



# MODELING BIOCHEMICALLY DRIVEN MINERAL PRECIPITATION IN ANAEROBIC BIOFILMS

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## ABSTRACT

A numerical model links the build-up of mineral precipitate (primarily  $\text{CaCO}_3$ ) and the anaerobic activity of biofilms, which occur in granular material permeated with leachate from a municipal solid waste landfill. The model represents the porous-media flow system as a collection of elements in which each element acts as a separate, fixed-film reactor. The model represents biofilm growth for microorganisms carrying out acetogenesis of propionate and methanogenesis of acetate. It also directly links substrate utilization to mineral precipitation and accounts for the accumulation of inert biomass on the porous media at any time or position along the length of the column. Thus, the model describes the ecological interactions among fermenters, methanogens, inert biomass, and mineral precipitate. Although substrate utilization by the active microorganisms drives the entire system, mineral precipitate becomes a dominant component in the biofilm.  
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## KEYWORDS

Biofilms; clogging; landfills; leachate collection systems; mineral precipitation; modelling.

## INTRODUCTION

The clogging of leachate collection systems in municipal solid waste landfills is a problem of considerable concern to engineers (eg. see Brune *et al.*, 1991; Rowe *et al.*, 1997). To date there is no published technique for predicting the rate of clogging of these systems. This paper represents a first step towards the modelling of the long-term performance of landfill leachate collection systems. It also provides important insights into ecological interactions among active and inert components of the anaerobic biofilms that develop in leachate collection systems.

The objective of the paper is to present a model for biochemically driven mineral precipitation that occurs in laboratory column experiments, performed using synthetic landfill leachate. The model is based on transient anaerobic, fixed-film biological processes (such as those considered in wastewater treatment modelling) coupled with deposition of mineral precipitate. A time-marching algorithm allows the evolution of the influent and effluent organic concentration, active biofilm species, inert biomass, mineral precipitate, and porosity to be modelled at any position or time. An example is given to illustrate predictions of the model.

## REPRESENTATION OF COLUMN FLOW

The porous medium of the flow system is represented using ideal spheres of equal diameter. This idealization allows geometric calculation of the porosity and specific surface as a function of the film thickness on the porous medium. The diameter of the spheres is assumed to be equal to the average diameter of the medium while the packing arrangement of the spheres is related to the initial porosity of the medium. The column is discretized into a single line of segments, where each segment is assumed to act as a separate, fixed-film reactor. Acting as a reactor, each segment reduces the concentration of substrate in the fluid, and the chemical energy is converted partially into bacterial cell mass. This growth of biomass forms an *active* film layer on the porous media. As explained later in this paper, this bacterial activity aids in the formation of a second film, an *inactive* film, which consists of inert biomass and mineral precipitate. As a first approximation, the *active* film grows on the outermost surface, whether that be the media or inactive film, and the *inactive* film forms directly on the porous media, behind the active layer. The influent substrate concentration and flow rate to the first segment is a boundary condition (which could vary with time). The influent substrate concentration to all other segments is equal to the effluent substrate concentration of the previous segment in the series. Saturated flow conditions are assumed for all segments. Flow (and hence substrate) is transferred from one segment to the next over time using a simple advection algorithm. Leachate may include a number of potential substrates; however the dominant substrates are acetic and propionic acid. The model, therefore, was designed to model separately acetogenesis of propionate and methanogenesis of acetate in a mixture of these two acids. Note that since the majority of electron flow is through acetate, hydrogen methanogens are not included in the model.

## BIOFILM IDEALIZATION

The biofilm is idealized as shown in Figure 1(a). The active portion of biofilm has a uniform thickness of  $L_{fa}$  [L, where L is length] and a uniform biofilm density of  $X_{fa}$  [ $M L^{-3}$ , where M is mass]. A liquid diffusion layer of thickness  $L_d$  [L] represents a theoretical uniform layer of stagnant liquid adjacent to the biofilm and offering mass-transport resistance between the bulk liquid and the biofilm surface. The bulk liquid is perfectly mixed. No significant biological activity occurs in the bulk fluid or diffusion layer (relative to that in the active biofilm). The inactive film lies between the active film and the attachment media and has a uniform thickness of  $L_{fi}$  [L] and a uniform solids density of  $X_{fi}$  [ $M L^{-3}$ ].

