO3--	G/MIN	3,65E-09	0,00E+00	3,28E-09	0,00E+00
N2	G/MIN	3,36E-04	0	2,13E-04	0
H2SO4	G/MIN	4,25E-18	0	3,82E-18	0
NAOH	G/MIN	0,00E+00	0	0,00E+00	0
NA+	G/MIN	0,073397	0,034671	0,065897	0,037368
NA2SO4	G/MIN	0	0	0	0
ETHANOL	G/MIN	0,003041	0	0,00273	0
ACETICAC	G/MIN	0,010243	0	0,009196	0
ACETATE	G/MIN	0,006839	0	0,00614	0
Component Mole Flow					
ZN++	MOL/H	0,004089	0	3,67E-05	0
ZNS	MOL/H	0,00E+00	0	0,00E+00	0
CU++	MOL/H	3,99E-05	0	3,58E-05	0
CUS	MOL/H	0,00E+00	0	0,00E+00	0
NI++	MOL/H	0	0	0	0
NIS	MOL/H	0	0	0	0
S--	MOL/H	1,92E-14	0	1,72E-14	0
WATER	MOL/H	1,95E+02	50,14497	1,75E+02	53,98313
H2S	MOL/H	0,109335	0	0,094292	0
HS-	MOL/H	0,000407	0	3,65E-04	0
CO2	MOL/H	6,57E-02	0	5,85E-02	0
HCO3-	MOL/H	1,19E-03	0	1,07E-03	0

H+	MOL/H	0,00E+00	0	0,00E+00	0
OH-	MOL/H	1,12E-09	0,090489	1,00E-09	0,097528
HSO4-	MOL/H	1,26E-04	0,00E+00	1,13E-04	0,00E+00
SO4--	MOL/H	9,56E-02	0	8,59E-02	0
H3O+	MOL/H	1,31E-04	1,20E-13	7,39E-03	1,90E-13
CO3--	MOL/H	3,65E-09	0,00E+00	3,28E-09	0,00E+00
N2	MOL/H	7,19E-04	0	4,57E-04	0
H2SO4	MOL/H	2,60E-18	0	2,34E-18	0
NAOH	MOL/H	0,00E+00	0	0,00E+00	0
NA+	MOL/H	0,19156	0,090489	0,171987	0,097528
NA2SO4	MOL/H	0	0,00E+00	0	0,00E+00
ETHANOL	MOL/H	0,003961	0	0,003556	0
ACETICAC	MOL/H	1,02E-02	0	9,19E-03	0
ACETATE	MOL/H	6,95E-03	0	6,24E-03	0
Mole Flow	MOL/H	1,95E+02	50,32595	1,75E+02	54,17819
Volume Flow	L/MIN	0,059295	0,015065	0,052727	0,016237

Appendix C – Aspen Plus Simulation Code

CALCULATOR BLOCK: CUS1

SAMPLED VARIABLES:

H2S	: H2S MOLEFLOW IN STREAM H2SG SUBSTREAM MIXED
EH2S	: H2S MOLEFLOW IN STREAM EXTRAGAS SUBSTREAM MIXED
COPPER	: CU++ MOLEFLOW IN STREAM LEACH SUBSTREAM MIXED
LEAFLOW	: STDVOL-FLOW IN STREAM LEACH SUBSTREAM MIXED
GASFLOW	: STDVOL-FLOW IN STREAM H2SG SUBSTREAM MIXED
EGASFLOW	: STDVOL-FLOW IN STREAM EXTRAGAS SUBSTREAM MIXED
INFLOW	: STDVOL-FLOW IN STREAM PH1,5IN SUBSTREAM MIXED
TEMP	: SENTENCE=PARAM VARIABLE=TEMP IN UOS BLOCK PH1,5
OXONIUM	: H3O+ MOLEFLOW IN STREAM PH1,5IN SUBSTREAM MIXED
RATEA	: SENTENCE=EXTENT-SPEC VARIABLE=EXTENT ID1=2 IN UOS BLOCK PH1,5

FORTRAN STATEMENTS:

```
      REAL H2S, EH2S, COPPER, OXONIUM
      REAL LEAFLOW, GASFLOW, EGASFLOW, INFLOW, TEMP
      REAL K, L, M, N, O, P
      REAL PH, RATEA
       A = .00000001
      IF (H2S .EQ. 0.) THEN
       H2S = H2S + A
      ENDIF
      IF (EH2S .EQ. 0.) THEN
       EH2S = EH2S + A
      ENDIF
      IF (COPPER .EQ. 0.) THEN
       COPPER = COPPER + A
      ENDIF
      IF (LEAFLOW .EQ. 0.) THEN
       LEAFLOW = LEAFLOW + A
      ENDIF
      IF (GASFLOW .EQ. 0.) THEN
       GASFLOW = GASFLOW + A
      ENDIF
      IF (EGASFLOW .EQ. 0.) THEN
       EGASFLOW = EGASFLOW + A
      ENDIF
      IF (INFLOW .EQ. 0.) THEN
       INFLOW = INFLOW + A
      ENDIF
      IF (TEMP .EQ. 0.) THEN
       TEMP = TEMP + A
      ENDIF
      IF (OXONIUM .EQ. 0.) THEN
```

```
      OXONIUM = OXONIUM + A
      ENDIF
      K = ( (H2S/GASFLOW) + (EH2S/EGASFLOW) )
      L = ( K * 0.082057338 * TEMP ) / 10.7
      M = ( 3600 )
      N = (0.00402 * 0.000170 ) / 2.6 * LEAFLOW
      O = ( COPPER/LEAFLOW + K ) * 1000
      PH = - ALOG10(OXONIUM/INFLOW)
C     PH = 1
      IF ( PH .LT. 2) THEN
       P = 1
      ELSE
       P = 0.00000001
      ENDIF
      RATEA = K * L * M * N * O * P
```

EXECUTE BEFORE BLOCK PH1,5

VALUES OF ACCESSED FORTRAN VARIABLES ON MOST RECENT SIMULATION PASS:

VARIABLE	VALUE READ	VALUE WRITTEN	UNITS
H2S	0.766854		MOL/HR
EH2S	0.560143E-02		MOL/HR
COPPER	0.397299E-02		MOL/HR
LEAFLOW	2.59678		L/HR
GASFLOW	0.884731E-01		L/HR
EGASFLOW	0.600000E-01		L/HR
INFLOW	2.74525		L/HR
TEMP	293.150		K
OXONIUM	0.102704		MOL/HR
RATEA	3715.01	3715.36	MOL/HR

CALCULATOR BLOCK: ZNS1

SAMPLED VARIABLES:

H2S	: H2S MOLEFLOW IN STREAM EXTRAGAS SUBSTREAM MIXED
METAL	: ZN++ MOLEFLOW IN STREAM LEACH SUBSTREAM MIXED
LEAFLOW	: STDVOL-FLOW IN STREAM PH1,5IN SUBSTREAM MIXED
GASFLOW	: STDVOL-FLOW IN STREAM EXTRAGAS SUBSTREAM MIXED
TEMP	: SENTENCE=PARAM VARIABLE=TEMP IN UOS BLOCK PH1,5
OXONIUM	: H3O+ MOLEFLOW IN STREAM PH1,5IN SUBSTREAM MIXED
RATEB	: SENTENCE=EXTENT-SPEC VARIABLE=EXTENT ID1=1 IN UOS BLOCK PH1,5

FORTRAN STATEMENTS:

```
      REAL H2S, METAL, GASFLOW, LEAFLOW, TEMP, RATEB
      REAL K, L, M, N, O
      REAL PH, P, OXONIUM
       A = .00000001
```

```
      IF (H2S .EQ. 0.) THEN
       H2S = H2S + A
      ENDIF
      IF (METAL .EQ. 0.) THEN
       METAL = METAL + A
      ENDIF
      IF (GASFLOW .EQ. 0.) THEN
       GASFLOW = GASFLOW + A
      ENDIF
      IF (LEAFLOW .EQ. 0.) THEN
       LEAFLOW = LEAFLOW + A
      ENDIF
      IF (TEMP .EQ. 0.) THEN
       TEMP = TEMP + A
      ENDIF
      IF (OXONIUM .EQ. 0.) THEN
       OXONIUM = OXONIUM + A
      ENDIF
      K = ((H2S/GASFLOW) * 0.082057338 * TEMP ) / 10.7
      L = ( 3600 )
      M = ( 0.00402 ) / ( 0.00130 )
      N = ( 0.000170 )
      O = ( METAL/LEAFLOW + K )
      PH = - ALOG10(OXONIUM/LEAFLOW)
C     PH = 1
      IF ( PH .LT. 4 .AND. PH .GT. 2) THEN
       P = 1
      ELSE
       RATE = 0.000001
      ENDIF
      RATEB = K * L * M * N * O * P

  READ VARIABLES:  GASFLOW   LEAFLOW   METAL     H2S      TEMP
OXONIUM

  WRITE VARIABLES: RATEB

  VALUES OF ACCESSED FORTRAN VARIABLES ON MOST RECENT SIMULATION PASS:
   VARIABLE       VALUE READ     VALUE WRITTEN    UNITS
   --------------      ----------------   ---------------------  - --------
   H2S              0.560143E-02                      MOL/HR
   METAL            0.408911E-02                      MOL/HR
   LEAFLOW          2.74525                            L/HR
   GASFLOW          0.600000E-01                       L/HR
   TEMP             293.150                            K
   OXONIUM          0.102705                          MOL/HR
   RATEB            0.00000             0.00000       MOL/HR

-------------------------------------------------------------------------------------------------------------------------------
------------------------------
```

