“Non-linearities and upscaling in porous media“

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A. Ebigbo
R. Helmig
A.B. Cunningham
H. Class
R. Gerlach

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Anozie Ebigbo\textsuperscript{a}, Rainer Helmig\textsuperscript{a}, Alfred B. Cunningham\textsuperscript{b}, Holger Class\textsuperscript{a}; Robin Gerlach\textsuperscript{b}

\textsuperscript{a}Department of Hydromechanics and Modelling of Hydrosystems, Universität Stuttgart, Pfaffenwaldring 61, 70569 Stuttgart, Germany.
\textsuperscript{b}Center for Biofilm Engineering, Montana State University, Bozeman, MT 59717, USA.

Abstract

The concentration of greenhouse gases – particularly carbon dioxide (CO\textsubscript{2}) – in the atmosphere has been on the rise in the past decades. One of the methods which have been proposed to help reduce anthropogenic CO\textsubscript{2} emissions is the capture of CO\textsubscript{2} from large, stationary point sources and storage in deep geological formations. The caprock is an impermeable geological layer which prevents the leakage of stored CO\textsubscript{2}, and its integrity is of utmost importance for storage security. Due to the high pressure build-up during injection, the caprock in the vicinity of the well is particularly at risk of fracturing. Biofilms could be used as biobarriers which help prevent the leakage of CO\textsubscript{2} through the caprock in injection well vicinity by blocking leakage pathways. The biofilm could also protect well cement from corrosion by CO\textsubscript{2}-rich brine.

The goal of this paper is to develop and test a numerical model which is capable of simulating the development of a biofilm in a CO\textsubscript{2} storage reservoir. This involves the description of the growth of the biofilm, flow and transport in the geological formation, and the interaction between the biofilm and the flow processes. Important processes which are accounted for in the model include the effect of biofilm growth on the permeability of the formation, the hazardous effect of supercritical CO\textsubscript{2} on suspended and attached bacteria, attachment and detachment of biomass, and two-phase fluid flow processes. The model is tested by comparing simulation results to experimental data.

Key words: biofilm growth, CO\textsubscript{2} storage, leakage
1. Introduction

The fundamental motive of this work is the incorporation of concepts and equations describing microbial biofilm processes into a simulator, which models two-phase fluid flow through porous media, with the purpose of examining the interactions between the fluid phases flowing through the porous medium, dissolved constituents, and microorganisms – either attached or suspended in a fluid. Many modelling studies exist in the literature which attempt to model biofilms in porous media. However most account for only one fluid phase (i.e., saturated flow), e.g., Foppen et al. (2007); Ham et al. (2007); Kim (2006); Cooke et al. (2005); Thullner et al. (2004); Murphy and Ginn (2000); Chen-Charpentier (1999); Clement et al. (1999, 1996); Tan et al. (1994); Hornberger et al. (1992); Taylor and Jaffé (1990b). Few studies describe models capable of simulating a system consisting of two fluid phases flowing through a porous medium containing a biofilm or suspended bacteria, e.g., Gargiulo et al. (2007); Maggi and Porporato (2007); Mostafa and Van Geel (2007); Yarwood et al. (2006); Rockhold et al. (2004, 2002); Schaefer et al. (1998); Wan et al. (1994). The work presented here models this system using a dual-continuum concept – assuming that the biofilm phase can contribute to flow – and empirically accounts for the effect of the presence of the two fluid phases on bacterial growth and decay. Many existing models focus on such applications as microbially enhanced oil recovery and bioremediation. The present work focuses on the application of the model to the mitigation of leakage from a geologic carbon dioxide (CO\textsubscript{2}) storage reservoir.

The effects of global warming on the environment are diverse and often beyond human control. Anthropogenic emissions of greenhouse gases, particularly CO\textsubscript{2}, have been made primarily responsible for the temperature increase. The use of more efficient technology and regenerative energy sources are ways of reducing emissions. Additionally, CO\textsubscript{2} could be captured from flue gases of power plants and stored in geological formations. Suitable storage formations should have the capacity to accommodate large amounts of CO\textsubscript{2} and guarantee a high storage security. Substantial leakage of CO\textsubscript{2} from a reservoir would render any storage operation useless and could even compromise groundwater resources and human life. Hence, the proper assessment of the risk of CO\textsubscript{2} leakage from a potential storage reservoir is a key issue that needs to be addressed (see Oldenburg, 2008; Kopp et al., 2009a). Minimising the risk of leakage could include sealing potential leakage pathways. Cunningham et al. (2009) propose the use of microbial biofilms to plug
such pathways. Experiments show that biofilms can significantly increase the resistance of a porous medium to flow (e.g., Taylor and Jaffé, 1990a; Vandevivere and Baveye, 1992; Mitchell et al., 2009). Setting up such a hydraulic barrier in the subsurface requires proper judgment of relevant flow, transport, and microbial processes. Numerical models are indispensable for the study of these processes and their interactions with each other.

In the following, the topics of microbial biofilms and CO₂ storage in geological formations are discussed in brief.

1.1. Microbial Biofilms

Bacteria and other microorganisms can exist as suspended or floating cells in a bulk fluid – planktonic. However, in natural environments, microbial cells tend to be sessile, i.e., attached to a solid surface. Attached cells are often embedded in a matrix of extrapolymeric substances (EPS) which protects the bacterial cells from environmentally harsh conditions. This assembly of EPS and microbial cells attached to a solid surface (substratum) is referred to as a biofilm.

The structure of biofilms is very heterogeneous. Cells within a biofilm tend to form clusters leaving open spaces within the structure. Biofilms in porous media grow on the surface of the solid matrix, occupying pore space and obstructing fluid flow through pore throats. Hence, the accumulation of biomass in a porous medium can lead to changes in the hydraulic properties (porosity, permeability) of the medium. This and the ability of attached bacteria to degrade certain compounds give rise to a range of applications in which biofilm-affected porous media are used as biofilters and biobarriers (Mitchell et al., 2009; Zekri, 2001; Rittmann, 1993; Cunningham et al., 1991).

1.2. CO₂ Storage in Geological Formations

Geological sites suitable for subsurface CO₂ storage include deep saline aquifers, depleted oil and gas reservoirs, and coal seams. The CO₂ is injected into geological formations at great depths (>800 m). Due to the high pressures and temperatures at such depths, the injected CO₂ would be either a liquid or a supercritical fluid. The injected CO₂, which is lighter and less viscous than the formation water (brine), would form a separate phase. The resulting CO₂ plume would, driven by the injection pressure, move radially into the formation. Due to buoyancy, it would also be driven upwards. An impermeable geological layer (caprock) is necessary to prevent the buoyant CO₂ plume from rising to the surface (see Figure 1). Fractures in the caprock
or leaky wells can act as leakage pathways for the injected CO$_2$ (Pruess, 2005; Nordbotten et al., 2005; Ebigbo et al., 2007). As an example, the reinjection of oily water into the Tordis subsea field in 2008 led to significant leakage of oil-contaminated formation water through fractures in the caprock into the North Sea$^1$.

Wells used for the injection of CO$_2$ into geological formations need to be able to withstand the high pressure build-up during injection and corrosion by CO$_2$-rich brine. The pressure increase due to injection is highest in the vicinity of the injection well. Its magnitude is dependent, among others, on the viscosities of CO$_2$ and brine, and on relative permeability effects. Due to low CO$_2$ saturations during the initial injection phase, the pressure build-up can be quite significant. This can cause fractures in the caprock. If the gas pressure exceeds the capillary entry pressure of the caprock, the CO$_2$ can penetrate the caprock. The injection rate can be regulated to prevent pres-$^1$

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sures that exceed some preestimated critical pressure. Injection well integrity can be undermined by corrosive CO\textsubscript{2}-water mixtures causing degradation of well cement.

Mitchell et al. (2009) have suggested the use of engineered biofilms to plug CO\textsubscript{2} leakage pathways. This would entail injecting microbial cells and nutrients at the caprock–aquifer interface before the injection of CO\textsubscript{2} into the formation with the intention of growing a biofilm which would plug potential leakage pathways. Cunningham et al. (2009) also propose the use of biofilms which are capable of actively precipitating calcium carbonate (CaCO\textsubscript{3}) minerals, in which case, a medium containing calcium ions would be injected after the formation of the biofilm.