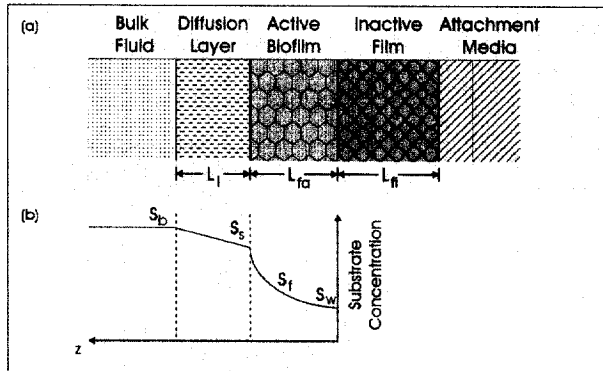


Figure 1. (a) Idealized biofilm and thicknesses, (b) substrate concentration profiles (modified from Rittmann and McCarty, 1980).

Figure 1(b) depicts the substrate concentration profile through the biofilm. Symbols  $S_b$ ,  $S_s$ ,  $S_f$ , and  $S_w$  in Figure 1(b) represent the substrate concentrations [ $M L^{-3}$ ] in the bulk liquid, at the outer surface of the biofilm, within the biofilm, and at the inactive film, respectively. The substrate concentration within the biofilm,  $S_f$ , only varies in the  $z$  direction, the direction normal to the surface of the biofilm. The substrate neither diffuses into, or is utilized by, the inactive film and attachment media.

The biofilm growth and loss model includes six processes occurring simultaneously. The six processes are: mass transport of the substrate across the diffusion layer, diffusion of the substrate in the biofilm, utilization of the substrate for cell growth (two types), subsequent growth of active cells, the growth of mineral film driven by the utilization of substrate, and loss of biomass due to detachment and decay of cell matter.

### MODEL PROCEDURES

The following describes the simulation of the processes occurring in each segment, during each time step. In addition, a simple advection algorithm is used to transport soluble substrates and products into and out of each segment for each time step.

Acetogenesis of propionate and methanogenesis of acetate are the key microbiological reactions, and they were described by a nonsteady-state biofilm model that simultaneously predicts the rates of propionate and acetate utilization, as well as the growth and loss of active acetogens and methanogens. The utilization rates of the two substrates, propionate and acetate, were each controlled by their own set of kinetic constants and concentrations. Each contributed to separate active and inactive films, which, when added together, comprised the active and inactive film thicknesses shown in Figure 1(a). Growth of cell matter was proportional to the flux  $J$  [ $M L^{-2} T^{-1}$ , where  $T$  is time] of each substrate into the biofilm, while losses occurred due to bacterial detachment and respiration decay (Rittmann, 1982; Rittmann and Brunner, 1984). The calculation of each flux of substrate into the biofilm was performed using a slightly modified version of the procedure outlined by Rittmann and McCarty (1981). The substrate flux into the biofilm was calculated according to the kinetic constants, a known bulk substrate concentration, and a known biofilm thickness for each substrate. Non-steady biofilm growth and loss due to a single substrate were then modelled using an algorithm modified from Rittmann and Brunner (1984). Finally, the "growth" of the two inert components, inert biomass and mineral precipitates, was computed from the substrate flux and amount of active biomass. All calculation methods are described in detail later.

Once the accumulation of biofilm was known, the new porosity  $n$  [-] and specific surface  $A_s$  [ $L^{-1}$ ] were calculated using equations based on a sphere model representing the porous media. The porosity and specific surface model was based on the work of Taylor (1990). However, Cooke and Rowe (1998) found that Taylor's equations gave erroneous porosity and specific surface values when the film thickness exceeded a threshold. Cooke and Rowe (1998) derived equations to be used within the region of error for each of four packing arrangements.