CALCULATOR BLOCK: ZNS2

```
------------------------------------------------------------------------------------------------------------------------------------------------------
------------------------------

  SAMPLED VARIABLES:
    H2S            : H2S MOLEFLOW IN STREAM H2SL SUBSTREAM MIXED
    METAL          : ZN++ MOLEFLOW IN STREAM PH1P4 SUBSTREAM MIXED
    LEAFLOW        : STDVOL-FLOW IN STREAM PH1P4 SUBSTREAM MIXED
    GASFLOW        : STDVOL-FLOW IN STREAM H2SL SUBSTREAM MIXED
    TEMP           : SENTENCE=PARAM VARIABLE=TEMP IN UOS BLOCK PH4,5
    OXONIUM        : H3O+ MOLEFLOW IN STREAM PH1P4 SUBSTREAM MIXED
    RATEC          : SENTENCE=EXTENT-SPEC VARIABLE=EXTENT ID1=1 IN UOS BLOCK PH4,5

  FORTRAN STATEMENTS:
        REAL H2S, METAL, GASFLOW, LEAFLOW, TEMP, RATEC
        REAL K, L, M, N, O
        REAL PH
         A = .00000001
        IF (H2S .EQ. 0.) THEN
         H2S = H2S + A
        ENDIF
        IF (METAL .EQ. 0.) THEN
         METAL = METAL + A
        ENDIF
        IF (GASFLOW .EQ. 0.) THEN
         GASFLOW = GASFLOW + A
        ENDIF
        IF (LEAFLOW .EQ. 0.) THEN
         LEAFLOW = LEAFLOW + A
        ENDIF
        IF (TEMP .EQ. 0.) THEN
         TEMP = TEMP + A
        ENDIF
        IF (OXONIUM .EQ. 0.) THEN
         OXONIUM = OXONIUM + A
        ENDIF
        K = ((H2S/GASFLOW) * 0.082057338 * TEMP ) / 10.7
        L = ( 3600 )
        M = ( 0.00488 * 0.000217 ) /2.6 * LEAFLOW
        N = ( METAL/LEAFLOW + K ) * 1000
        PH = - ALOG10(OXONIUM/LEAFLOW)
  C      PH = 3
        IF ( PH .LT. 4 .AND. PH .GT. 2) THEN
         O = 1
        ELSE
         O = 0.00000001
        ENDIF
        RATEC = K * L * M * N * O

  EXECUTE BEFORE BLOCK PH4,5

  VALUES OF ACCESSED FORTRAN VARIABLES ON MOST RECENT SIMULATION PASS:
    VARIABLE      VALUE READ      VALUE WRITTEN    UNITS
```

H2S	0.684953E-02		MOL/HR
METAL	0.410904E-02		MOL/HR
LEAFLOW	3.54918		L/HR
GASFL	0.242750E-01		L/HR
TEMP	293.150		K
OXONIUM	0.122418E-03		MOL/HR
RATEC	0.209760E-07	0.209787E-07	MOL/HR

CALCULATOR BLOCK: ETH

SAMPLED VARIABLES:
VOLFLOW : STDVOL-FLOW IN STREAM BIN SUBSTREAM MIXED
ETHANOL : ETHANOL MOLEFLOW IN STREAM BIN SUBSTREAM MIXED
SULFATE : SO4-- MOLEFLOW IN STREAM BIN SUBSTREAM MIXED
OXONIUM : H3O+ MOLEFLOW IN STREAM BIN SUBSTREAM MIXED
KINETIC : SENTENCE=RATE-CON VARIABLE=PRE-EXP ID1=1 IN REACTION R-1

FORTRAN STATEMENTS:

```
      REAL VOLFLOW, ETHANOL, SULFATE, OXONIUM
      REAL KINETIC, M, N, O, P
      REAL A
      REAL PH, R
           A = .00000001
      IF (VOLFLOW .EQ. 0.) THEN
       VOLFLOW = VOLFLOW + A
      ENDIF
      IF (ETHANOL .EQ. 0.) THEN
       ETHANOL= ETHANOL + A
      ENDIF
      IF (SULFATE .EQ. 0.) THEN
       SULFATE = SULFATE + A
      ENDIF
      IF (OXONIUM .EQ. 0.) THEN
       OXONIUM = OXONIUM + A
      ENDIF
      M = (0.013/0.25) / 3600
      N = ( 1. / ( 1. + 0.045 / ( ETHANOL / VOLFLOW ) ) )
      O = ( SULFATE / VOLFLOW )
      P = ( 1. / ( 1. + 0.085 / O ) )
      PH = - ALOG10(OXONIUM/VOLFLOW)
C     PH = 6.5
      R = (EXP ( -3 * ( (PH-6.75) / (6.75-1.3) )**2))
      KINETIC = M * N * O * P * R
```

EXECUTE BEFORE BLOCK BATCHETH

VALUES OF ACCESSED FORTRAN VARIABLES ON MOST RECENT SIMULATION PASS:

VARIABLE	VALUE READ	VALUE WRITTEN	UNITS
VOLFLOW	5.52861		L/HR
ETHANOL	7.75926		MOL/HR
SULFATE	9.40124		MOL/HR
OXONIUM	0.511870E-05		MOL/HR
KINETIC	0.215203E-04	0.215208E-04	

CALCULATOR BLOCK: ACE

SAMPLED VARIABLES:

VOLFLOW : STDVOL-FLOW IN STREAM ETHL SUBSTREAM MIXED
ACETATE : ACETATE MOLEFLOW IN STREAM ETHL SUBSTREAM MIXED
SULFATE : SO4-- MOLEFLOW IN STREAM ETHL SUBSTREAM MIXED
OXONIUM : H3O+ MOLEFLOW IN STREAM ETHL SUBSTREAM MIXED
KINETICA : SENTENCE=RATE-CON VARIABLE=PRE-EXP ID1=1 IN REACTION R-2

FORTRAN STATEMENTS:

```
      REAL VOLFLOW, ACETATE, SULFATE, OXONIUM, KINETICA
      REAL M, N, O, P
      REAL A
      REAL PH, R
           A = .00000001
      IF (VOLFLOW .EQ. 0.) THEN
       VOLFLOW = VOLFLOW + A
      ENDIF
      IF (ACETATE .EQ. 0.) THEN
       ACETATE= ACETATE + A
      ENDIF
      IF (SULFATE .EQ. 0.) THEN
       SULFATE = SULFATE + A
      ENDIF
      IF (OXONIUM .EQ. 0.) THEN
       OXONIUM = OXONIUM + A
      ENDIF
      M = (0.01/0.25) / 3600
      N = ( 1. / ( 1. + 0.0603 / ( ACETATE / VOLFLOW ) ) )
      O = ( 1. / ( 1. + 0.087 / ( SULFATE / VOLFLOW ) ) )
      PH = - ALOG10(OXONIUM/VOLFLOW)
C     PH = 6.5
      R = (EXP ( -3 * ( (PH-6.75) / (6.75-1.3) )**2))
      KINETICA = M * N * O * R
```

EXECUTE BEFORE BLOCK BATCHACE

VALUES OF ACCESSED FORTRAN VARIABLES ON MOST RECENT SIMULATION PASS:

VARIABLE	VALUE READ	VALUE WRITTEN	UNITS

VOLFLOW	5.62249		L/HR
ACETATE	6.89821		MOL/HR
SULFATE	5.90932		MOL/HR
OXONIUM	0.348929E-05		MOL/HR
KINETICA	0.949419E-05	0.949418E-05	

