

GRAY BOX MODELING OF MSW DEGRADATION: REVEALING ITS DOMINANT (BIO)CHEMICAL MECHANISM

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SUMMARY: In this paper we present an approach to describe organic degradation within immobile water regions of Municipal Solid Waste (MSW) landfills which is best described by the term “gray box” model. We use a simplified set of dominant (bio)chemical and physical reactions and realistic environmental conditions. All equations, relationships and inhibitions are based on semi-empirical or fundamental relationships which have proven to be applicable in the peer reviewed literature. As much as possible parameter values are obtained from thermodynamic relationships and literature, a minimum set of parameters needs to be identified by fitting. Modeled emissions of biogas, Volatile Fatty Acids (VFA), pH and ammonium are in good agreement with the experimental data. The model is able to describe the delay in methanogenic activity, the dynamics in pH and the partial pressures in the gas phase. Results from a parameter optimization indicate a missing transport limitation. Our aim is to include the model as a bio(geo)chemical module in other models because of its computational efficiency.

1. INTRODUCTION

Completion of landfill aftercare requires a quantitative estimate of the remaining emission potential present in the waste body. Knowing the emission potential is also relevant when implementing management scenarios aiming to stabilize the waste body (infiltration, leachate recirculation, aeration etc.). An important part of landfill stabilization is the degradation of the available organic matter in the waste body.

We hypothesize that most of the organic degradation takes place in immobile water regions or ‘water pockets’ within Municipal Solid Waste (MSW) landfills. As such these regions are an important source for biogas, leachate compounds. A good understanding of the processes occurring within these ‘water pockets’ is therefore essential for accurate prediction of landfill emission behavior.

More insight in to the complex mechanisms within such a water pocket can be obtained by modeling. However, due to the large scale and high heterogeneity within full-scale landfills it is difficult to choose a proper modeling approach. Detailed mechanistic models (white box) require large sets of well identified parameters which are impossible to obtain at full landfill scale. As a consequence the inherent large uncertainty in parameters would severely reduce the reliability of the model. On the other hand, simplifying the processes within the ‘water pocket’ to a fully empirical first order relation (black box) is not satisfying as we do have quite detailed knowledge of the processes that may occur. In addition we need to incorporate complex interactions between the different reactions and environmental conditions in order to be able to use models for realistic representation of the biodegradation in order to make predictions about future emission behavior.

In this paper we present an approach to describe the processes within a ‘water pocket’ which is best described by the term “gray box” model. We use a simplified set of dominant (bio)chemical and physical reactions and realistic environmental conditions. All equations, relationships and inhibitions are based on semi-empirical or fundamental relationships which have proven to be applicable in the peer reviewed literature. As much as possible parameter values are obtained from thermodynamic relationships and literature, a minimal set of parameters needs to be identified by fitting. Maintaining the balance between the use of proven relationships and simplified process description allows us to maintain a general applicability.

2. MODEL DESCRIPTION

The gray box approach we developed is verified with data obtained from an experiment carried out by R. Valencia (2009) in which leachate was recirculated in a bioreactor filled with shredded MSW (volume of 750 liter). In order to keep things as simple as possible we assume that the system can be described as a continous stirred reactor which is well mixed, i.e. we disregard effects of transport within the column. We assume that biodegradation, associated redox reactions and exchange with the gas phase are relatively slow processes compared to the inorganic geochemical speciation in our system. The main reason for this is that certain inhibiting conditions for biodegradation occur in the system.

2.1. General framework

The model numerically integrates mass balances in time via solvers in MATLAB for the liquid and gas phase. Considered compounds in liquid and gas phase are either dynamic or constant and listed in Table 1. The lumped VFA_x represents a constant ratio between the products of acidogenesis and acetogenesis during the experiment.