1.3. Objective

The objective of this work is the development of a numerical model which can aid in assessing the feasibility of the use of biobarriers to increase CO\textsubscript{2} storage security. To this end, a model is described in Section 2 and tested against experiments in Section 3. Finally, it is applied to a field-scale test case in Section 4 in which leakage through the caprock of a formation is mitigated using biofilms.

2. Physical and Mathematical Model

This section focuses on the description of a conceptual model capable of representing the relevant processes involved in a system which consists of a natural porous medium, two fluid phases (water and CO\textsubscript{2}), and a biofilm (see Figure 2). Such a system is typically characterised by a hierarchy of length scales (e.g., Golfier et al., 2009; Kapellos et al., 2007; Wood and Ford, 2007). On the cell scale (characteristic length \( \sim 1 \, \mu\text{m} \)), individual bacterial cells and EPS, which make up the biofilm, can be identified. These cells form clusters held together by EPS. Given that the clusters are sufficiently large compared to the individual cells, one can treat these as a continuum, giving rise to the biofilm scale. The void spaces within a biofilm can serve as channels (characteristic pore diameter \( \sim 10 \, \mu\text{m} \)) for advective flow (see Stoodley et al., 1994; De Beer et al., 1994). If the thickness of the biofilm phase is sufficiently large compared to the size of the channels/voids within the biofilm, the flow processes through the biofilm may be described on the average with effective properties. These channels contribute to the overall flow of fluids through the porous medium/rock (characteristic pore diameter
Figure 2: For flow and transport processes involving two fluid phases and a biofilm within a porous medium, various characteristic length scales can be identified. The figure shows a conceptual model of how the fluids (water and CO$_2$) may be distributed within the porous medium (on the pore scale, characteristic pore diameter $\sim 100 \, \mu m$) and within the biofilm (on the biofilm scale, characteristic pore diameter $\sim 10 \, \mu m$).

$\sim 100 \, \mu m$). Obviously, flow processes as well as concentrations of solutes and bacterial cells within and outside the biofilm may differ significantly leading to strong gradients across the biofilm–fluid interface.

On the pore scale (microscale), the grains of the porous medium, which make up the solid phase, are impermeable. The biofilm is attached to the solid phase and occupies part of the porous medium’s void space. The rest of this space is occupied by the fluids. Pore-scale flow processes can be averaged (e.g., van Noorden et al., 2010; Golfier et al., 2009) on a larger scale (Darcy scale) giving rise to effective, macroscale parameters and equations which describe the porous medium and the interaction between the fluid, biofilm, and solid phases. Depending on the application in mind, one may or may not explicitly account for the flow and transport processes in the biofilm on the macroscale. In this work, the characteristic flow rates through the open pores of the porous medium and through the biofilm have direct consequences for the permeability changes caused by biofilm growth, the transport of nutrients, and the potential presence of CO$_2$ inside the biofilm. These are important factors which are difficult to describe properly without explicitly accounting for flow through the biofilm. Hence, a distinction is made here between two different components of the flow processes – fast flow through the open pores of the porous medium and slow flow through the biofilm within the porous medium. This can be seen in analogy to the dual-continuum concepts of
fractured porous media. Two continua can be defined as shown in Figure 3. Continuum $P$ accounts for flow through the open pores and Continuum $F$ for flow through the biofilm embedded in the porous medium. Mass balance equations can be set up for each continuum and the variables of both continua linked by mass transfer terms.

Figure 3: Schematic diagram of dual-continuum concept applied to biofilm-affected porous media. Continuum $P$ accounts for flow through the pores of the porous medium and Continuum $F$ for flow through the biofilm. Note that the model presented in this article is defined entirely on the macroscale, and no upscaling techniques have been applied for its derivation.

Definitions of the volume fractions which describe the proportions of each component of the system (see Figure 4) are given in the following.

- The original porosity $\phi_0$ of the porous medium is defined as the pore volume of the porous medium unaffected by the biofilm within a representative elementary volume (REV) divided by the bulk volume of the REV.

- The porosity $\phi_p$ of Continuum $P$ is defined as the pore volume of the porous medium excluding biofilm pores divided by the bulk volume of the REV.

- The porosity $\phi_f$ of Continuum $F$ is defined as the volume of pores within the biofilm divided by the bulk volume of the REV.

- The biofilm porosity $\varepsilon$ is defined as the volume of pores within the biofilm divided by the total biofilm volume. It is related to $\phi_f$ and $\phi_p$ in the following way:

$$\varepsilon = \frac{\phi_f}{\phi_0 - \phi_p}. \quad (1)$$
2.1. Mass Conservation Equations

In the following, continuity equations for the fluid phases, biomass, and a substrate are given. Note that the formulation of these equations in this work is heuristic.

2.1.1. Conservation of Mass of Water and CO$_2$

The mass balance equation for each phase $\alpha$ within the continuum $\kappa$ reads

$$\frac{\partial (\phi_\kappa S_{\alpha,\kappa} \rho_{\alpha,\kappa})}{\partial t} + \nabla \cdot (\rho_{\alpha,\kappa} \mathbf{v}_{\alpha,\kappa}) = q_{\alpha,\kappa} + e_{\alpha,\kappa};$$

$$\alpha \in \{w, n\}, \quad \kappa \in \{p, f\},$$

where $S_{\alpha,\kappa}$ and $\rho_{\alpha,\kappa}$ are saturation and density, respectively. Water is the wetting phase $w$, and CO$_2$ is the non-wetting phase $n$. Sources and sinks are represented by $q_{\alpha,\kappa}$, and $e_{\alpha,\kappa}$ accounts for the exchange of mass between two continua. Both continua are treated as porous media in which the Darcy equation is valid (conditions for validity of the Darcy equation, e.g., low Reynolds numbers, can be found, e.g., in Helmig (1997)). The Darcy velocities $\mathbf{v}_{\alpha,\kappa}$ are calculated as

$$\mathbf{v}_{\alpha,\kappa} = -\frac{k_{\alpha,\kappa}}{\mu_{\alpha,\kappa}} K_\kappa (\nabla P_{\alpha,\kappa} - \rho_{\alpha,\kappa} \mathbf{g}),$$

where $k_{\alpha,\kappa}$ is relative permeability, $\mu_{\alpha,\kappa}$ is dynamic viscosity, $P_{\alpha,\kappa}$ is pressure, $K_\kappa$ is intrinsic permeability, and $\mathbf{g}$ is the vector of acceleration due to gravity. The dissolution of CO$_2$ in water and water in CO$_2$ is neglected. Dissolved CO$_2$ may have a detrimental effect on bacterial cells. Due to this simplification, such an effect would not be explicitly accounted for by the model.
Note that Equation (3) is supplemented by the equations and constitutive relationships given below.

\[
\begin{align*}
1 &= S_{w,\kappa} + S_{n,\kappa} \\
p_{c,\kappa}(S_{w,\kappa}) &= p_{n,\kappa} - p_{w,\kappa} \\
k_{\alpha,\kappa} &= k_{\alpha,\kappa}(S_{w,\kappa})
\end{align*}
\tag{4}
\]

Capillary pressure \( p_{c,\kappa} \) and relative permeabilities are calculated using Brooks-Corey relationships (e.g., Corey, 1994). The Brooks-Corey formulation of the capillary pressure–saturation relationship is advantageous here since it explicitly accounts for entry pressure. It is worth noting that capillary pressure as used here is a Darcy-scale quantity (see Korteland et al., 2009). The above equations assume that each continuum can be characterised with a set of parameters such as porosity \( \phi_{\kappa} \), entry pressure \( p_{d,\kappa} \), and pore-size distribution index \( \lambda_{\kappa} \) as can be seen in Equation (15).

### 2.1.2. Conservation of Biomass

Conservation equations for the biomass in the system also need to be formulated. Again, this is done for each continuum. At this point, the following assumptions are made.

- **In Continuum \( P \)**, biomass exists only as suspended cells within the water phase and can be accounted for with a concentration \( C^b_w \) [kg/m\(^3\)]. Biomass in the \( \text{CO}_2 \) phase is neglected since supercritical \( \text{CO}_2 \) is a biocide (Mitchell et al., 2008).

- **In Continuum \( F \)**, biomass exists only in the biofilm, i.e., attached. The properties of the biofilm, namely, biofilm density \( \rho_b \) and biofilm porosity \( \varepsilon \) are taken to be constant. See Equation (1) for the definition of \( \varepsilon \). Here, biofilm density \( \rho_b \) is defined as the amount of biomass per volume of biofilm including the biofilm pore volume.