Full Model Input Code

```
;Input Summary created by Aspen Plus Rel. 34.0 at 09:39:14 Tue May 23, 2017
;Directory \\fs-n.net.lth.se\home\bte12hkv\Documents\Exjobb\Aspen\MERGEDworking  Filename
C:\Users\bte12hkv\AppData\Local\Temp\~ap15bb.txt
;


DYNAMICS
   DYNAMICS RESULTS=ON

TITLE 'Precipitation of metalsulfides'

IN-UNITS MET

DEF-STREAMS MIXCIPSD ALL

SIM-OPTIONS MASS-BAL-CHE=YES FLASH-TOL=0.01 HF-FL3-DAMP=NO  &
      MASS-BAL-TOL=0.01 OPER-YEAR=8766.000000

MODEL-OPTION

SYS-OPTIONS TRACE=YES

DATABANKS 'APV88 ASPENPCD' / 'APV88 AQUEOUS' / 'APV88 SOLIDS' &
       / 'APV88 INORGANIC' / 'APEOSV88 AP-EOS' /  &
      'APV88 PURE32'

PROP-SOURCES 'APV88 ASPENPCD' / 'APV88 AQUEOUS' / 'APV88 SOLIDS' &
       / 'APV88 INORGANIC' / 'APEOSV88 AP-EOS' /  &
      'APV88 PURE32'

COMPONENTS
   ZN++ ZN+2 /
   ZNS ZNS-2 /
   CU++ CU+2 /
   CUS CUS /
   NI++ NI+2 /
   NIS NIS /
   S-- S-2 /
   WATER H2O /
   H2S H2S /
   HS- HS- /
   CO2 CO2 /
   HCO3- HCO3- /
   H+ H+ /
   OH- OH- /
   HSO4- HSO4- /
   SO4-- SO4-2 /
   H3O+ H3O+ /
   CO3-- CO3-2 /
   N2 N2 /
```

```
   H2SO4 H2SO4 /
   NAOH NAOH /
   NA+ NA+ /
   NA2SO4 NA2SO4 /
   ETHANOL C2H6O-2 /
   ACETICAC C2H4O2-1 /
   ACETATE CH3COO-

CISOLID-COMPS ZNS CUS NIS

HENRY-COMPS GLOBAL CO2 H2S N2

SOLVE
   RUN-MODE MODE=SIM

CHEMISTRY GLOBAL
   PARAM GAMMA-BASIS=UNSYMMETRIC
   DISS NAOH OH- 1 / NA+ 1
   DISS NA2SO4 SO4-- 1 / NA+ 2
   STOIC 1 ACETICAC -1 / WATER -1 / ACETATE 1 / H3O+ 1
   STOIC 2 WATER -1 / HSO4- -1 / H3O+ 1 / SO4-- 1
   STOIC 3 H2SO4 -1 / WATER -1 / H3O+ 1 / HSO4- 1
   STOIC 4 WATER -1 / HCO3- -1 / CO3-- 1 / H3O+ 1
   STOIC 5 WATER -2 / CO2 -1 / HCO3- 1 / H3O+ 1
   STOIC 6 WATER -1 / HS- -1 / H3O+ 1 / S-- 1
   STOIC 7 WATER -1 / H2S -1 / H3O+ 1 / HS- 1
   STOIC 8 WATER -2 / OH- 1 / H3O+ 1
   K-STOIC 4 A=216.050446 B=-12431.700195 C=-35.481899 D=0
   K-STOIC 5 A=231.465439 B=-12092.099609 C=-36.781601 D=0
   K-STOIC 6 A=-9.741963 B=-8585.469727 C=0 D=0
   K-STOIC 7 A=214.582443 B=-12995.400391 C=-33.5471 D=0
   K-STOIC 8 A=132.89888 B=-13445.900391 C=-22.477301 D=0

FLOWSHEET
   BLOCK PH1,5 IN=PH1,5IN OUT=PH1G PH1P1
   BLOCK PH4,5 IN=PH1P4 OUT=PH2G PH2P1
   BLOCK M1 IN=PH1P2 OUT=PH1P3
   BLOCK M3 IN=NAOH0,1 S1 OUT=PH1P4
   BLOCK C1 IN=PH1P1 OUT=PH1P2 CUS
   BLOCK C2 IN=PH2P1 OUT=PH2P2 ZNS
   BLOCK SUBSPLIT IN=PH2P2 OUT=CIDSID PH2P3
   BLOCK M4 IN=PH2P4 2NAOH0,1 OUT=REC
   BLOCK BATCHETH IN=BIN OUT=BP1
   BLOCK BACE IN=BP2 OUT=ACG ACL
   BLOCK BATCHACE IN=ETHL OUT=BP2
   BLOCK M2 IN=PH1P3 H2SL OUT=S1
   BLOCK M5 IN=REC ETOH OUT=S2
   BLOCK BETH IN=BP1 OUT=ETHG ETHL
   BLOCK MG IN=ACG ETHG OUT=H2SG
   BLOCK SEP2 IN=S OUT=H2SL PURGE2
   BLOCK SEP1 IN=PH2P3 OUT=PH2P4 PURGE1
   BLOCK M6 IN=S2 SO4 OUT=BIN
```

```
   BLOCK SEPW IN=ACL OUT=W S
   BLOCK M0 IN=EXTRAGAS LEACH H2SG OUT=PH1,5IN

PROPERTIES ELECNRTL HENRY-COMPS=GLOBAL CHEMISTRY=GLOBAL  &
      TRUE-COMPS=YES
   PROPERTIES NRTL / RK-SOAVE / SOLIDS / STEAMNBS

PROP-DATA PCES-1
   IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
      INVERSE-PRES='1/bar'
   PROP-LIST VLSTD
   PVAL ZNS 298.9063450

PROP-DATA REVIEW-1
   IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
      INVERSE-PRES='1/bar'
   PROP-LIST CHARGE / RKTZRA / VLSTD
   PVAL ZNS 0 / .2918596200 / 23.83
   PROP-LIST CHARGE / VLSTD
   PVAL CUS 0 / 20.08
   PVAL NIS 0 / 23.83
   PROP-LIST CHARGE
   PVAL NA2SO4 0
   PROP-LIST DGAQHG / DHAQHG / DHVLB / OMEGHG / RGYR /  &
      S25HG / VB / VLSTD
   PVAL H2SO4 -1.7782794E+5 / -2.1717541E+5 / 13890.79966 /  &
      26729.66466 / 2.5372000E-10 / 4.800802522 / 65.75890000 / &
      53.63720000
   PROP-LIST VLSTD
   PVAL NAOH 20.85950000
   PVAL ZN++ 9.17
   PVAL CU++ 7.09
   PVAL NI++ 9.17
   PVAL S-- 53.5578
   PVAL HS- 53.5578
   PVAL HCO3- 53.5578
   PVAL H+ 18.05
   PVAL OH- 18.05
   PVAL HSO4- 53.6372
   PVAL SO4-- 53.6372
   PVAL H3O+ 18.05
   PVAL CO3-- 53.5578
   PVAL NA+ 20.8595
   PVAL ACETATE 57.63

PROP-DATA MULAND-1
   IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
      INVERSE-PRES='1/bar'
   PROP-LIST MULAND
   PVAL ZNS 81.00275458 -12127.32210 -10.25255770 1126.850000  &
      1706.850000
```

```
PROP-DATA SIGDIP-1
  IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
    INVERSE-PRES='1/bar'
  PROP-LIST SIGDIP
  PVAL NAOH 812.5318210 1.222222670 -1.4235885E-6  &
    1.53005362E-6 -5.5171520E-7 1554.760000 1686.850000

PROP-DATA HOCETA-1
  IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
    INVERSE-PRES='1/bar'
  PROP-LIST HOCETA
  BPVAL WATER WATER 1.700000000
  BPVAL WATER H2S .7000000000
  BPVAL WATER CO2 .3000000000
  BPVAL WATER ETHANOL 1.550000000
  BPVAL WATER ACETICAC 2.500000000
  BPVAL H2S WATER .7000000000
  BPVAL H2S CO2 .1000000000
  BPVAL H2S ETHANOL .7000000000
  BPVAL H2S ACETICAC .5000000000
  BPVAL CO2 WATER .3000000000
  BPVAL CO2 H2S .1000000000
  BPVAL CO2 CO2 .1600000000
  BPVAL CO2 ETHANOL .3000000000
  BPVAL CO2 ACETICAC .5000000000
  BPVAL ETHANOL WATER 1.550000000
  BPVAL ETHANOL H2S .7000000000
  BPVAL ETHANOL CO2 .3000000000
  BPVAL ETHANOL ETHANOL 1.400000000
  BPVAL ETHANOL ACETICAC 2.500000000
  BPVAL ACETICAC WATER 2.500000000
  BPVAL ACETICAC H2S .5000000000
  BPVAL ACETICAC CO2 .5000000000
  BPVAL ACETICAC ETHANOL 2.500000000
  BPVAL ACETICAC ACETICAC 4.500000000

PROP-DATA HENRY-1
  IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
    INVERSE-PRES='1/bar'
  PROP-LIST HENRY
  BPVAL H2S WATER 149.5490745 -8226.500000 -20.23070000  &
    -1.2940500E-3 -.1500000000 59.85000000 0.0
  BPVAL CO2 WATER 159.8650745 -8741.550000 -21.66900000  &
    1.10259000E-3 -.1500000000 79.85000000 0.0
  BPVAL N2 WATER 164.9940745 -8432.770000 -21.55800000  &
    -8.4362400E-3 -.1500000000 72.85000000 0.0
  BPVAL CO2 ETHANOL 89.58307554 -5018.799805 -11.89100000 0.0  &
    10.00000000 40.00000000 0.0
  BPVAL N2 ETHANOL -1.930195465 -22.08200100 2.206100000  &
    -8.8300000E-3 -60.00000000 50.00000000 0.0
  BPVAL H2S ACETICAC 9.695774535 -1828.199951 0.0 0.0  &
    25.00000000 60.00000000 0.0
```

```
   BPVAL CO2 ACETICAC -76.15792246 2162.300049 12.88900000 0.0  &
     18.00000000 36.00000000 0.0
   BPVAL N2 ACETICAC 7.972975535 74.05300100 0.0 0.0  &
     20.00000000 25.00000000 0.0

PROP-DATA NRTL-1
   IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
     INVERSE-PRES='1/bar'
   PROP-LIST NRTL
   BPVAL WATER H2S -3.674000000 1155.900000 .2000000000 0.0  &
     0.0 0.0 0.0 150.0000000
   BPVAL H2S WATER -3.674000000 1155.900000 .2000000000 0.0  &
     0.0 0.0 0.0 150.0000000
   BPVAL WATER CO2 10.06400000 -3268.135000 .2000000000 0.0  &
     0.0 0.0 0.0 200.0000000
   BPVAL CO2 WATER 10.06400000 -3268.135000 .2000000000 0.0  &
     0.0 0.0 0.0 200.0000000

PROP-DATA RKSKBV-1
   IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
     INVERSE-PRES='1/bar'
   PROP-LIST RKSKBV
   BPVAL WATER H2S .0100000000 0.0 0.0 -273.1500000  &
     726.8500000
   BPVAL H2S WATER .0100000000 0.0 0.0 -273.1500000  &
     726.8500000
   BPVAL WATER CO2 .0737000000 0.0 0.0 -273.1500000  &
     726.8500000
   BPVAL CO2 WATER .0737000000 0.0 0.0 -273.1500000  &
     726.8500000
   BPVAL H2S CO2 .0989000000 0.0 0.0 -273.1500000 726.8500000
   BPVAL CO2 H2S .0989000000 0.0 0.0 -273.1500000 726.8500000
   BPVAL H2S N2 .1696000000 0.0 0.0 -273.1500000 726.8500000
   BPVAL N2 H2S .1696000000 0.0 0.0 -273.1500000 726.8500000
   BPVAL CO2 N2 -.0315000000 0.0 0.0 -273.1500000 726.8500000
   BPVAL N2 CO2 -.0315000000 0.0 0.0 -273.1500000 726.8500000

PROP-DATA VLCLK-1
   IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
     INVERSE-PRES='1/bar'
   PROP-LIST VLCLK
   BPVAL H+ HSO4- 54.80395000 20.24347000
   BPVAL H3O+ HSO4- 54.80395000 20.24347000
   BPVAL NA+ HCO3- 23.70637000 30.40776000
   BPVAL NA+ OH- -13.79420000 72.92090000
   BPVAL NA+ SO4-- 8.675527000 123.2671000
   BPVAL NA+ CO3-- -5.411850000 94.55199000

PROP-DATA GMELCC-1
   IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
     INVERSE-PRES='1/bar'
   PROP-LIST GMELCC
```