Since the above procedures required that the bulk substrate concentration within the segment,  $S_b$  (a function of the influent and effluent substrate concentrations,  $S_0$  and  $S_e$ ) be known, an iterative procedure was implemented to ensure that the value best reflects the conditions throughout the segment. First, initial estimates were made for  $S_b$ ,  $L_i$ , and the total loss coefficient,  $b'$  [ $T^{-1}$ ]. Using these values and the active film thickness corresponding to the substrate,  $L_{fa}$ , the flux, biofilm and mineral film thicknesses, and change in porosity and specific surface were calculated. A mass balance was used to calculate a revised effluent substrate concentration  $S_e$ , upon which a new estimate of  $S_b$  was made. Because degradation of propionic acid produces acetic acid, the following mass balance was used to calculate the effluent acetate concentration,  $S_{e,a}$ :

$$S_{e,a} = S_{0,a} + 0.5714 \frac{J_p V A_s}{Q} - \frac{J_a V A_s}{Q} \quad (1)$$

where  $S_{0,a}$  is the influent acetate concentration,  $J_p$  and  $J_a$  are the flux of propionate and acetate, respectively,  $V$  [ $L^3$ ] is the segment volume,  $A_s$  is the specific surface of the beads,  $Q$  [ $L^3 T^{-1}$ ] is the flow rate and 0.5714 is the ratio of mass (in COD) of acetic acid created per mass of propionic acid degraded. The mass balance for propionic acid required no term for production from degradation of other substrates. The calculations were repeated until convergence of the estimated and calculated effluent concentrations occurred. Based on the converged values of substrate flux, film thicknesses, porosity, and specific surface, the loss due to detachment coefficient,  $b_d$  (and thus total loss coefficient,  $b'$ ), and diffusion layer thickness,  $L_i$  (if considered variable), were recalculated.

## CALCULATION OF BIOFILM AND MINERAL GROWTH AND LOSS

Non-steady growth and loss of biofilm

The change in thickness of the active biofilm,  $L_{fa}$ , and change in thickness of the mineral and inert film, which added together form the inactive film, were calculated separately for each segment and time step. The model utilized the expression of non-steady growth and loss of biofilm developed by Rittmann and Brunner (1984):

$$\frac{d X_{fa} L_{fa}}{dt} = Y J - b' X_{fa} L_{fa}$$

where  $t$  is time [T] and  $Y$  [ $M M^{-1}$ ] is the active biomass yield coefficient. Because the time increment  $\Delta t$  was small and  $J$  and  $b'$  did not change significantly, the new active film thickness was calculated for each time step using:

$$L_{fa,New} = L_{fa} + \Delta t \frac{Y J - b' X_{fa} L_{fa}}{X_{fa}}$$

where  $\Delta t$  is the time step length and the flux  $J$  used in the equation is calculated as outlined in the previous section, and the biofilm thickness  $L_{fa}$  is the thickness calculated in the previous time step for this segment. A very small initial estimation of  $L_{fa}$  was required for the first time step, since the calculation of substrate flux  $J$  requires a non-zero thickness of biofilm. The initial film thickness was  $0.05 \mu m$ , which according to Rittmann and Brunner (1984) represents about 5% surface coverage for a monolayer of bacteria.

Mineral precipitation and inert biomass accumulation

The composition of the inorganic portion of clog material is predominately calcium carbonate,  $CaCO_3$  (Brune *et al.*, 1991; Rowe *et al.*, 1995; Fleming *et al.*, 1998). Rittmann *et al.* (1996) reported a relationship between the microbial oxidation of COD and inorganic carbon to the mass of calcium carbonate precipitated out of landfill leachate. Laboratory experiments performed using coarse gravel permeated with landfill leachate indicated that the removal of COD (mostly acetic acid) and its partial conversion to  $H_2CO_3$  resulted in an increase in pH and total carbonate, which together caused a large increase in  $CO_3^{2-}$  concentration, allowing or accelerating  $CaCO_3$  precipitation. Further testing using synthetic leachate resulted in similar trends, and test data (for a column test conducted in triplicate using 6 mm glass beads as the porous medium) are summarized in Figure 2

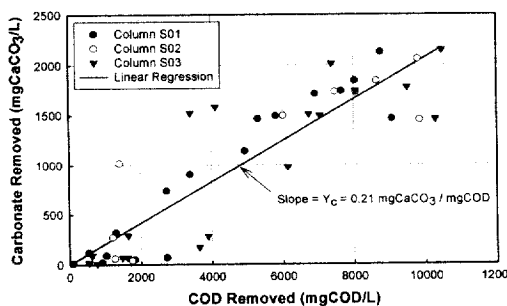


Figure 2. Measured calcium carbonate removed versus COD removed and calculation of  $Y_c$  by linear regression for columns fed synthetic leachate ( $r = 0.90$ ).