Thus, the conservation equation for biomass in Continuum \( P \) (suspended) reads

\[
\frac{\partial (\phi_p C^b_w S_{w,p})}{\partial t} + \nabla \cdot (C^b_w \mathbf{v}_{w,p}) - \nabla \cdot (D^b_p \nabla C^b_w) = q^b_p + e^b_p.
\tag{5}
\]

\( C^b_w \) is the concentration of biomass in the water phase, \( q^b_p \) is a source/sink term with which biomass growth and decay can be accounted for, and \( e^b_p \) is an
exchange term. The coefficient of molecular diffusion of suspended biomass in the water phase $D_b^p$ within a porous medium varies with porosity and saturation (e.g., Bear, 1979); $D_b^p = \hat{D}_b^p \phi_p S_{w,p}$. $\hat{D}_b^p$ is a constant diffusion coefficient. Here, the effects of changes in tortuosity with respect to saturation have been neglected. Mechanical dispersion is not included, and this may lead to errors in the calculation of the diffusive fluxes. The accuracy of the calculated diffusive fluxes is further reduced by numerical dispersion which may depend on the spatial and temporal resolution of a given simulation and on the velocity of the fluid.

In Continuum $F$, biomass is immobile, therefore, the mass balance equation consists of only storage and source/sink terms.

$$\frac{\partial ([\phi_0 - \phi_p] q_b)}{\partial t} = q_f^b + e_f^b \tag{6}$$

Inserting Equation (1), yields

$$\left( \frac{q_b}{\varepsilon} \right) \frac{\partial \phi_f}{\partial t} = q_f^b + e_f^b \tag{7}$$

$\varepsilon$ and $q_b$ have been pulled out of the differential because they are taken to be constant. Note that

$$e_f^b = -e_p^b. \tag{8}$$

2.1.3. Conservation of Mass of Growth-Limiting Substrate

Bacterial cells, both attached and floating, need the appropriate pH, temperature, salinity etc. to survive. They also need energy, carbon, and an electron acceptor source for metabolism and reproduction. However, it is assumed here that the availability of one substrate limits bacterial growth. Therefore, the growth of biomass is essentially a function of the concentration of this substrate in water. The validity of this assumption depends strongly on the specific conditions in the aquifer and on the characteristics of the bacteria. For example, it could well be that soluble electron acceptors (e.g., oxygen) get used up quickly at which point the available electron acceptors in the aquifer exist as solid minerals which are only available to the biofilm and not to the planktonic cells. In this case, biomass growth would only be possible by the biofilm, and that would violate the assumption made above. However, if a soluble electron acceptor is injected with the substrate, such a situation would not arise.
A mass balance of the growth-limiting substrate gives

\[
\frac{\partial (\phi_N S_{w,N} C_{w,N}^s)}{\partial t} + \nabla \cdot (C_{w,N}^s \mathbf{v}_{w,N}) - \nabla \cdot (D_N^s \nabla C_{w,N}^s) = q_{w,N}^s + e_{w,N}^s.
\]

(9)

\(D_N^s\) is a porosity-dependent diffusion coefficient: \(D_N^s = \hat{D}_N^s \phi_N S_{w,N}\), where \(\hat{D}_N^s\) is a constant diffusion coefficient.

In Equation (9), the dissolution of substrate in \(\text{CO}_2\) has been neglected. Depending on the substrate, its solubility in supercritical \(\text{CO}_2\) may not be negligible. In that case, a balance equation which accounts for the transfer of substrate between the phases would be necessary.

2.2. Simplifying Assumptions and Exchange Terms

A total of eight conservation equations, four in each continuum, were set up in Section 2.1. Some of the equations can be linked by exchange terms which describe the flow of mass from one continuum to the other as a function of a difference in potential. Some assumptions can also be made which significantly reduce the complexity, while bearing in mind the consequences this has on accuracy.

2.2.1. Fluid Exchange

Mass exchange of water and \(\text{CO}_2\) between the continua can be achieved with an exchange term \(e_\alpha\) [kg/(m\(^3\)s)] which is a function of the pressure difference between the two continua.

\[
e_\alpha = a_\alpha (p_{\alpha,p} - p_{\alpha,f}),
\]

with \(e_{\alpha} = -e_{\alpha,p} = e_{\alpha,f}\).

(10)

\(a_\alpha\) is a parameter which describes the rate at which the exchange takes place.

For simplicity and as a first step in the development of this model, the pressures in the two continua are assumed to be equal. The consequence of this simplification is that fluid exchange takes place instantaneously, and it is not possible to quantify the exchange rate which may be important for the determination of solute exchange. In this work, solute exchange is assumed to be driven primarily by concentration gradients (see Section 2.2.5). The topic of further work has to be the investigation of the importance of solute exchange due to advection and the implementation into the model.
As stated above, it is assumed that for each local REV
\[ p_{\alpha,p} = p_{\alpha,f} = p_{\alpha}. \]  
(11)
Since fluid properties depend on pressure, the following expressions are direct consequences of Equation (11).
\[ \varrho_{\alpha,p} = \varrho_{\alpha,f} = \varrho_{\alpha} \]
\[ \mu_{\alpha,p} = \mu_{\alpha,f} = \mu_{\alpha} \]  
(12)

The capillary pressures at the interface between the two continua have to be the same.
\[ p_{c,p} = p_{c,f} = p_c \]  
(13)
Note that no wettability changes will be accounted for in this work, i.e., both the porous medium and the biofilm are taken to be hydrophilic media. Capillary pressure \( p_c \) can be expressed as a function of either of the effective saturations \( S_{e,p} \) or \( S_{e,f} \). Thus, \( S_{e,p} \) and \( S_{e,f} \) are not independent. Note that
\[ S_{e,\kappa} = \frac{S_{w,\kappa} - S_{wr,\kappa}}{1 - S_{wr,\kappa}}. \]  
(14)
If one of the two is known (e.g., \( S_{e,p} \)), the other can be calculated as a function of \( p_c \) in the following manner (see also Figure 5).
\[ p_c = p_{d,p}S_{e,p}^{-\frac{1}{\lambda_p}}, \]
\[ S_{e,f} = \left( \frac{p_{d,f}}{p_c} \right)^{\frac{1}{\lambda_f}} \]  
if \( p_c > p_{d,f} \),
\[ S_{e,f} = 1 \]  
otherwise.  
(15)
This means that the distribution of the two fluids within the two continua is determined by capillary forces. It is assumed that \( p_{d,f} > p_{d,p} \), so that the non-wetting phase invades Continuum \( P \) first before Continuum \( F \), and for a given range of \( \text{CO}_2 \) saturations in Continuum \( P \), no \( \text{CO}_2 \) is present in Continuum \( F \). This results from the assumption that the largest pores of the porous medium are larger than those of the biofilm.

Equation (3) for the water phase becomes
\[ \frac{\partial (\varphi_p S_{w,p} \varrho_w)}{\partial t} + \nabla \cdot (\varrho_w \boldsymbol{v}_{w,p}) = q_{w,p} - e_{\alpha} \]  
(16)
Figure 5: $S_{e,p}$ and $S_{e,f}$ resulting from one $p_c$-value. $\lambda_p = 2$, $\lambda_f = \frac{1}{2}$, $p_{d,f} = 2.5 \cdot p_{d,p}$.

and

$$\frac{\partial(\phi_f S_{w,f} \rho_w)}{\partial t} + \nabla \cdot (\rho_w v_{w,f}) = q_{w,f} + e_n. \quad (17)$$

Adding Equations (16) and (17), gives

$$\frac{\partial([\phi_p S_{w,p} + \phi_f S_{w,f}] \rho_w)}{\partial t} + \nabla \cdot (\rho_w [v_{w,p} + v_{w,f}]) = q_w, \quad (18)$$

where $q_w = q_{w,p} + q_{w,f}$. Similar reformulations can be done for the CO$_2$ phase.

$$\frac{\partial([\phi_p S_{n,p} + \phi_f S_{n,f}] \rho_n)}{\partial t} + \nabla \cdot (\rho_n [v_{n,p} + v_{n,f}]) = q_n \quad (19)$$

2.2.2. Biomass Growth and Decay

The terms $q^b_f$ and $q^b_p$, from Equations (5) and (7), comprise biomass growth $r_{g,\kappa}$, biomass decay $r_{b,\kappa}$, and external sources or sinks $q^b_\kappa$.