PPVAL WATER (H+ S--) 8.045000000
PPVAL (H+ S--) WATER -4.072000000
PPVAL WATER (H+ HS-) 8.045000000
PPVAL (H+ HS-) WATER -4.072000000
PPVAL WATER (H+ HCO3-) 8.045000000
PPVAL (H+ HCO3-) WATER -4.072000000
PPVAL WATER (H+ OH-) 8.045000000
PPVAL (H+ OH-) WATER -4.072000000
PPVAL WATER (H+ HSO4-) 11.01100000
PPVAL (H+ HSO4-) WATER -5.366000000
PPVAL WATER (ZN++ SO4--) 8.189000000
PPVAL (ZN++ SO4--) WATER -4.058000000
PPVAL WATER (H3O+ S--) 8.045000000
PPVAL (H3O+ S--) WATER -4.072000000
PPVAL WATER (H3O+ HS-) 8.045000000
PPVAL (H3O+ HS-) WATER -4.072000000
PPVAL WATER (H3O+ HCO3-) 8.045000000
PPVAL (H3O+ HCO3-) WATER -4.072000000
PPVAL WATER (H3O+ OH-) 8.045000000
PPVAL (H3O+ OH-) WATER -4.072000000
PPVAL WATER (H3O+ HSO4-) 6.362000000
PPVAL (H3O+ HSO4-) WATER -3.749000000
PPVAL WATER (H3O+ SO4--) 8.000000000
PPVAL (H3O+ SO4--) WATER -4.000000000
PPVAL H2S (H3O+ S--) 15.00000000
PPVAL (H3O+ S--) H2S -8.000000000
PPVAL H2S (H3O+ HS-) 15.00000000
PPVAL (H3O+ HS-) H2S -8.000000000
PPVAL H2S (H3O+ HCO3-) 15.00000000
PPVAL (H3O+ HCO3-) H2S -8.000000000
PPVAL H2S (H3O+ OH-) 15.00000000
PPVAL (H3O+ OH-) H2S -8.000000000
PPVAL CO2 (H3O+ S--) 15.00000000
PPVAL (H3O+ S--) CO2 -8.000000000
PPVAL CO2 (H3O+ HS-) 15.00000000
PPVAL (H3O+ HS-) CO2 -8.000000000
PPVAL CO2 (H3O+ HCO3-) 15.00000000
PPVAL (H3O+ HCO3-) CO2 -8.000000000
PPVAL CO2 (H3O+ OH-) 15.00000000
PPVAL (H3O+ OH-) CO2 -8.000000000
PPVAL WATER (H+ CO3--) 8.045000000
PPVAL (H+ CO3--) WATER -4.072000000
PPVAL WATER (H3O+ CO3--) 8.045000000
PPVAL (H3O+ CO3--) WATER -4.072000000
PPVAL H2S (H3O+ CO3--) 15.00000000
PPVAL (H3O+ CO3--) H2S -8.000000000
PPVAL CO2 (H3O+ CO3--) 15.00000000
PPVAL (H3O+ CO3--) CO2 -8.000000000
PPVAL H2SO4 (H3O+ HSO4-) 12.99200000
PPVAL (H3O+ HSO4-) H2SO4 -2.981000000
PPVAL H2SO4 (H3O+ SO4--) 8.000000000
PPVAL (H3O+ SO4--) H2SO4 -4.000000000

```
  PPVAL WATER ( NA+ HCO3- ) 7.834000000
  PPVAL ( NA+ HCO3- ) WATER -4.031000000
  PPVAL WATER ( NA+ OH- ) 6.737997000
  PPVAL ( NA+ OH- ) WATER -3.771221000
  PPVAL WATER ( NA+ HSO4- ) 7.663000000
  PPVAL ( NA+ HSO4- ) WATER -3.944000000
  PPVAL WATER ( NA+ SO4-- ) 1.954500000
  PPVAL ( NA+ SO4-- ) WATER -2.033257000
  PPVAL WATER ( NA+ CO3-- ) -4.833000000
  PPVAL ( NA+ CO3-- ) WATER .9770000000
  PPVAL ( NA+ OH- ) ( NA+ SO4-- ) 0.0
  PPVAL ( NA+ SO4-- ) ( NA+ OH- ) 0.0
  PPVAL WATER ( NA+ ACETATE ) 8.401078000
  PPVAL ( NA+ ACETATE ) WATER -4.491110000

PROP-DATA GMELCD-1
  IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
    INVERSE-PRES='1/bar'
  PROP-LIST GMELCD
  PPVAL WATER ( H3O+ HSO4- ) 1958.200000
  PPVAL ( H3O+ HSO4- ) WATER -583.2000000
  PPVAL WATER ( H3O+ SO4-- ) 0.0
  PPVAL ( H3O+ SO4-- ) WATER 0.0
  PPVAL H2S ( H3O+ S-- ) 0.0
  PPVAL ( H3O+ S-- ) H2S 0.0
  PPVAL H2S ( H3O+ HS- ) 0.0
  PPVAL ( H3O+ HS- ) H2S 0.0
  PPVAL H2S ( H3O+ HCO3- ) 0.0
  PPVAL ( H3O+ HCO3- ) H2S 0.0
  PPVAL H2S ( H3O+ OH- ) 0.0
  PPVAL ( H3O+ OH- ) H2S 0.0
  PPVAL CO2 ( H3O+ S-- ) 0.0
  PPVAL ( H3O+ S-- ) CO2 0.0
  PPVAL CO2 ( H3O+ HS- ) 0.0
  PPVAL ( H3O+ HS- ) CO2 0.0
  PPVAL CO2 ( H3O+ HCO3- ) 0.0
  PPVAL ( H3O+ HCO3- ) CO2 0.0
  PPVAL CO2 ( H3O+ OH- ) 0.0
  PPVAL ( H3O+ OH- ) CO2 0.0
  PPVAL H2S ( H3O+ CO3-- ) 0.0
  PPVAL ( H3O+ CO3-- ) H2S 0.0
  PPVAL CO2 ( H3O+ CO3-- ) 0.0
  PPVAL ( H3O+ CO3-- ) CO2 0.0
  PPVAL H2SO4 ( H3O+ HSO4- ) -1732.900000
  PPVAL ( H3O+ HSO4- ) H2SO4 -162.3000000
  PPVAL H2SO4 ( H3O+ SO4-- ) 0.0
  PPVAL ( H3O+ SO4-- ) H2SO4 0.0
  PPVAL WATER ( NA+ OH- ) 1420.242000
  PPVAL ( NA+ OH- ) WATER -471.8202000
  PPVAL WATER ( NA+ SO4-- ) 1762.185000
  PPVAL ( NA+ SO4-- ) WATER -537.9684000
  PPVAL WATER ( NA+ CO3-- ) 4018.400000
```

```
  PPVAL ( NA+ CO3-- ) WATER -1547.000000
  PPVAL ( NA+ OH- ) ( NA+ SO4-- ) 0.0
  PPVAL ( NA+ SO4-- ) ( NA+ OH- ) 0.0

PROP-DATA GMELCE-1
  IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
    INVERSE-PRES='1/bar'
  PROP-LIST GMELCE
  PPVAL WATER ( H3O+ HSO4- ) -4.599000000
  PPVAL ( H3O+ HSO4- ) WATER 4.472000000
  PPVAL H2S ( H3O+ S-- ) 0.0
  PPVAL ( H3O+ S-- ) H2S 0.0
  PPVAL H2S ( H3O+ HS- ) 0.0
  PPVAL ( H3O+ HS- ) H2S 0.0
  PPVAL H2S ( H3O+ HCO3- ) 0.0
  PPVAL ( H3O+ HCO3- ) H2S 0.0
  PPVAL H2S ( H3O+ OH- ) 0.0
  PPVAL ( H3O+ OH- ) H2S 0.0
  PPVAL CO2 ( H3O+ S-- ) 0.0
  PPVAL ( H3O+ S-- ) CO2 0.0
  PPVAL CO2 ( H3O+ HS- ) 0.0
  PPVAL ( H3O+ HS- ) CO2 0.0
  PPVAL CO2 ( H3O+ HCO3- ) 0.0