A linear relationship between COD removal and  $CaCO_3$  precipitation is clear and provides an empirical yield coefficient,  $Y_c$  [ $M_{CaCO_2} M_{COD}^{-1}$ ] of  $0.21 \text{ mg } CaCO_3 \text{ precipitated per mg COD consumed}$ . Further research is being completed to study the effects of loading rate, temperature, and chemical constituents on  $Y_c$ . Of course, precipitation of  $CaCO_3$  depends on the presence of  $Ca^{2+}$ , which is one of the dominant ions

in leachate. The empirical yield coefficient and the substrate fluxes gave the rate of mineral precipitation of  $\text{CaCO}_3$ :

$$\frac{d(X_f L_f)_{\text{mineral}}}{dt} = Y_c J$$

where  $J$  is the flux of COD into the active biofilm, and  $(X_f L_f)_{\text{mineral}}$  is the mass of mineral accumulated per unit area.

Inert biomass is non-degradable organic solids produced as part of biomass decay. The accumulation of inert biomass was found by first assuming a fraction of the active biomass,  $f_d$ , is degradable due to decay, while the remaining fraction,  $(1-f_d)$ , is not degradable. The rate of accumulation of inert biomass was calculated from:

$$\frac{d(X_f L_f)_{\text{inert}}}{dt} = (1 - f_d) b X_{fa} L_{fa}$$

where  $b$  is the decay coefficient of the active biofilm and  $(X_f L_f)_{\text{inert}}$  is the mass of inert material accumulated per unit area. The new thickness of the inactive film was found by the addition of the new mineral and inert film accumulations, as calculated in Equations 4 and 5, and implemented in the model using:

$$L_{fi, \text{New}} = L_{fi} + \Delta t \frac{Y_c J + (1 - f_d) b X_{fa} L_{fa}}{X_{fi}}$$

where  $X_{fi}$  is the density of the inactive film.

Table 1. Kinetic constants for hypothetical column experiment

Parameter	Acetic Acid	Propionic Acid	Units
$K_S$	1700	2800	mgCOD / L
$Y$	0.038	0.042	mgVS / mgCOD
$q^*$	3.9	3.0	mgCOD / mgVS-d
$b$	0.066	0.066	$\text{d}^{-1}$
$D_f$	0.47	0.52	$\text{cm}^2 / \text{d}$
$D_f/D_0$	0.31	0.41	-

#### APPLICATION OF THE MODEL

The model was applied to a hypothetical column experiment performed using a synthetic leachate. Although this application is hypothetical, it closely resembles column studies in terms of design and results (Cooke, 1997). The effective section of the column was 76.0 cm long, 5.1 cm in diameter, and filled with 0.6 cm diameter spherical glass beads. The column was operated with synthetic leachate at a continuous flow rate of 1.0 L/d. The density of the active and inactive films, measured from autopsies performed on column experiments conducted using real leachate (Cooke, 1997), were  $X_{fa} = 70 \text{ mgVS/cm}^3$  and  $X_{fi} = 2700 \text{ mgTS/cm}^3$ , respectively. The half-maximum rate substrate concentration,  $K_S$  [ $\text{M L}^{-3}$ ], maximum yield coefficient,  $Y$ , maximum specific rate of substrate utilization,  $q^*$  [ $\text{M M}^{-1} \text{T}^{-1}$ ], biomass decay coefficient,  $b$  [ $\text{T}^{-1}$ ], internal diffusion coefficient  $D_f$  [ $\text{L}^2 \text{T}^{-1}$ ] and diffusion ratio  $D_f/D_0$  for acetic and propionic acid were selected based on a number of experimentally measured values from literature, modified for laboratory temperature when applicable. They are summarized in Table 1. The calcium carbonate yield coefficient,  $Y_c$ ,

was 0.21 mgCaCO<sub>3</sub>/mgCOD as explained above and shown in Figure 2. The number of time steps, length of time step, and number of segments were varied to guarantee accuracy and stability of the model output. Space does not permit a discussion of the selection of parameters of this example; however, details are in Cooke (1997).