$$q^b_\kappa = r_{g,\kappa} - r_{b,\kappa} + q^b_\kappa \quad (20)$$

The growth of biomass $r_{g,\kappa}$ is a function of the biomass concentration or density and a growth rate $\mu_\kappa$.

$$r_{g,p} = \mu_p \phi_p S_{w,p} C_b, \quad r_{g,f} = \mu_f (\phi_f / \varepsilon) \rho_b \quad (21)$$
The growth rate $\mu_{\kappa}$ depends on the concentration of the growth-limiting substrate and is traditionally modelled with Monod kinetics.

$$\mu_{\kappa} = k_{\mu} Y \frac{C_{w,\kappa}^s}{K_s + C_{w,\kappa}^s}$$

(22)

$k_{\mu}$ is the maximum substrate utilisation rate, and $Y$ is the yield coefficient which accounts for the fraction of substrate actually used for growth. A great deal of the utilised substrate goes into cell maintenance. Notice that both $k_{\mu}$ and $Y$ have been assumed to be the same for both continua, i.e., for both planktonic and sessile cells. A review by van Loosdrecht et al. (1990) finds no conclusive evidence that the attachment of bacterial cells to solid surfaces directly affects metabolism (see also Clement et al., 1999). $K_s$ is the Monod half-saturation coefficient. It is the value of $C_{w,\kappa}^s$ at which $\mu_{\kappa} = k_{\mu} Y / 2$. These three parameters are species-specific.

Similar functions are used for biomass decay, $r_{b,\kappa}$.

$$r_{b,p} = b_p \phi_p S_{w,p} C_{w}^b$$
$$r_{b,f} = b_f (\phi_f / \epsilon) \rho_b$$

(23)

The decay rate $b_{\kappa}$ comprises a constant endogenous decay rate $b_0$ and a death rate $b_{c,\kappa}$ caused by the cells’ exposure to toxic supercritical CO$_2$.

$$b_{\kappa} = b_0 + b_{c,\kappa}$$

(24)

Zhang et al. (2006) and Mitchell et al. (2008) suggest likely mechanisms involved in cell inactivation by CO$_2$. On the one hand, low intracellular pH caused by CO$_2$ dissolution within a cell may disrupt processes essential for cell activity or cause enzyme denaturation. On the other hand, supercritical CO$_2$, which is a good solvent, can cause the extraction of intracellular material. In experiments conducted by Mitchell et al. (2009) to investigate the effect of supercritical CO$_2$ on bacterial cells, biofilm cells proved to be more resilient than planktonic cells. This was attributed to the interaction of CO$_2$ molecules with the EPS matrix leading to an immobilisation of the molecules.

$b_{c,\kappa}$ is a lumped parameter accounting for the different mechanisms responsible for the increased biomass decay due to exposure to CO$_2$. The most obvious macroscale parameter with which this exposure may be quantified is saturation. Hence, $b_{c,\kappa}$ is assumed to be a function of $S_{n,\kappa}$.

$$b_{c,\kappa} = c_S S_{n,\kappa}^m$$

(25)
where \( c_c \) and \( n_c \) are empirical values which may depend on the bacterial species and on the properties of the natural porous medium and biofilm. Note that while \( p_c \leq p_{d,f} \), \( S_{n,f} = 0 \) and thus \( b_{c,f} = 0 \). This means that \( S_{n,p} \) has to exceed a critical value before CO\(_2\) can invade Continuum \( F \) and cause damage to the biofilm. Before this happens, it is assumed that the free-phase CO\(_2\) does not come in contact with the hydrophilic biofilm. In Continuum \( P \), bacterial cells which attach to the CO\(_2\)-water interface are assumed to be inactivated immediately and are included in the saturation-dependent decay term. It must be stated that the transport of dissolved CO\(_2\) is not accounted for in the model and is important for the inactivation processes. Even though these processes are well understood for planktonic cells, it is not clear which mechanisms are important in a biofilm. Given further advancement in this field, it is intended that the model be extended to account for the dissolution of CO\(_2\) in water and to include the dependence of \( b_{c,n} \) on the concentration of CO\(_2\) in water.

Once biomass decays, it is no longer accounted for in the model. In effect, therefore, decayed biomass simply disappears causing slight changes in pressure. It is assumed here that the process of growth and decay of biofilm occurs much slower than the flow processes which would equilibrate any such changes in pressure.

### 2.2.3. Biomass Exchange

The exchange terms \( e_p^b \) and \( e_f^b \) from Equations (5) and (7), describe the mass transfer between suspended biomass in Continuum \( P \) and attached biomass in Continuum \( F \).

\[
e^b = e_f^b = -e_p^b = \frac{k_a \phi_p S_{w,p} C_w^b - k_d (\phi_f / \varepsilon) \theta_b}{r_a} \tag{26}
\]

\( r_a \) is the rate of attachment of suspended biomass to the solid or biofilm, and \( r_d \) is the rate at which biomass detaches from the biofilm. \( k_a \) and \( k_d \) are attachment and detachment functions, respectively. They are an attempt to account for microscale processes leading to either attachment or detachment on the macroscale.

**Attachment Function.** There are a number of different processes, occurring simultaneously, responsible for the attachment of microbial cells in a porous medium. See Corapcioglu and Haridas (1984) for a description of these processes.
Due to the strong effect large amounts of biofilm within the porous medium would have on the attachment function, it is imperative that the attachment function should account for variations in attachment with changes in the volume fraction of pore space occupied by attached biomass. Thus, the function by Taylor and Jaffé (1990b) is used in this work.

\[ k_a = c_{a,1} + c_{a,2} \phi_f / \varepsilon \]  

(27)

c_{a,1} and c_{a,2} are empirical parameters.

In two-phase fluid flow, microorganisms also attach to the interface between the two fluids. This is often incorporated in models with an additional attachment term (Rockhold et al., 2004; Schaefer et al., 1998; Gargiulo et al., 2007). The attachment rate at the fluids' interface is then a function of the interfacial area between the two fluids. This interfacial area can be estimated from the pore-size distribution of the porous medium and is a non-linear function of the wetting-phase saturation (Niemet et al., 2002; Cary, 1994). However, in this work, one of the fluid phases is a biocide which means that cells attached to the fluids' interface are exposed to the toxic fluid. These are then accounted for by decay term \( b_{c,p} \) (see Equation (25)).

**Detachment Function.** Detachment processes, relevant to this work, include erosion and sloughing (Bryers, 2000). Rittmann (1982) relates detachment to shear stress. In this case, changes in the force exerted on the biofilm (shear stress) are accounted for as well as the reduction in the strength of the biofilm with increasing thickness. Speitel and DiGiano (1987) suggest that an additional detachment term be added to that of Rittmann (1982). This is motivated by experimental data suggesting that fast-growing biofilms detach more readily than slow-growing biofilms. This could be as a result of differences in the production rate of EPS compared to cell reproduction. It could also result from an increasingly uneven growth as growth rate increases. Piccioreanu et al. (2001) could show, using numerical simulations, that differences in shape and structure between fast and slow-growing biofilms is one reason for the differences in susceptibility to shear.

The detachment function given in Equation (28) is a function of the magnitude of the water-phase pressure gradient \( |\nabla p_w| \). It is assumed that the pressure gradient accounts for the shear forces exerted on the biofilm by the water phase. It is also assumed, as discussed above, that a higher growth rate increases biofilm susceptibility to shear. This is accounted for,
as suggested by Speitel and DiGiano (1987), by the term \( k_d^\mu \).

\[
k_d = \frac{c_{d,1}(\phi_p S_{w,p}|\nabla P_w|)^{n_d}}{k_d^\tau} + \frac{c_{d,2}\mu_f(\phi_f/\varepsilon)\theta_b}{k_d^\mu}
\]  

(28)

c_{d,1}, c_{d,2}, and \( n_d \) are empirical parameters. Assuming the dependence of \( k_d^\tau \) on the pressure gradient behaves in the same way as its dependence on shear stress, the exponent \( n_d \) can be taken from Rittmann (1982) to be \( n_d = 0.58 \). The detachment term \( k_d^\mu \) is proportional to the rate of biofilm growth. Speitel and DiGiano (1987) give values for the proportionality factor \( c_{d,2} \) ranging from 0.319 to 0.665 depending, for example, on the substrate. In this work, it is assumed that the proportionality between \( k_d^\mu \) and growth rate varies with the amount of biofilm in place \( \phi_f/\varepsilon \).

\[
c_{d,2} = \tilde{c}_{d,2}\phi_f/\varepsilon
\]  

(29)

The dependence of \( c_{d,2} \) on \( \phi_f/\varepsilon \) accounts for the increase in variation of the substrate distribution within the biofilm with increase in biofilm thickness resulting in uneven biofilm growth, and hence in greater detachment.