  PPVAL ( H3O+ HCO3- ) CO2 0.0
  PPVAL CO2 ( H3O+ OH- ) 0.0
  PPVAL ( H3O+ OH- ) CO2 0.0
  PPVAL H2S ( H3O+ CO3-- ) 0.0
  PPVAL ( H3O+ CO3-- ) H2S 0.0
  PPVAL CO2 ( H3O+ CO3-- ) 0.0
  PPVAL ( H3O+ CO3-- ) CO2 0.0
  PPVAL H2SO4 ( H3O+ HSO4- ) -30.12600000
  PPVAL ( H3O+ HSO4- ) H2SO4 .8060000000
  PPVAL WATER ( NA+ OH- ) 3.013932000
  PPVAL ( NA+ OH- ) WATER 2.136557000
  PPVAL WATER ( NA+ SO4-- ) 7.552416000
  PPVAL ( NA+ SO4-- ) WATER 6.91975000E-3
  PPVAL WATER ( NA+ CO3-- ) 88.56000000
  PPVAL ( NA+ CO3-- ) WATER -32.40000000
  PPVAL ( NA+ OH- ) ( NA+ SO4-- ) 0.0
  PPVAL ( NA+ SO4-- ) ( NA+ OH- ) 0.0

PROP-DATA GMELCN-1
  IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
    INVERSE-PRES='1/bar'
  PROP-LIST GMELCN
  PPVAL WATER ( H3O+ HSO4- ) .2000000000
  PPVAL H2S ( H3O+ S-- ) .1000000000
  PPVAL H2S ( H3O+ HS- ) .1000000000
  PPVAL H2S ( H3O+ HCO3- ) .1000000000
  PPVAL H2S ( H3O+ OH- ) .1000000000
  PPVAL CO2 ( H3O+ S-- ) .1000000000
  PPVAL CO2 ( H3O+ HS- ) .1000000000
```

```
   PPVAL CO2 ( H3O+ HCO3- ) .1000000000
   PPVAL CO2 ( H3O+ OH- ) .1000000000
   PPVAL H2S ( H3O+ CO3-- ) .1000000000
   PPVAL CO2 ( H3O+ CO3-- ) .1000000000
   PPVAL H2SO4 ( H3O+ HSO4- ) .2000000000
   PPVAL WATER ( NA+ OH- ) .2000000000
   PPVAL WATER ( NA+ SO4-- ) .2000000000
   PPVAL WATER ( NA+ CO3-- ) .2000000000

DEF-STREAMS LOAD

PROP-SET PS-1 PH SUBSTREAM=MIXED PHASE=L

PROP-SET PS-2 PH SUBSTREAM=MIXED PHASE=L

STREAM 2NAOH0,1
   SUBSTREAM MIXED TEMP=298.15 <K> PRES=0.9869232667  &
      STDVOL-FLOW=0.0001 SOLVENT=WATER FREE-WATER=NO NPHASE=1  &
      PHASE=L
   MOLE-CONC NAOH 0.1 <mol/l>

STREAM ETOH
   IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
      INVERSE-PRES='1/bar'
   SUBSTREAM MIXED TEMP=30. PRES=1. STDVOL-FLOW=0.458525 <l/hr>  &
      FREE-WATER=NO NPHASE=1 PHASE=L
   MOLE-FRAC WATER 0.05 / ETHANOL 0.95

STREAM EXTRAGAS
   SUBSTREAM MIXED TEMP=293.1500000 PRES=.9869232667  &
      STDVOL-FLOW=0.001 FREE-WATER=NO NPHASE=1 PHASE=V
   STDVOL-FRAC H2S 0.005 / N2 0.995

STREAM LEACH
   SUBSTREAM MIXED TEMP=293.1500000 PRES=.9869232667  &
      VOLUME-FLOW=2.6 <l/hr> SOLVENT=WATER FREE-WATER=NO  &
      NPHASE=1 PHASE=L CONC-TREF=30. <C> VOL-TREF=30. <C>
   MOLE-CONC ZN++ 0.001574 <mol/l> / CU++ 0.0015293 <mol/l> /  &
      OH- 0.0062066 <mol/l> / H2SO4 0.0326 <mol/l>

STREAM NAOH0,1
   SUBSTREAM MIXED TEMP=293.1500000 PRES=.9869232667  &
      STDVOL-FLOW=0.001 SOLVENT=WATER FREE-WATER=NO NPHASE=1  &
      PHASE=L
   MOLE-CONC NAOH 1.00000000E-4

STREAM SO4
   SUBSTREAM MIXED TEMP=30. <C> PRES=1. STDVOL-FLOW=0.6 <l/hr>  &
      FREE-WATER=NO NPHASE=2 PHASE=V
   MOLE-FRAC WATER 0.3 / NA2SO4 0.7

STREAM SO42
```

```
   SUBSTREAM MIXED TEMP=30. <C> PRES=1. STDVOL-FLOW=2. <l/hr>  &
      SOLVENT=WATER FREE-WATER=NO NPHASE=1 PHASE=L
   MOLE-CONC NA2SO4 0.5 <mol/l>

BLOCK M0 MIXER
   PARAM

BLOCK M1 MIXER
   PARAM

BLOCK M2 MIXER
   PARAM

BLOCK M3 MIXER
   PARAM

BLOCK M4 MIXER
   PARAM MAXIT=50

BLOCK M5 MIXER
   PARAM

BLOCK M6 MIXER
   PARAM

BLOCK MG MIXER
   PARAM

BLOCK SEP1 FSPLIT
   VOL-LIMIT PURGE1 0.006
   STREAM-ORDER PURGE1 1

BLOCK SEP2 FSPLIT
   VOL-LIMIT H2SL 0.006
   STREAM-ORDER H2SL 1

BLOCK BACE SEP
   PARAM
   FRAC STREAM=ACG SUBSTREAM=MIXED COMPS=H2S CO2 N2 FRACS= &
      0.15 0.5 1.

BLOCK BETH SEP
   PARAM
   FRAC STREAM=ETHG SUBSTREAM=MIXED COMPS=H2S CO2 N2 FRACS= &
      0.15 0.5 1.
   FLASH-SPECS ETHG TEMP=25. <C> PRES=1. NPHASE=1  &
      FREE-WATER=NO PHASE=V

BLOCK SEPW SEP
   PARAM
   FRAC STREAM=S SUBSTREAM=MIXED COMPS=WATER FRACS=0.8
```

```
BLOCK PH1,5 REQUIL
  PARAM NREAC=2 TEMP=293.1500000 PRES=.9869232667 NPHASE=2
  STOIC 1 ZN++ -1. * / H2S -1. * / WATER -2. * / ZNS  &
    1. S / H3O+ 2. *
  STOIC 2 CU++ -1. * / H2S -1. * / WATER -2. * / CUS  &
    1. S / H3O+ 2. *
  EXTENT-SPEC 1 1E-007 <mol/hr> / 2 8. <mol/hr>
  FRAC CIPSD

BLOCK PH4,5 REQUIL
  PARAM NREAC=1 TEMP=293.1500000 PRES=.9869232667  &
    CHEM-MAXIT=50 CHEM-TOL=0.02 MAXIT=50 TOL=0.01  &
    MB-TOLFAC=0.01
  STOIC 1 ZN++ -1. * / H2S -1. * / WATER -2. * / ZNS  &
    1. S / H3O+ 2. *
  EXTENT-SPEC 1 0.1 <mol/hr>
  FRAC CIPSD

BLOCK BATCHACE RBATCH
  IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
    INVERSE-PRES='1/bar'
  PARAM TYPE=T-SPEC PRINT-TIME=0.5 <hr> CYCLE-TIME=30.1237 <hr>  &
    MAX-TIME=30. <hr> MAX-NPOINT=62 PRES=1. TEMP=30.  &