Mass balances for component i in both the liquid and gas phase are given in equations 1 and 2 respectively. The mass change in liquid is the total of the mass change per biochemical reaction j including the exchange of mass with the gas phase. The parameters R , S , f , k_1a and C^* represent maximum degradation rate constant, stoichiometric coefficient, inhibition coefficient, mass transfer constant and maximum solubility in the liquid phase, respectively. V_l denotes the liquid phase volume and is assumed to be constant. Mass change in gas is the resultant of mass transfer from liquid to gas and mass transport to the environment. The parameters x and F_{out} represent mass fraction and total gasflow to the environment respectively. Gas volume and pressure are assumed constant. Total gasflow therefore equals the total mass transfer in.

$$\frac{dM_{i,l}(t)}{dt} = \sum_{j=1}^n \frac{dM_{i,j,l}(t)}{dt} = \left(\sum_{j=1}^n \left(R_{j,\max} \cdot \prod_{a=1}^n f_{a,j}(t) \cdot S_{i,j} \right) \cdot C_{ss/x}(t) + k_1 a \cdot (C_{i,l}^* - C_{i,l}) \right) \cdot V_1 \quad (1)$$

$$\frac{dM_{i,g}(t)}{dt} = k_1 a \cdot (C_{i,l}^* - C_{i,l}) \cdot V_1 - X_{i,g} \cdot F_{out} \quad (2)$$

2.2. Biochemistry

Four biochemical kinetic steps are considered in the model and listed in Table 2. The composition of organic solid substrate ($CH_{1.79}O_{0.63}N_{0.06}$) and VFA_x ($C_{2.36}H_{4.72}O_{1.72}$) are derived from the measurements. The hydrolysis reaction is a lumped form of hydrolysis, acidogenesis and acetogenesis. Its reaction stoichiometry is balanced according to the constant VFA ratio and the net hydrogen production of zero. To ensure mass-balance in the experiment we needed to assume that 80 % of the organic solid substrate is degradable and 20 % remains as soluble inert material.

Both methanogenesis and sulphate reduction are lumped with acetogenesis and use VFA_x as a substrate. The biomass is assumed to decay to the same composition as organic solid substrate. A general formula ($CH_{1.4}O_{0.4}N_{0.2}$) for biomass is considered and the growth yield for each reaction is estimated with the energy dissipation method and thermodynamics relationships. Inhibiting compounds for each reaction are listed in Table 3. Additionally a first order Ammonium oxidation reaction is considered that only consumes Ammonium.

Dominant (inhibiting) conditions and slow kinetic steps in anaerobic degradation were included and taken from validated waste water models. The speciation of the chemical system is described by the major ions and minerals present. Chemical equilibrium is considered instantaneous for the time scale investigated. For accurate description of the inhibition effects (like pH) chemical equilibrium is updated at each time step of the numerical integration. This is done by a very efficient coupling of MATLAB and ORCHESTRA (J.C.L. Meeussen (2003)).

Table 1. Compounds considered in the model

Dynamic compounds in liquid	Total protons (H^+)	Chloride (Cl^-)
Organic solid substrate (C_{ss})	Methanogenic biomass (C_x)	Dynamic compounds in gas
Methane (CH_4)	Total Ammonium ($NH_3 + NH_4^+$)	Methane (CH_4)
Total Sulfide ($H_2S + HS^- + S^{2-}$)	Total Sulfate ($H_2SO_4 + HSO_4^- + SO_4^{2-}$)	Carbon dioxide (CO_2)
Lumped Volatile Fatty Acid (VFA_x)	Sulfate reducing biomass (C_x)	Ammonia (NH_3)
Water (H_2O)	Constant compounds in liquid	Water (H_2O)
Acidogenic biomass (C_x)	Calcium (Ca^{+2})	Nitrogen (N_2)
Total Carbonates ($H_2CO_3 + HCO_3^- + CO_3^{2-}$)	Sodium (Na^+)	Dihydrogen sulfide (H_2S)

2.3. Mineral & Speciation Chemistry

The speciation and mineral reactions considered in the calculations of the chemical equilibrium done by ORCHESTRA for each time step are listed in Table 4. Activity corrections are calculated with Davies equation. The speciation of VFA_x is modelled as the speciation of Acetic acid.