### 2.2.4. Substrate Consumption

Substrate is utilised by biomass in both continua. Therefore, \( q_{w,\kappa}^s \) in Equation (9) is a sink and a function of the bacterial substrate utilisation rates.

\[
q_{w,\kappa}^s = -r_{g,\kappa}/Y
\]  

(30)

### 2.2.5. Substrate Exchange

The transfer of substrate between the two continua is accounted for by the term \( e_{w,\kappa}^s \) in Equation (9). It is a function of the difference in substrate concentration in the two continua.

\[
e_{w}^s = -e_{w,p}^s = -e_{w,f}^s = a_w^s(C_{w,p}^s - C_{w,f}^s)
\]  

(31)

The parameter \( a_w^s \) describes the rate at which the exchange takes place. This process is often assumed to be mainly diffusive. In dual-continuum models, such exchange terms often take the form (e.g., Gerke and van Genuchten, 1996):

\[
e_{w}^s = D_{dff}^s \frac{\beta}{L_2^2}(C_{w,p}^s - C_{w,f}^s).
\]  

(32)
$L$ is a characteristic length over which the concentration difference exists, and $\beta$ is a dimensionless, geometry-dependent coefficient. These two parameters are difficult to determine and have to be estimated. One way to estimate $\beta/L^2$ could be by assuming that mass transfer occurs across the specific surface $M$ of the porous medium over a characteristic length which is equivalent to the characteristic pore radius $d_r/2$. This gives

$$e_w^s = D_{eff}^s \frac{M}{d_r/2} (C_{w,p}^s - C_{w,f}^s).$$  \hspace{1cm} (33)

$D_{eff}^s$ can be interpreted as the effective diffusivity of the solute in the biofilm (Stewart, 1998; Wood et al., 2002).

2.3. Clogging

Many studies have focused on deriving a mathematical expression linking the permeability of a porous medium to its porosity, e.g., Taylor et al. (1990), Vandevivere (1995), Clement et al. (1996), Seki and Miyazaki (2001), Thullner et al. (2002). There are also some studies on the effect of bacterial accumulation on changes in permeability or pore-size distribution in an unsaturated porous medium, e.g., Rockhold et al. (2002), Maggi and Porporato (2007), Mostafa and Van Geel (2007). In experiments, the effect of biofilm growth on permeability has been shown (Cunningham et al., 1991; Vandevivere and Baveye, 1992). They generally show a strong initial decrease in intrinsic permeability with decrease in porosity followed by a region in which only minor changes in permeability are observed (see Figure 6). The shape of the permeability–porosity curve is dependent on both the properties of the porous medium and of the biofilm.

In the model described here, two permeabilities exist. Each continuum is assigned a permeability. With a summation of the individual fluxes within a control volume, it can be shown that for saturated flow and with the assumption made in Section 2.2.1 (equal pressures in both continua), that the total intrinsic permeability $K$ as measured in the experiments (e.g., by Cunningham et al. (1991)) is equivalent to the sum of the permeabilities of the two continua.

$$K = K_p + K_f$$ \hspace{1cm} (34)

This means that one can determine the individual permeability–porosity relationships for each continuum and sum them up for comparison with experimental values. Obviously, the permeability of a porous medium with small
amounts of biofilm is mainly dependent on $K_p$, while that of a biofilm-filled porous medium is mainly dependent on $K_f$. Thus, the following expressions have to be fulfilled.

$$
\begin{align*}
\text{If } \phi_p = \phi_0 \text{ and } K &= K_0 \quad \Rightarrow \quad K_p = K_0 \text{ and } K_f = 0, \\
\text{if } \phi_p = 0 \text{ and } K &= K_{\text{min}} \quad \Rightarrow \quad K_p = 0 \text{ and } K_f = K_{\text{min}},
\end{align*}
$$

(35)

$K_0$ is the permeability of the biofilm-free porous medium, while $K_{\text{min}}$ is the permeability of the biofilm-filled porous medium.

The permeability of Continuum $P$ can be described using the expression given by Xu et al. (2004).

$$
K_p/K_0 = \left(\frac{\phi_p - \phi_{p,c}}{\phi_0 - \phi_{p,c}}\right)^{n_k} \text{ if } \phi_p > \phi_{p,c}, \\
K_p = 0 \quad \text{otherwise.}
$$

(36)

$\phi_{p,c}$ is the porosity at which $K_p = 0$, and $n_k$ is an empirical parameter which is strongly dependent on the geometry of the porous medium. From the experimental data in Figure 6, one can determine values of $K_{\text{min}}$ for the various sands, and since these values are relatively constant, it seems appropriate to assign $K_f$ the constant value $K_{\text{min}}$. However, at $\phi_p = \phi_0$, $K_f$ has to be zero. Thus, one could think of a $\phi_p = \phi'_{p,c}$ for which the following holds.

$$
\begin{align*}
K_f &= K_{\text{min}} \quad \text{if } \phi_p \leq \phi'_{p,c}, \\
K_f < K_{\text{min}} \quad \text{otherwise.}
\end{align*}
$$

(37)

For the region in which $K_f < K_{\text{min}}$, there could be a number of different concepts to describe the behaviour of $K_f$. However, the concept used is not very important because its contribution to the overall flow process is very small within that region. A simple concept is to have $K_f$ continuously increase from zero to $K_{\text{min}}$ as $\phi_p$ decreases from $\phi_0$ to $\phi'_{p,c}$. The resulting permeability–porosity relationship is shown in Figure 6.

Vandevivere (1995) describes a similar expression for the permeability–porosity relationship. He identifies two clogging mechanisms, and their weighted contributions are summed to get the permeability of the porous medium.

2.3.1. Neglected Effects of Biofilm Growth on Porous Medium

Biofilm growth in a porous medium would probably also change the pore-size distribution represented in this work by the pore-size distribution index $\lambda$. Maggi and Porporato (2007) introduces concepts with which one could account for these changes. Such changes in pore-size distribution are not
Figure 6: Mathematical description of permeability decrease with increase in biomass fitted to data from Cunningham et al. (1991) with two sands of different median particle sizes (0.54 mm and 0.70 mm). $K$ as used for the $y$-axis is the sum of $K_p$ and $K_f$. The values of the parameters used are $\phi_{p,c}/\phi_0 = 0.6$, $\phi'_{p,c}/\phi_0 = 0.8$, $K_{\text{min}} = 0.025 \cdot K_0$ and $n_k = 3$. $K_f$ is assumed to increase linearly from zero with decreasing $\phi_p$ until $\phi'_{p,c}$ at which point $K_f = K_{\text{min}}$.

included in the presented model. Also neglected are potential changes in entry pressure due to biofilm growth.

2.4. System of Equations

As a summary of Section 2, the equations which describe the model concept are given in Table 1. The primary variables of the system of equations are $S_{w,p}$, $P_n$, $C^b_w$, $C'_w$, $C^s_w$, and $C^s_{w,f}$.

2.5. Numerical Model

The balance equations in Table 1 form a system of strongly coupled, non-linear partial differential equations. The complexity of the system of equations calls for a numerical solution. The numerical model used in this work is implemented within the framework of the multiphase flow simulator MUFTE-UG (Multiphase Flow, Transport, and Energy model on Unstructured Grids). A vertex-centred finite volume method is used for spatial discretisation, while the time discretisation is done with a fully implicit Euler scheme.