    NPHASE=2 INT-TOL=0.01 FLASH=NO
  INTEG-PARAMS EXACT=YES
  STOP 1 REACTOR CONVERSION 0.75 FROM-BELOW COMP=ACETATE  &
    SSID=MIXED
  STOP 2 REACTOR TIME 20.
  BLOCK-OPTION STREAM-LEVEL=6 FREE-WATER=NO
  REACTIONS RXN-IDS=R-2

BLOCK BATCHETH RBATCH
  IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
    INVERSE-PRES='1/bar'
  PARAM TYPE=T-SPEC PRINT-TIME=0.5 <hr> CYCLE-TIME=30. <hr>  &
    MAX-TIME=30. <hr> MAX-NPOINT=62 PRES=1. TEMP=30.  &
    NPHASE=2 INT-TOL=0.01 HINIT=0.01 FLASH=NO
  INTEG-PARAMS EXACT=YES IE-TOLFAC=0.01
  STOP 1 REACTOR CONVERSION 0.9 FROM-BELOW COMP=ETHANOL  &
    SSID=MIXED
  STOP 2 REACTOR TIME 40.
  BLOCK-OPTION STREAM-LEVEL=6 FREE-WATER=NO
  REACTIONS RXN-IDS=R-1

BLOCK SUBSPLIT SSPLIT
  FRAC CIPSD CIDSID 1.
  FRAC MIXED PH2P3 1.

BLOCK C1 CFUGE
  PARAM TYPE=DECANTER FLASH-MAXIT=50 FLASH-TOL=0.01  &
    TINIT=20. <C>
  CAKE-PROPS WETNESS=0.1
```

```
BLOCK C2 CFUGE
   PARAM TYPE=DECANTER TINIT=20. <C>
   CAKE-PROPS WETNESS=0.1

DESIGN-SPEC PH
   DEFINE PH4 STREAM-PROP STREAM=PH1P4 PROPERTY=PS-1
   SPEC "PH4" TO "4.5"
   TOL-SPEC "0.2"
   VARY STREAM-VAR STREAM=NAOH0,1 SUBSTREAM=MIXED  &
      VARIABLE=STDVOL-FLOW UOM="l/min"
   LIMITS "0.001" "0.1" STEP-SIZE=0.001

DESIGN-SPEC PH7
   DEFINE PH7 STREAM-PROP STREAM=REC PROPERTY=PS-2
   SPEC "PH7" TO "7"
   TOL-SPEC "0.8"
   VARY STREAM-VAR STREAM=2NAOH0,1 SUBSTREAM=MIXED  &
      VARIABLE=STDVOL-FLOW UOM="l/min"
   LIMITS "0.0001" "0.1" STEP-SIZE=0.0001

EO-CONV-OPTI

CALCULATOR ACE
   IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
      INVERSE-PRES='1/bar'
F     REAL VOLFLOW, ACETATE, SULFATE, KINETICA
F     REAL M, N, O, P
F     REAL A
F     REAL PH, R
   DEFINE VOLFLOW STREAM-VAR STREAM=ETHL SUBSTREAM=MIXED  &
      VARIABLE=STDVOL-FLOW UOM="l/hr"
   DEFINE ACETATE MOLE-FLOW STREAM=ETHL SUBSTREAM=MIXED  &
      COMPONENT=ACETATE UOM="mol/hr"
   DEFINE SULFATE MOLE-FLOW STREAM=ETHL SUBSTREAM=MIXED  &
      COMPONENT=SO4-- UOM="mol/hr"
   DEFINE KINETICA REACT-VAR REACTION=R-2 VARIABLE=PRE-EXP  &
      SENTENCE=RATE-CON ID1=1
F          A = .00000001
F     IF (VOLFLOW .EQ. 0.) THEN
F      VOLFLOW = VOLFLOW + A
F     ENDIF
F     IF (ACETATE .EQ. 0.) THEN
F      ACETATE= ACETATE + A
F     ENDIF
F     IF (SULFATE .EQ. 0.) THEN
F      SULFATE = SULFATE + A
F     ENDIF
F     M = (0.01/0.25) / 3600
F     N = ( 1. / ( 1. + 0.0603 / ( ACETATE / VOLFLOW ) ) )
F     O = ( 1. / ( 1. + 0.087 / ( SULFATE / VOLFLOW ) ) )
F     PH = 6.5
```

```
F      R = (1.+2.*10.**(.5*(6.-7.)))/(1.+10.**(PH-7.)+10.**(6.-PH))
F      KINETICA = M * N * O * R
   READ-VARS VOLFLOW ACETATE SULFATE
   WRITE-VARS KINETICA
   EXECUTE BEFORE BLOCK BATCHACE
   BLOCK-OPTION VAR-LEVEL=6 TVAR-LEVEL=6

;This block describes the formation of copper sulfide. The data is based on Tokuda et al.,
;The units are as follows:
;
;L=S_H2St=(S_H2S*R*T)/H_H2S [
;M = [sec/hr]
;N = (kLa) [m^2]*[m/s]
;O = (S_H2St+S_Me) [mol/l] *1000 -> [mol/m3]
;
;RATE = mol/hr

CALCULATOR CUS1
;  "copper conversion"

F      REAL H2S, EH2S, COPPER, OXONIUM
F      REAL LEAFLOW, GASFLOW, EGASFLOW, INFLOW, TEMP
F      REAL K, L, M, N, O, P
F      REAL PH, RATEA
   DEFINE H2S MOLE-FLOW STREAM=H2SG SUBSTREAM=MIXED  &
      COMPONENT=H2S UOM="mol/hr"
   DEFINE EH2S MOLE-FLOW STREAM=EXTRAGAS SUBSTREAM=MIXED  &
      COMPONENT=H2S UOM="mol/hr"
   DEFINE COPPER MOLE-FLOW STREAM=LEACH SUBSTREAM=MIXED  &
      COMPONENT=CU++ UOM="mol/hr"
   DEFINE LEAFLOW STREAM-VAR STREAM=LEACH SUBSTREAM=MIXED  &
      VARIABLE=STDVOL-FLOW UOM="l/hr"
   DEFINE GASFLOW STREAM-VAR STREAM=H2SG SUBSTREAM=MIXED  &
      VARIABLE=STDVOL-FLOW UOM="l/hr"
   DEFINE EGASFLOW STREAM-VAR STREAM=EXTRAGAS SUBSTREAM=MIXED  &
      VARIABLE=STDVOL-FLOW UOM="l/hr"
   DEFINE INFLOW STREAM-VAR STREAM=PH1,5IN SUBSTREAM=MIXED  &
      VARIABLE=STDVOL-FLOW UOM="l/hr"
   DEFINE TEMP BLOCK-VAR BLOCK=PH1,5 VARIABLE=TEMP  &
      SENTENCE=PARAM UOM="K"
   DEFINE OXONIUM MOLE-FLOW STREAM=PH1,5IN SUBSTREAM=MIXED  &
      COMPONENT=H3O+ UOM="mol/hr"
   DEFINE RATEA BLOCK-VAR BLOCK=PH1,5 VARIABLE=EXTENT  &
      SENTENCE=EXTENT-SPEC ID1=2 UOM="mol/hr"
F       A = .00000001
F      IF (H2S .EQ. 0.) THEN
F       H2S = H2S + A
F      ENDIF
F      IF (EH2S .EQ. 0.) THEN
F       EH2S = EH2S + A
F      ENDIF
F      IF (COPPER .EQ. 0.) THEN
```

```
F      COPPER = COPPER + A
F     ENDIF
F     IF (LEAFLOW .EQ. 0.) THEN