2.4. Physics

Instantaneous physical equilibrium is assumed between solid and liquid phase for all compounds. Once the organic solid substrate is hydrolyzed it is immediately soluble. Mass transfer from liquid to gas is kinetically modelled with a transfer rate constant k_{la} as presented in equation 1 and 2. The reactor is assumed perfectly mixed and fully saturated. Gas/liquid volume and pressure are considered constant.

Table 2. (Lumped) biochemical reactions considered in the model.

Hydrolysis:	$1C_{1.179}H_{4.72}O_{1.72}N_{0.06} + 0.078H_2O \rightarrow 0.3C_{2.36}H_{4.72}O_{1.72} + 0.01CO_2 + 0.024NH_3 + 0.18C_{1.14}H_{1.4}O_{0.4}N_{0.2}$
Methanogenesis:	$1C_{2.36}H_{4.72}O_{1.72} + 0.24H_2O + 0.027NH_3 \rightarrow 1.27CH_4 + 0.95CO_2 + 0.13C_{1.14}H_{1.4}O_{0.4}N_{0.2}$
Sulfate reduction:	$1C_{2.36}H_{4.72}O_{1.72} + 1.15H_2SO_4 + 0.003NH_3 \rightarrow 1.15H_2S + 1.99CO_2 + 0.014C_{1.14}H_{1.4}O_{0.4}N_{0.2} + 2.35H_2O$
Biomass decay:	$1C_{1.14}H_{1.4}O_{0.4}N_{0.2} + 0.34H_2O \rightarrow 0.92C_{1.179}H_{4.72}O_{1.72}N_{0.06} + 0.08CO_2 + 0.14NH_3$

Table 3. Compounds that cause inhibition of the respective reaction.

Hydrolysis:	pH and VFA_x
Methanogenesis:	VFA_x (substrate limitation), pH, NH_3 and H_2S
Sulfate reduction:	SO_4^{-2} (substrate limitation) and H_2S

Table 4. Speciation and mineral reactions calculation by ORCHESTRA.

$C_2H_4O_2 \rightleftharpoons C_2H_3O_2^- + H^+$	$H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \rightleftharpoons CO_3^{-2} + H^+$
$Na(C_2H_3O_2) \rightleftharpoons Na^+ + C_2H_3O_2^-$	$Ca(C_2H_3O_2)^+ \rightleftharpoons Ca^{+2} + C_2H_3O_2^-$
$NaHCO_3 \rightleftharpoons Na^+ + HCO_3^-$	$NaCO_3^- \rightleftharpoons Na^+ + CO_3^{-2}$
$CaHCO_3^+ \rightleftharpoons Ca^{+2} + HCO_3^-$	$H_2O \rightleftharpoons OH^- + H^+$
$NH_4^+ \rightleftharpoons NH_3 + H^+$	Calcite $\rightleftharpoons Ca^{+2} + CO_3^{-2}$
Natron $\rightleftharpoons 3Na^+ + HCO_3^- + CO_3^{-2}$	$Ca(NH_3)_2^{+2} \rightleftharpoons Ca^{+2} + 2NH_3$
$CaNH_3^{+2} \rightleftharpoons Ca^{+2} + NH_3$	$CaOH^+ \rightleftharpoons Ca^{+2} + OH^-$
Gypsum $\rightleftharpoons Ca^{+2} + SO_4^{-2}$	$HSO_4^- + H^+ \rightleftharpoons SO_4^{-2} + H^+$
$H_2S \rightleftharpoons HS^- + H^+ \rightleftharpoons S^{-2} + H^+$	$NH_4SO_4^- \rightleftharpoons NH_4^+ + SO_4^{-2}$
$NaSO_4^- \rightleftharpoons Na^+ + SO_4^{-2}$	

2.5. Parameters

Intrinsic, validated, fitted process parameters and initial conditions estimated from the measurements are listed in Table 5. The K_s value for VFA_x is assumed to be equal to the K_s value for Acetic acid. The amount of Calcite is set such that it is not depleted during the simulation. The initial concentrations in the gas phase are derived from initial concentration in the liquid phase according to Henry's law.