3. Attempts at Model Validation

Two experiments have been chosen from literature which deal with problems relevant to this work and with which the model presented in the previous
Continuum $q \sum_k v_k \partial K_p q + \nabla \cdot (g [v_{w,p} + v_{w,f}]) = q_w$

CO$_2$

Biomass $q^n_b = r_{g,n} - r_{b,n} + \hat{q}^b_n$

Substrate $q^n_s = -r_{g,n}/Y$

Exchange terms $e^b = r_a - r_d$

Supplementary equations and constitutive relationships $e^a_w = D_{eff} \frac{M}{a_{w,f}^2} (C_{w,p}^s - C_{w,f}^s)$

<table>
<thead>
<tr>
<th>Table 1: System of equations ($\kappa \in {p, f}, \alpha \in {w, n}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Continuum $P$</td>
</tr>
<tr>
<td>Mass balance equations</td>
</tr>
<tr>
<td>Water $\frac{\partial [\phi_p S_{w,p} + \phi_f S_{w,f}] [\phi_w]}{\partial t} + \nabla \cdot (g_w [v_{w,p} + v_{w,f}]) = q_w$</td>
</tr>
<tr>
<td>CO$<em>2$ $\frac{\partial [\phi_p S</em>{w,p} + \phi_f S_{w,f}] [\phi_w]}{\partial t} + \nabla \cdot (g_n [v_{n,p} + v_{n,f}]) = q_n$</td>
</tr>
<tr>
<td>Biomass $\frac{\partial \phi_p C^b_{w,p} [\phi_w]}{\partial t} + \nabla \cdot (C^b_p v_{w,p}) - \nabla \cdot (D^b_p \nabla C^b_w) = q^b_p - e^b$</td>
</tr>
<tr>
<td>Substrate $\frac{\partial \phi_p S_{w,p} C^s_w [\phi_w]}{\partial t} + \nabla \cdot (C^s_p w_{w,p}) - \nabla \cdot (D^s_p \nabla C^s_w) = q^s_w - e^s_w$</td>
</tr>
<tr>
<td>Sources and sinks</td>
</tr>
<tr>
<td>Biomass $r_{g,p} = \mu_p \phi_p S_{w,p} C^b_w$</td>
</tr>
<tr>
<td>$\mu_n = k_n Y$</td>
</tr>
<tr>
<td>$b_n = b_0 + c_n S^s_n$</td>
</tr>
<tr>
<td>Substrate</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Exchange terms</td>
</tr>
<tr>
<td>Biomass $e^b = r_a - r_d$</td>
</tr>
<tr>
<td>$k_a = c_{a,1} + c_{a,2} \phi_f / \varepsilon$</td>
</tr>
<tr>
<td>$k_{a,2} = \varepsilon$</td>
</tr>
<tr>
<td>Substrate</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Volume fractions</td>
</tr>
<tr>
<td>Saturations</td>
</tr>
<tr>
<td>Capillary pressure</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Intr. perm.</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Rel. perms.</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Velocities</td>
</tr>
</tbody>
</table>
section will be tested. They include an experiment with water-saturated flow through a biofilm-affected porous medium by Taylor and Jaffé (1990a) and one by Mitchell et al. (2009) which deals with the effect of CO$_2$ on a biofilm grown in a porous medium. The first experiment focuses particularly on the interaction between fluid flow and biofilm growth, while the second experiment focuses on the effect of supercritical CO$_2$ on the development of a biofilm.

3.1. One-Phase Flow Experiments by Taylor and Jaffé (1990a)

3.1.1. General Description

Two columns were packed with sand, and biofilms were grown in these columns over several months under constant flow conditions. The columns were inoculated with methanol-utilising bacteria for a few hours after which a constant methanol concentration was maintained in the influent. Pressure was measured at regular intervals along the column, and thus the permeability changes could be quantified.

3.1.2. Simulation Parameters

In Table 2, a list of parameters as used in the experiments by Taylor and Jaffé (1990a) is given. In Column 1, the flow rate and the influent substrate concentration were reduced after 149 days, whereas only the influent substrate concentration was reduced in Column 2.

Taylor and Jaffé (1990b) developed a numerical model with which they simulated part of the experiment described above. The parameters used in those simulations are listed in Table 3. The experiments have been simulated with the model developed in Section 2. However, since this is a one-phase flow problem, the mass balance equation for CO$_2$ is not necessary.

The initial and boundary conditions for the problem are given in Table 4. The domain is discretised with 22 uniform elements, i.e., a discretisation length of 0.0236 m. In Section 2.3, the parameters needed to describe changes in permeability were fitted to data given by Cunningham et al. (1991) for sands with median grain sizes of 0.54 mm and 0.70 mm. The permeabilities of these sands were $2.17 \times 10^{-10}$ m$^2$ and $3.19 \times 10^{-10}$ m$^2$, respectively. These values are very close to those of the sand used by Taylor and Jaffé (1990a) (mean grain size: 0.70 mm, permeability: $2.93 \times 10^{-10}$ m$^2$). Thus, the set of parameters from Section 2.3 shown in Figure 6 are deemed appropriate for the description of changes in permeability in this experiment. They include $\phi_{p,c}/\phi_0 = 0.6$, $n_k = 3$, and $\phi_{p,c}'/\phi_0 = 0.8$. However, $K_{\text{min}}$ is assumed to

22
Table 2: Parameters for experiments by Taylor and Jaffé (1990a).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Column 1</th>
<th>Column 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column length</td>
<td>0.52 m</td>
<td></td>
</tr>
<tr>
<td>Column diameter</td>
<td>0.0508 m</td>
<td></td>
</tr>
<tr>
<td>Sand porosity $\phi_0$</td>
<td>0.347</td>
<td></td>
</tr>
<tr>
<td>Sand permeability $K_0$</td>
<td>$2.93 \times 10^{-10}$ m$^2$</td>
<td></td>
</tr>
<tr>
<td>Mean grain diameter of sand</td>
<td>0.7 mm</td>
<td></td>
</tr>
<tr>
<td>Specific surface of sand $M$</td>
<td>$4.85 \times 10^3$ m$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>15 °C</td>
<td></td>
</tr>
<tr>
<td>Total operation time</td>
<td>284 days</td>
<td>356 days</td>
</tr>
</tbody>
</table>

For $t \leq 149$ days

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value 1</th>
<th>Value 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Influent substrate concentration</td>
<td>$7.20 \times 10^{-3}$ kg/m$^3$</td>
<td>$5.59 \times 10^{-3}$ kg/m$^3$</td>
</tr>
<tr>
<td>Flow rate</td>
<td>$2.22 \times 10^{-5}$ m$^3$/s</td>
<td>$7.38 \times 10^{-6}$ m$^3$/s</td>
</tr>
</tbody>
</table>

For $t > 149$ days

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value 1</th>
<th>Value 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Influent substrate concentration</td>
<td>$5.20 \times 10^{-3}$ kg/m$^3$</td>
<td>$4.70 \times 10^{-3}$ kg/m$^3$</td>
</tr>
<tr>
<td>Flow rate</td>
<td>$1.37 \times 10^{-5}$ m$^3$/s</td>
<td>$7.38 \times 10^{-6}$ m$^3$/s</td>
</tr>
</tbody>
</table>

Table 3: Parameters used for simulation in Taylor and Jaffé (1990b).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water viscosity $\mu_w$</td>
<td>$1.139 \times 10^{-3}$ Pa $\cdot$ s</td>
</tr>
<tr>
<td>Maximum substrate utilisation rate $k_{\mu}$</td>
<td>$8.91 \times 10^{-5}$ s$^{-1}$</td>
</tr>
<tr>
<td>Monod half-saturation coefficient $K_s$</td>
<td>$7.99 \times 10^{-4}$ kg/m$^3$</td>
</tr>
<tr>
<td>Yield coefficient $Y$</td>
<td>0.0975 kg/kg</td>
</tr>
<tr>
<td>Endogenous decay rate $b_0$</td>
<td>$3.18 \times 10^{-7}$ s$^{-1}$</td>
</tr>
<tr>
<td>Biofilm density $\rho_b$</td>
<td>3 kg/m$^3$</td>
</tr>
<tr>
<td>Attachment rate parameter $c_{a,1}$</td>
<td>$7.40 \times 10^{-3}$</td>
</tr>
<tr>
<td>Attachment rate parameter $c_{a,2}$</td>
<td>$7.88 \times 10^{-2}$</td>
</tr>
</tbody>
</table>
Table 4: Initial and boundary conditions, and fitted parameters for simulation of experiments by Taylor and Jaffé (1990a).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Column 1</td>
</tr>
<tr>
<td><strong>Initial conditions</strong></td>
<td></td>
</tr>
<tr>
<td>$p_w$</td>
<td></td>
</tr>
<tr>
<td>$C_w$</td>
<td></td>
</tr>
<tr>
<td>$C_{w,p}$</td>
<td></td>
</tr>
<tr>
<td>$C_{w,f}$</td>
<td></td>
</tr>
<tr>
<td><strong>Boundary conditions at</strong> $x = 0$ m</td>
<td></td>
</tr>
<tr>
<td>Water flux (Neumann)</td>
<td></td>
</tr>
<tr>
<td>$C_w$ (Dirichlet)</td>
<td></td>
</tr>
<tr>
<td>(Neumann)</td>
<td></td>
</tr>
<tr>
<td>$C_{w,p}$ (Dirichlet)</td>
<td></td>
</tr>
<tr>
<td>$C_{w,f}$ (Neumann)</td>
<td></td>
</tr>
<tr>
<td><strong>Boundary conditions at</strong> $x = 0.52$ m</td>
<td></td>
</tr>
<tr>
<td>$p_w$ (Dirichlet)</td>
<td></td>
</tr>
<tr>
<td>$C_w$ (Dirichlet)</td>
<td></td>
</tr>
<tr>
<td>$C_{w,p}$ (Dirichlet)</td>
<td></td>
</tr>
<tr>
<td>$C_{w,f}$ (Dirichlet)</td>
<td></td>
</tr>
<tr>
<td><strong>Values of parameters fitted to Column 1</strong></td>
<td></td>
</tr>
<tr>
<td>$c_{d,1}$</td>
<td></td>
</tr>
<tr>
<td>$c_{d,2}$</td>
<td></td>
</tr>
<tr>
<td>$K_{\text{min}}$</td>
<td></td>
</tr>
</tbody>
</table>
be unknown and will be fitted to the experimental results. The sand used by Taylor and Jaffé (1990a) had a declared permeability of $2.93 \times 10^{-10}$ m$^2$. However, judging from their results, the measured permeabilities of the sands unaffected by biomass was a bit lower than $K_0$. For this reason, in the simulations, the maximum permeability is taken to be $1.42 \times 10^{-10}$ m$^2$.