F      LEAFLOW = LEAFLOW + A
F     ENDIF
F     IF (GASFLOW .EQ. 0.) THEN
F      GASFLOW = GASFLOW + A
F     ENDIF
F     IF (EGASFLOW .EQ. 0.) THEN
F      EGASFLOW = EGASFLOW + A
F     ENDIF
F     IF (INFLOW .EQ. 0.) THEN
F      INFLOW = INFLOW + A
F     ENDIF
F     IF (TEMP .EQ. 0.) THEN
F      TEMP = TEMP + A
F     ENDIF
F     IF (OXONIUM .EQ. 0.) THEN
F      OXONIUM = OXONIUM + A
F     ENDIF
F     K = ( (H2S/GASFLOW) + (EH2S/EGASFLOW) )
F     L = ( K * 0.082057338 * TEMP ) / 10.7
F     M = ( 3600 )
F     N = (0.00402 * 0.000170 ) / 2.6 * LEAFLOW
F     O = ( COPPER/LEAFLOW + K ) * 1000
C     PH = - ALOG10(OXONIUM/INFLOW)
F     PH = 1
F     IF ( PH .LT. 2) THEN
F      P = 1
F     ELSE
F      P = 0.00000001
F     ENDIF
F     RATEA = K * L * M * N * O * P
   READ-VARS H2S COPPER LEAFLOW TEMP OXONIUM GASFLOW EGASFLOW  &
      EH2S INFLOW
   WRITE-VARS RATEA
   EXECUTE BEFORE BLOCK PH1,5
   BLOCK-OPTION VAR-LEVEL=6 TVAR-LEVEL=6

CALCULATOR ETH
   IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
      INVERSE-PRES='1/bar'
F     REAL VOLFLOW, ETHANOL, SULFATE
F     REAL KINETIC, M, N, O, P
F     REAL A
F     REAL PH, R

   DEFINE VOLFLOW STREAM-VAR STREAM=BIN SUBSTREAM=MIXED  &
      VARIABLE=STDVOL-FLOW UOM="l/hr"
   DEFINE ETHANOL MOLE-FLOW STREAM=BIN SUBSTREAM=MIXED  &
      COMPONENT=ETHANOL UOM="mol/hr"
   DEFINE SULFATE MOLE-FLOW STREAM=BIN SUBSTREAM=MIXED  &
```

```
      COMPONENT=SO4-- UOM="mol/hr"
   DEFINE KINETIC REACT-VAR REACTION=R-1 VARIABLE=PRE-EXP  &
      SENTENCE=RATE-CON ID1=1
F          A = .00000001
F     IF (VOLFLOW .EQ. 0.) THEN
F      VOLFLOW = VOLFLOW + A
F     ENDIF
F     IF (ETHANOL .EQ. 0.) THEN
F      ETHANOL= ETHANOL + A
F     ENDIF
F     IF (SULFATE .EQ. 0.) THEN
F      SULFATE = SULFATE + A
F     ENDIF
F     M = (0.013/0.25) / 3600
F     N = ( 1. / ( 1. + 0.045 / ( ETHANOL / VOLFLOW ) ) )
F     O = ( SULFATE / VOLFLOW )
F     P = ( 1. / ( 1. + 0.085 / O ) )
F     PH = 6.5
F     R = (1.+2.*10.**(.5*(6.-7.)))/(1.+10.**(PH-7.)+10.**(6.-PH))
F     KINETIC = M * N * O * P * R
   READ-VARS VOLFLOW ETHANOL SULFATE
   WRITE-VARS KINETIC
   EXECUTE BEFORE BLOCK BATCHETH
   BLOCK-OPTION VAR-LEVEL=6 TVAR-LEVEL=6

;R=0.082057338 l atm K^(-1)  mol^(-1)
;H_(H_2 S)=10.7 atm l mol^(-1)
;
;
;r_ZnS=-A_b/V k_L (S_(Zn^(2+))^t+S_(H_2 S)^0 )
;S_(H_2 S)^0=(S_(H_2 S_g)^t*R*T)/H_(H_2 S)

CALCULATOR ZNS1
F     REAL H2S, METAL, GASFLOW, LEAFLOW, TEMP, RATEB
F     REAL K, L, M, N, O
F     REAL PH, P, OXONIUM
   DEFINE H2S MOLE-FLOW STREAM=EXTRAGAS SUBSTREAM=MIXED  &
      COMPONENT=H2S UOM="mol/hr"
   DEFINE METAL MOLE-FLOW STREAM=LEACH SUBSTREAM=MIXED  &
      COMPONENT=ZN++ UOM="mol/hr"
   DEFINE LEAFLOW STREAM-VAR STREAM=LEACH SUBSTREAM=MIXED  &
      VARIABLE=STDVOL-FLOW UOM="l/hr"
   DEFINE GASFLOW STREAM-VAR STREAM=EXTRAGAS SUBSTREAM=MIXED  &
      VARIABLE=STDVOL-FLOW UOM="l/hr"
   DEFINE TEMP BLOCK-VAR BLOCK=PH1,5 VARIABLE=TEMP  &
      SENTENCE=PARAM UOM="K"
   DEFINE OXONIUM MOLE-FLOW STREAM=PH1P1 SUBSTREAM=MIXED  &
      COMPONENT=H3O+ UOM="mol/hr"
   DEFINE RATEB BLOCK-VAR BLOCK=PH1,5 VARIABLE=EXTENT  &
      SENTENCE=EXTENT-SPEC ID1=1 UOM="mol/hr"
F       A = .00000001
F     IF (H2S .EQ. 0.) THEN
```

```
F      H2S = H2S + A
F     ENDIF
F     IF (METAL .EQ. 0.) THEN
F      METAL = METAL + A
F     ENDIF
F     IF (GASFLOW .EQ. 0.) THEN
F      GASFLOW = GASFLOW + A
F     ENDIF
F     IF (LEAFLOW .EQ. 0.) THEN
F      LEAFLOW = LEAFLOW + A
F     ENDIF
F     IF (TEMP .EQ. 0.) THEN
F      TEMP = TEMP + A
F     ENDIF
F     IF (OXONIUM .EQ. 0.) THEN
F      OXONIUM = OXONIUM + A
F     ENDIF
F     K = ((H2S/GASFLOW) * 0.082057338 * TEMP ) / 10.7
F     L = ( 3600 )
F     M = ( 0.00402 ) / ( 0.00130 )
F     N = ( 0.000170 )
F     O = ( METAL/LEAFLOW + K )
F     PH = - ALOG10(OXONIUM/LEAFLOW)
F     PH = 1
F     IF ( PH .LT. 4 .AND. PH .GT. 2) THEN
F      P = 1
F     ELSE
F      RATE = 0.000001
F     ENDIF
F     RATEB = K * L * M * N * O * P
   READ-VARS GASFLOW LEAFLOW METAL H2S TEMP OXONIUM
   WRITE-VARS RATEB
   BLOCK-OPTION VAR-LEVEL=6 TVAR-LEVEL=6

CALCULATOR ZNS2
F     REAL H2S, METAL, GASFLOW, LEAFLOW, TEMP, RATEC
F     REAL K, L, M, N, O
F     REAL PH
   DEFINE H2S MOLE-FLOW STREAM=H2SL SUBSTREAM=MIXED  &
      COMPONENT=H2S UOM="mol/hr"
   DEFINE METAL MOLE-FLOW STREAM=PH1P4 SUBSTREAM=MIXED  &
      COMPONENT=ZN++ UOM="mol/hr"