Most of the intrinsic processes include validated parameters. However, ammonium oxidation and parameters for initial concentration of bacteria and mass transfer from liquid to gas (k_{1a}) were fitted to the experimental data. They could not be estimated or described fundamentally because of insufficient experimental or literature data. In order to accurately describe the measured ammonium dynamics ammonium degradation is modeled during the experiment as a first order reaction ($k = 0.006 \text{ d}^{-1}$). It was important to include this degradation for accurate description of ammonia inhibition effects. The initial amount of methanogenic/sulphate reducing bacteria is set to 2.2 mol L^{-1} . The rate constant, k_{1a} , for mass transfer from liquid to gas is set to 0.8 d^{-1} .

3. RESULTS & DISCUSSION

The modeled emissions of biogas ($p\text{CO}_2$, $p\text{CH}_4$, and cumulative production of landfill gas), Volatile Fatty Acids (VFA), pH and ammonium are presented together with the experimental data in Figure 1. Considering the heterogeneity and scale of the experiment the model results are in good agreement with the experimental data. This indicates that the gray modeling approach simplifies the heterogeneity of this system correctly. The fact that the model is based on fundamental relations (and intrinsic parameters) suggests that the model may have a general applicability for simulating 'water pockets' under other experimental conditions as well.

Detailed modeling of biochemical stoichiometry using the experimentally determined initial composition of the waste, in combination with including inhibition effects acting on both hydrolysis and methanogenesis enables the model to correctly describe the delay in methanogenic activity, the dynamics in pH and the ratio between $p\text{CH}_4$ and $p\text{CO}_2$. In order to achieve this result it was essential to update the chemical system including all possible equilibrium reactions for every time step.

Table 5. Intrinsic, validated, fitted process parameters and initial conditions in the model.

Intrinsic/Literature		$K_{i,\text{H}_2\text{S}(\text{sulf})}$	$2.5 \times 10^{-3} \text{ mol L}^{-1}$	$C_{\text{H}+(\text{tot}),\text{ini}}$	-2.21 mol L^{-1}
k_{hyd}	0.108 d^{-1}	Process (Measurements)		$C_{\text{SO}_4(\text{tot}),\text{ini}}$	0.07 mol L^{-1}
qS_{meth}^m	$1.79 \text{ mol Cmol}^{-1} \text{ d}^{-1}$	T	303 K	$C_{\text{H}_2\text{S}(\text{tot}),\text{ini}}$	0 mol L^{-1}
qS_{sulf}^m	$22.5 \text{ mol Cmol}^{-1} \text{ d}^{-1}$	P	1 atm	Process (fitted)	
$K_{s,\text{meth}}$	$0.00018 \text{ mol L}^{-1}$	V_1	325 L	k_{NH_4}	0.006 d^{-1}
$K_{s,\text{sulf}}$	$0.00018 \text{ mol L}^{-1}$	V_g	80 L	k_{1a}	0.8 d^{-1}
$K_{i,\text{pH}(\text{hyd})}$	$1 \times 10^{-5} \text{ mol L}^{-1}$	$C_{\text{ss},\text{ini}}$	7.25 mol L^{-1}	$C_{x(\text{meth}),\text{ini}}$	$0.0022 \text{ mol L}^{-1}$
$K_{i,\text{pH}(\text{meth})}$	$5 \times 10^{-7} \text{ mol L}^{-1}$	$C_{\text{VFA}_x,\text{ini}}$	0.2 mol L^{-1}	$C_{x(\text{sulf}),\text{ini}}$	$0.0022 \text{ mol L}^{-1}$
K_{i,NH_3}	$1.21 \times 10^{-3} \text{ mol L}^{-1}$	$C_{\text{H}_2\text{CO}_3(\text{tot}),\text{ini}}$	1.08 mol L^{-1}	$C_{x(\text{ace}),\text{ini}}$	0 mol L^{-1}
K_{i,VFA_x}	$2.34 \times 10^{-2} \text{ mol L}^{-1}$	$C_{\text{NH}_3(\text{tot}),\text{ini}}$	0.065 mol L^{-1}		
$K_{i,\text{H}_2\text{S}(\text{meth})}$	$4.7 \times 10^{-3} \text{ mol L}^{-1}$	$C_{\text{CH}_4,\text{ini}}$	0 mol L^{-1}		