Other parameters used in the simulation include water density $\rho_w = 1000$ kg/m$^3$, the diffusion coefficients $D_p^b = \hat{D}_s^b = 10^{-8}$ m$^2$/s and the effective diffusion coefficient $D_{eff}^s = \varepsilon \times 10^{-9}$ m$^2$/s. The average pore diameter of the sand is estimated using the empirical relation $d_r = 6\phi_0/M$, therefore, $d_r = 0.43$ mm. Zhang and Bishop (1994) observed variations in biofilm porosity $\varepsilon$ ranging from 0.58 to 0.93. Here, $\varepsilon$ is assigned a value of 0.8. However, the results of the simulation were not very sensitive to changes in $\varepsilon$. The attachment parameters $c_{a,1}$ and $c_{a,2}$ were fitted in the simulations by Taylor and Jaffé (1990a) (see Table 2).

A total of three parameters were fitted in the simulation of Column 1 and remained unchanged for Column 2 (see Table 4).

3.1.3. Results

Figure 7 shows the results of the simulations. The logarithmic reduction of permeability caused by biofilm growth is plotted over distance into the columns. The biofilm grows by utilising the substrate at the inlet causing a decrease in permeability. Since the inflow rate is kept constant, this results in a pressure build-up near the inlet. High pressure gradients cause high biomass detachment from the biofilm. Detached cells get transported downstream, where they reattach. This results in an encroachment of the biofilm into the column, the extent of which is dependent on the inflow rate. The simulated permeability reduction in Column 1 was less than observed in the experiments. In Column 2, the simulated biofilm advanced further into the column than in the experiments. The differences between simulations and experiments may result from shortcomings of the model concept, e.g., the assumption that the biofilm density is constant or the way biofilm decay is treated. Biofilm density may vary with biofilm age and external conditions. This is not accounted for in the model. In the model concept, decay of biomass within the biofilm immediately leads to a reduction of the pore space occupied by the biofilm. In reality, obviously, it may take some amount of time for dead biomass to be removed. However, during the experiments, there were problems with the water source (Taylor and Jaffé, 1990b), and thus the aim of this comparison is mostly qualitative. Column 1 is affected
by biomass throughout the column, whereas the biofilm affects only part of Column 2. This can be seen in both the experimental and the simulated results. The permeability values of both experimental and numerical results near the inlet fluctuate in space. However, these fluctuations are more pronounced in the simulation. This is probably due to the instability of the solution just before or after Continuum $P$ becomes fully clogged ($K_P = 0$). This is however exaggerated by the logarithmic scale.

![Simulation vs Experiment](attachment:image1.png)

(a) Column 1

![Simulation vs Experiment](attachment:image2.png)

(b) Column 2

Figure 7: Comparison of simulated permeability reduction to the experimental results of Taylor and Jaffé (1990a). The parameters $c_d, \tilde{c}_d, \tilde{c}^2_d,$ and $K_{\min}$ were fitted to the experimental data in Column 1. Possible reasons for the differences between simulations and experimental results are discussed in Section 3.1.3 The mean absolute error in permeability reduction between the simulation and experimental data is 0.8 % in Column 1 and 8 % in Column 2.

Concluding, even tough the model can qualitatively reproduce and predict the experiments, a quantitative validation was not possible. This calls for further work in this regard as discussed in the Outlook (Section 6).

3.2. Experiments by Mitchell et al. (2009) with Two Phases

3.2.1. General Description

These experiments were conducted at high pressure (89 bar) and moderate temperature (32 °C). Two sandstone cores were inoculated with *Shewanella frigidimarina*. The general strategy in the experiments was to grow a biofilm in the sandstone core and challenge the biofilm with supercritical CO$_2$. A saline nutrient medium was injected once or twice a day in pulses lasting between 20 and 200 minutes. With each pulse, the permeability of
Table 5: Parameters for experiments by Mitchell et al. (2009).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Experiment 1</th>
<th>Experiment 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column length</td>
<td>0.0508 m</td>
<td>0.1185 m</td>
</tr>
<tr>
<td>Sandstone porosity $\phi_0$</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>Sandstone permeability $K_0$</td>
<td>$38.96 \times 10^{-15}$ m$^2$</td>
<td>$47.13 \times 10^{-15}$ m$^2$</td>
</tr>
<tr>
<td>Pressure</td>
<td>89 bar</td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>32 °C</td>
<td></td>
</tr>
<tr>
<td>Total operation time</td>
<td>20.67 days</td>
<td>34.58 days</td>
</tr>
</tbody>
</table>

Table 6: Duration of the different phases of the experiments by Mitchell et al. (2009).

<table>
<thead>
<tr>
<th></th>
<th>Growth</th>
<th>Starvation</th>
<th>CO$_2$</th>
<th>Starvation</th>
<th>CO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I</td>
<td>II</td>
<td>III</td>
<td>IV</td>
<td>V</td>
</tr>
<tr>
<td>Experiment 1</td>
<td>20 days</td>
<td>-</td>
<td>0.67 days</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Experiment 2</td>
<td>12.5 days</td>
<td>15.13 days</td>
<td>4.21 days</td>
<td>0.75 days</td>
<td>2 days</td>
</tr>
</tbody>
</table>

the core was calculated. The bacteria species *S. fridgidimarina* which was used to inoculate the cores was succeeded by other species originally present in the cores, namely, *Bacillus mojavensis* and *Citrobacter* sp.

3.2.2. Simulation Parameters

The properties of the sandstone cores and the conditions at which the experiments were run are given in Table 5. Also given in the table is the duration of each experiment. The experiments can be divided into different phases depending on the medium. Initially, a saline nutrient medium was injected into the cores at intervals as mentioned in Section 3.2.1 (growth phase). In Experiment 1, the growth phase was followed directly by a flooding of the core with CO$_2$. After the growth phase in Experiment 2, a nutrient-depleted saline solution was injected (starvation phase). This was followed by the injection of CO$_2$, a second starvation phase, and another CO$_2$ challenge. The different phases of the experiments are summarised in Table 6.

Due to lack of information and for simplicity, the following assumptions will be made in the simulation.

- The periods of flow through the core are neglected. This means that no spatial discretisation is necessary since there are no spatial gradients.
- The effect of suspended biomass is neglected. This implies that the
balance equation for biomass in Continuum \( P \) is omitted, and there are no attachment or detachment rates.

- During the growth phase, the nutrients needed by the bacterial cells are abundantly available, i.e., the growth rate is independent of the substrate concentration, \( \mu_f = k_p Y \). The opposite is the case during the starvation phase, \( \mu_f = 0 \). Therefore, no balance equations for substrate are solved.