   DEFINE LEAFLOW STREAM-VAR STREAM=PH1P4 SUBSTREAM=MIXED  &
      VARIABLE=STDVOL-FLOW UOM="l/hr"
   DEFINE GASFLOW STREAM-VAR STREAM=H2SL SUBSTREAM=MIXED  &
      VARIABLE=STDVOL-FLOW UOM="l/hr"
   DEFINE TEMP BLOCK-VAR BLOCK=PH4,5 VARIABLE=TEMP  &
      SENTENCE=PARAM UOM="K"
   DEFINE OXONIUM MOLE-FLOW STREAM=PH1P4 SUBSTREAM=MIXED  &
      COMPONENT=H3O+ UOM="mol/hr"
   DEFINE RATEC BLOCK-VAR BLOCK=PH4,5 VARIABLE=EXTENT  &
      SENTENCE=EXTENT-SPEC ID1=1 UOM="mol/hr"
```

```
F       A = .00000001
F      IF (H2S .EQ. 0.) THEN
F       H2S = H2S + A
F      ENDIF
F      IF (METAL .EQ. 0.) THEN
F       METAL = METAL + A
F      ENDIF
F      IF (GASFLOW .EQ. 0.) THEN
F       GASFLOW = GASFLOW + A
F      ENDIF
F      IF (LEAFLOW .EQ. 0.) THEN
F       LEAFLOW = LEAFLOW + A
F      ENDIF
F      IF (TEMP .EQ. 0.) THEN
F       TEMP = TEMP + A
F      ENDIF
F      IF (OXONIUM .EQ. 0.) THEN
F       OXONIUM = OXONIUM + A
F      ENDIF
F      K = ((H2S/GASFLOW) * 0.082057338 * TEMP ) / 10.7
F      L = ( 3600 )
F      M = ( 0.00488 * 0.000217 ) /2.6 * LEAFLOW
F      N = ( METAL/LEAFLOW + K ) * 1000
C      PH = - ALOG10(OXONIUM/LEAFLOW)
F      PH = 3
F      IF ( PH .LT. 4 .AND. PH .GT. 2) THEN
F       O = 1
F      ELSE
F       O = 0.00000001
F      ENDIF
F      RATEC = K * L * M * N * O
    READ-VARS GASFLOW METAL H2S TEMP OXONIUM LEAFLOW
    WRITE-VARS RATEC
    EXECUTE BEFORE BLOCK PH4,5
    BLOCK-OPTION VAR-LEVEL=6 TVAR-LEVEL=6

CONV-OPTIONS
    PARAM FLASH=YES

BLOCK-REPORT COMPBAL

STREAM-REPOR MOLEFLOW MASSFLOW

PROPERTY-REP PCES NOPARAM-PLUS

REACTIONS PRECACBA POWERLAW
    REAC-DATA 1 EQUIL
    REAC-DATA 2 EQUIL
    REAC-DATA 3 EQUIL
    REAC-DATA 4 EQUIL
    REAC-DATA 5 EQUIL
    REAC-DATA 6 EQUIL
```

```
  STOIC 1 MIXED WATER -2. / H3O+ 1. / OH- 1.
  STOIC 2 MIXED WATER -2. / CO2 -1. / H3O+ 1. / HCO3-  &
    1.
  STOIC 3 MIXED HCO3- -1. / WATER -1. / CO3-- 1. / H3O+  &
    1.
  STOIC 4 MIXED WATER -1. / H2S -1. / H3O+ 1. / HS- 1.
  STOIC 5 MIXED WATER -1. / HS- -1. / S-- 1. / H3O+ 1.
  STOIC 6 MIXED HSO4- -1. / WATER -1. / H3O+ 1. / SO4--  &
    1.

REACTIONS PRECREAC POWERLAW
  REAC-DATA 1
  REAC-DATA 2
  RATE-CON 1 PRE-EXP=0.001 ACT-ENERGY=0.0 T-REF=571.1500000
  RATE-CON 2 PRE-EXP=0.001 ACT-ENERGY=0.0 T-REF=571.1500000
  STOIC 1 MIXED H2S -1. / ZN++ -1. / ZNS 1. / H+ 2.
  STOIC 2 MIXED H2S -1. / CU++ -1. / CUS 1. / H+ 2.

REACTIONS R-1 GENERAL
  IN-UNITS MET PRESSURE=bar TEMPERATURE=C DELTA-T=C PDROP=bar  &
    INVERSE-PRES='1/bar'
  REAC-DATA 1 NAME=ETHANOL CBASIS=MOLARITY RBASIS=REAC-VOL  &
    REVERSIBLE=NO
  RATE-CON 1 PRE-EXP=0.1 ACT-ENERGY=0. T-REF=298. <K>
  STOIC 1 MIXED SO4-- -0.5 / ETHANOL -1. / S-- 0.5 /  &
    H3O+ 1. / ACETATE 1.

REACTIONS R-2 GENERAL
  REAC-DATA 1 NAME=ACETATE REAC-CLASS=POWERLAW STATUS=ON
  RATE-CON 1 PRE-EXP=0.1 ACT-ENERGY=0. T-REF=298. <K>
  STOIC 1 MIXED ACETATE -1. / SO4-- -1. / CO2 2. / S--  &
    1. / OH- 1. / WATER 1.
  REAC-ACT 1

PROP-TABLE PH1,5 FLASHCURVE
  IN-UNITS MET PRESSURE=bar TEMPERATURE=C PDROP=atm
  STREAM PH1P1
  VARY PRES
  RANGE LIST=1.013250000
  VARY TEMP
  RANGE LOWER=0 UPPER=50. NPOINT=20
  PARAM
  TABULATE PROPERTIES=PS-1

PROP-TABLE PH3 FLASHCURVE
  IN-UNITS MET PRESSURE=bar TEMPERATURE=C PDROP=atm
  STREAM PH1P4
  VARY PRES
  RANGE LIST=1.013250000
  VARY TEMP
  RANGE LOWER=0 UPPER=50. NPOINT=20
  PARAM
```

```
   TABULATE PROPERTIES=PS-1

PROP-TABLE SPROP-1 FLASHCURVE
   STREAM PH2P4
   VARY PRES
   RANGE LIST=1.000000000
   VARY TEMP
   RANGE LOWER=273.1500000 UPPER=373.1500000 NPOINT=20
   PARAM
   TABULATE PROPERTIES=PS-1

PROP-TABLE SPROP-2 FLASHCURVE
   STREAM S1
   VARY PRES
   RANGE LIST=1.000000000
   VARY TEMP
   RANGE LOWER=273.1500000 UPPER=373.1500000 NPOINT=20
   PARAM
   TABULATE PROPERTIES=PS-1

PROP-TABLE SPROP-3 FLASHCURVE
   STREAM PH1P1
   VARY PRES
   RANGE LIST=1.000000000
   VARY TEMP
   RANGE LOWER=273.1500000 UPPER=373.1500000 NPOINT=20
   PARAM
   TABULATE PROPERTIES=PS-1

PROP-TABLE SPROP-4 FLASHCURVE
   STREAM PH1P3
   VARY PRES
   RANGE LIST=1.000000000
   VARY TEMP
   RANGE LOWER=273.1500000 UPPER=373.1500000 NPOINT=20
   PARAM
   TABULATE PROPERTIES=PS-1

PROP-TABLE SPROP-5 FLASHCURVE
   STREAM PH1,5IN
   VARY PRES
   RANGE LIST=1.000000000
   VARY TEMP
   RANGE LOWER=273.1500000 UPPER=373.1500000 NPOINT=20
   PARAM
   TABULATE PROPERTIES=PS-1
```

Appendix D – Aspen Plus flowchart