The difference in experimental and modeled biogas production after $t = 580$ indicates that a slow hydrolyzing substrate is missing in the model. This slow hydrolyzing step is important to incorporate in the model for investigation of the waste over longer time periods. Comparing the modeled pH with the experimental pH shows that the model is not able to capture the gradual increase in pH. This is an indication that some kind of mass transport limitation is missing in the model. Results from an optimization of all parameters in which the model results are fitted to the experimental data within a Bayesian framework also indicates a high value for the methanogenic K_s . In biochemistry high K_s values are often used to compensate for a missing transport limitation.

4. OUTLOOK

Lab-scale (2L) and lysimeter experiments (750 L) are planned to obtain more insight in uncertain processes/parameters of the gray model such as ammonium degradation, initial concentration of bacteria and $k_{i,a}$. A set of experiments in which increased mass transfer limitation is imposed will be performed in order to establish a semi-empirical mass transfer relation. The lysimeter experiments will also be used to test different treatment methods such as irrigation/recirculation and aeration for enhanced biodegradation. The combination of experiments and gray modeling gives the opportunity to investigate the methods applied to reduce emission potential in a more fundamental framework. Once verified, the gray box model may provide a relative accurate tool for prediction of ‘water pockets’ behavior. Our aim is to include it as a bio(geo)chemical module in other models because of its computational efficiency.

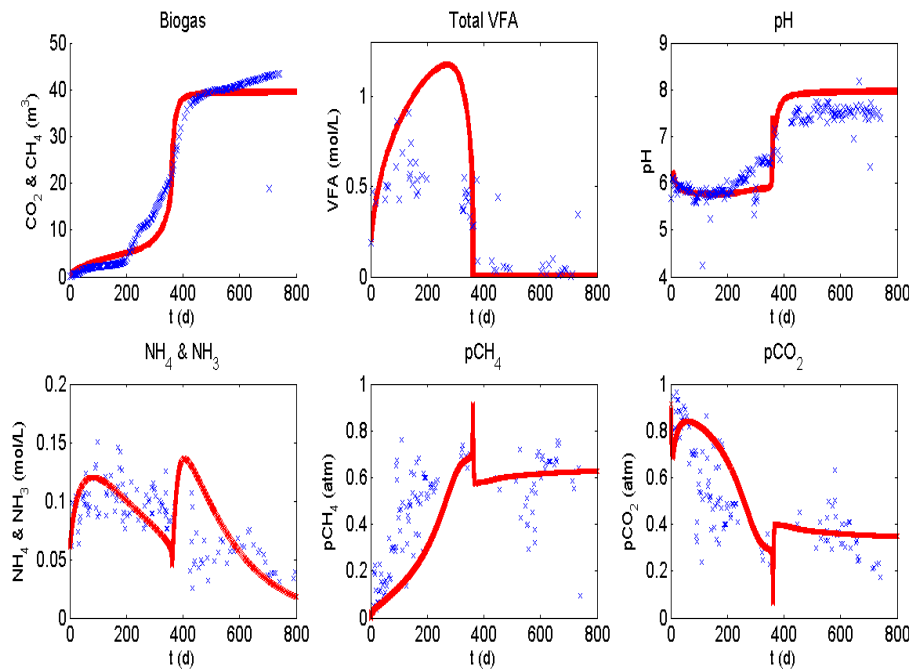


Figure 1. Experimental data and model results represented in blue and red respectively.

5. REFERENCES

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