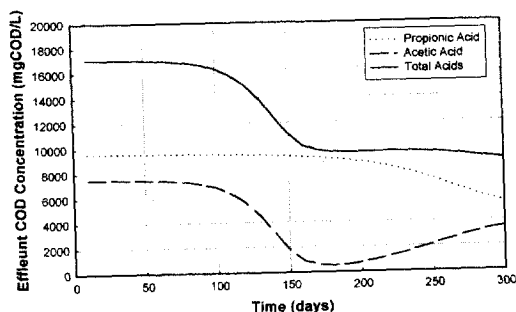


Figure 3. Change in predicted effluent COD concentrations of propionic and acetic acid, and the total COD over time.

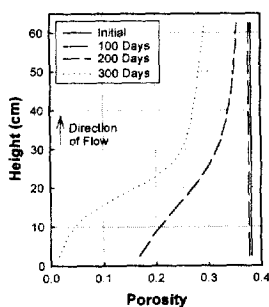


Figure 4. Predicted change in porosity due to active and inactive film growth along the column at 100 day intervals.

Figures 3 and 4 illustrate the predicted loss of organic substrates and build up of the clog material. Figure 3 shows the predicted total COD, propionic-acid COD, and acetic-acid COD concentrations in the effluent versus time. The model predicts an initial lag period, an increase in substrate removal, and then a final, relatively constant removal period for total COD. However, the model predicts a gradual shift within the active biomass, as the propionate utilizers develop more slowly than the acetoclastic methanogens. This is indicated by the later degradation of propionate relative to acetic acid, which causes an increase in the acetic-acid COD. Figure 4 shows the predicted porosities along the length of the column during the period at 100 day intervals. Rapid accumulation of clog material occurs throughout the column, but is most important near the inlet, where COD concentrations are greatest.

The ecological history predicted by the model illustrates the change in dominance in the system from biofilm growth to mineral precipitation. Figure 5 shows that the biofilm ecology eventually becomes dominated by inert materials, especially near the inlet, where medium clogging is most significant. The model also predicts a strong ecological distribution by location. Figure 6 demonstrates that the propionate-utilizer community is located largely near the acetate-starved outlet of the column, while a considerably larger acetate community is located at the inlet.

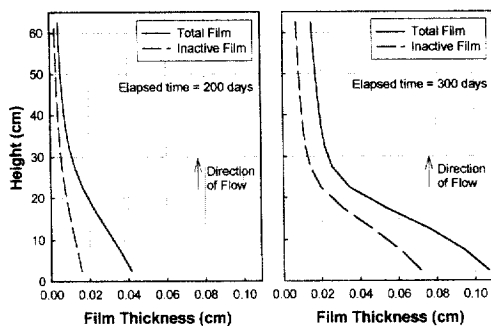


Figure 5. Predicted inactive and total film thickness profiles along the column after 200 and 300 days. The inactive film is dominated by  $\text{CaCO}_3$  precipitate.

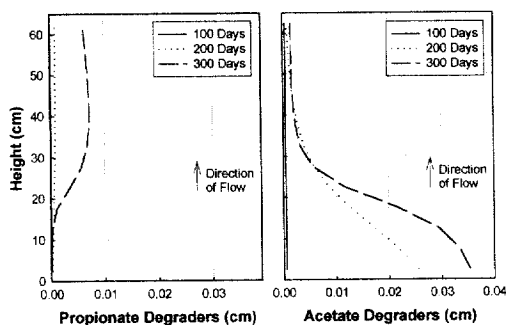


Figure 6. Predicted (a) propionate and (b) acetate degrader film thickness profiles along the column at 100 day intervals.

## CONCLUSIONS

A model was developed for predicting the change in porosity in column test experiments fed synthetic leachate. The model considers the growth of two types of active biofilm (propionate fermenters and acetoclastic methanogens) and two types of inert material (inert biomass and  $\text{CaCO}_3$  precipitate). The mineral growth was linearly related to substrate utilization, at a rate established empirically. The ecological history of the column was predicted with respect to acetogenic and methanogenic film growth, acetate and propionate removal, calcium carbonate precipitation, and total effect on porosity and clogging. For conditions relevant to synthetic leachate, the model gave these insights about the microbial ecology: (1) the propionate fermenters developed much more slowly than did the acetate methanogens; (2) the propionate fermenters tended to accumulate near the acetate-starved outlet of the column; and (3) the part of the column that became seriously clogged was populated by acetoclastic methanogens, but the dominant compound in the biofilm was the mineral precipitate.

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