- The pore-size distribution and entry pressure of the rock and the biofilm are unknown. The same goes for the amount of \( \text{CO}_2 \) in the cores during the flooding of the cores with \( \text{CO}_2 \). Obviously, any fitting of parameters would not be unique. Instead, it will be assumed that \( \lambda_\kappa \) and \( p_{d,\kappa} \) are known, and the \( \text{CO}_2 \) saturation at the start of the \( \text{CO}_2 \) challenge is fitted to the experimental data.

With the above assumptions, the mass balance equations from Table 1 simplify to the following.

\[
\frac{d(\phi_p S_{w,p} + \phi_f S_{w,f})}{dt} = q_w / \varrho_w \tag{38}
\]

\[
\frac{d(\phi_p S_{n,p} + \phi_f S_{n,f})}{dt} = q_n / \varrho_n \tag{39}
\]

\[
\frac{1}{\phi_f} \frac{d\phi_f}{dt} = \mu_f - b_0 - c_w S_{n,f} \tag{40}
\]

The source/sink term \( q_w \) is chosen in such a way that the water-phase pressure \( p_w \) remains unchanged (accounting for the transfer of intracellular to extracellular water as the biofilm decays), whereas, \( q_n = 0 \).

In Table 7, the set of parameters used for the simulation of the two experiments are listed. Some of the parameters are estimated based on values from literature. As mentioned above, assumptions have been made for the pore-size distribution indices, entry pressures, and residual saturations of the two phases in the two continua. Three parameters have been fitted to the results of Experiment 2.

The growth phase is initialised, in the experiments, by injecting bacteria suspended in water into the cores and letting the bacteria attach to the rock. In the simulation, the porosity of Continuum \( F \) is initialised with \( \phi_f = 10^{-4} \cdot \varepsilon \).
Table 7: Parameters for simulation of experiments by Mitchell et al. (2009).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Growth rate $\mu_f$</td>
<td>$4.63 \times 10^{-5}$ s$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Endogenous decay rate $b_0$</td>
<td>$3.18 \times 10^{-7}$ s$^{-1}$</td>
<td>from Taylor and Jaffé (1990b)</td>
</tr>
<tr>
<td>Decay rate parameter $c_c$</td>
<td>$8.7 \times 10^{-4}$ s$^{-1}$</td>
<td>estimated from Mitchell et al. (2008)</td>
</tr>
<tr>
<td>Decay rate parameter $n_c$</td>
<td>3</td>
<td>fitted to Experiment 2</td>
</tr>
<tr>
<td>Permeability parameter $\phi_{p,c}/\phi_0$</td>
<td>0.35</td>
<td>fitted to Experiment 2</td>
</tr>
<tr>
<td>Permeability parameter $n_k$</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Minimum permeability $K_{\text{min}}$</td>
<td>$5.0 \times 10^{-16}$ m$^2$</td>
<td>taken from experimental data</td>
</tr>
<tr>
<td>Biofilm porosity $\varepsilon$</td>
<td>0.8</td>
<td>estimated from Zhang and Bishop (1994)</td>
</tr>
<tr>
<td>Pore-size distribution indices</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\lambda_p$</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>$\lambda_f$</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Entry pressures</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$p_{d,p}$</td>
<td>0.1 bar</td>
<td></td>
</tr>
<tr>
<td>$p_{d,f}$</td>
<td>0.25 bar</td>
<td></td>
</tr>
<tr>
<td>Residual saturations</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$S_{wr,p}$</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>$S_{wr,f}$</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>$S_{nr,p}$</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>$S_{nr,f}$</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>$S_n,p$ at start of each CO$_2$ challenge</td>
<td>0.8</td>
<td>fitted to Experiment 2</td>
</tr>
</tbody>
</table>
3.2.3. Results

The growth of biofilm within the sandstone core causes a permeability reduction. At some point, a minimum permeability value is achieved. In the experiments, this occurs after a small increase in permeability (see Figure 8). In both experiments, this occurs at about $t \approx 5$ days. The reason for this increase is not clear. Possibly, it occurs due to nutrient limitations at that point. Since no nutrient limitations are accounted for in the simulation, no such increase was modelled. Instead, the permeability decreases monotonously and stagnates at the minimum value of $5 \times 10^{-16}$ m$^2$. In Experiment 1, the growth phase is followed directly by a CO$_2$ challenge in which a slight increase in permeability was observed. The simulation does not show this increase in permeability. However, the effect of the CO$_2$ on the biofilm can be seen in the sharp decrease in the amount of pore space occupied by the biofilm $\phi_f/\varepsilon$ (see Figure 8). In Experiment 2, the growth phase is followed by a starvation phase. In the first starvation phase, the permeability remains constantly low. The simulation shows a steady decrease in $\phi_f/\varepsilon$ corresponding to the endogenous decay rate. This first starvation phase is followed by the first CO$_2$ challenge, a second short starvation phase, and finally the second CO$_2$ challenge. Both the experiment and simulation show slight increases in permeability in each of the last three phases.

Due the lack of experiments dealing with the processes required for a proper validation of the model, it is not possible at the current stage of research in this field to adequately validate the model. However, the experiments by Mitchell et al. (2009) do provide a means of calibration for the parameters which describe the interaction between CO$_2$ and the biofilm in the model.

3.3. Remarks

The model described in this paper was tested by modelling experiments from literature and comparing the simulations to experimental results. In order to model these experiments numerically, a number of assumptions and simplifications had to be made. Each of the experiments consisted of two runs, each with a different set of parameters and conditions. The model was fitted to one of the two runs and used to predict the results of the other. The values of the fitted parameters may not be unique. This may question the capability of these comparisons to validate the model. However, it is an excellent way of testing the model and getting a feel for the important parameters and the implications of the modelling assumptions.
Figure 8: Comparison of simulated permeability changes to the experimental results of Mitchell et al. (2009). Three parameters were fitted to Experiment 2 and remained unchanged for the simulation of Experiment 1. The symbols show the measured permeabilities of the sandstone cores in the experiments by Mitchell et al. (2009), and the continuous lines show the permeabilities of the cores in the simulation. The dashed lines show the volume fractions of pore space occupied by attached biomass, which is equivalent to $\phi_f/\varepsilon$. The experiments are divided into various phases, I, II, III, IV, and V. These are described in Table 6 on page 27.

4. Model Application

In the following, the model presented here will be applied in simulations of processes in the vicinity of a CO$_2$ injection well.

4.1. General Description

The problem set-up is similar to that used in the leakage simulations run by Kopp et al. (2009b) with which they investigated the thermal effects of leaking CO$_2$ (see also Pruess, 2004). In this work, however, the interest is on the caprock and the target formation which are both included in the model domain as is shown in Figure 9. The caprock around the well is assumed to have been damaged, for example, during the drilling of the well or as a result of high pressures during injection. The damaged caprock is a leakage pathway for CO$_2$ from the storage reservoir. In the following, three simulations are shown which demonstrate the use of biofilms to reduce leakage from the reservoir.
4.2. Description of Model Domain and Simulation Parameters

The model domain is radially symmetric, i.e., two-dimensional \((r, z)\), with a radius of 100 m and a thickness of 20 m. The bottom of the domain is at 1000 m depth. As shown in Figure 10, the caprock and the storage aquifer both have a thickness of 10 m, and the caprock is damaged up to a radius of 0.5 m. The simulation parameters including formation and fluid properties, and biological parameters are summarised in Table 8. The properties of brine are assumed to be constant, whereas those of \(\text{CO}_2\) vary with pressure. Biomass attachment and detachment parameters \((c_{a,1}, c_{a,2}, c_{d,1}, \tilde{c}_{d,2})\) have been taken from the simulations in Section 3.1. Capillary pressure and relative permeabilities are calculated with the parameters given in Table 7 on page 29. Other parameters include the specific surface area of the rock formation \(M = 2.2 \times 10^4 \text{ m}^{-1}\), the diffusion coefficients \(\tilde{D}^b = \tilde{D}^s = 10^{-8} \text{ m}^2/\text{s}\), and the effective diffusion coefficient \(D_{\text{eff}}^s = \varepsilon \times 10^{-9} \text{ m}^2/\text{s}\).

Even though the model domain has a radius of 100 m, only the first 10 m are of interest and are finely meshed. This is done to capture relevant processes and strong gradients of the primary variables near the well. The mesh in the outer region \((r > 10 \text{ m})\) is very coarse (see Figure 11) and only supposed to reduce the influence of the lateral boundary conditions,
Table 8: Simulation parameters.

<table>
<thead>
<tr>
<th>Property/Parameter</th>
<th>Value</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formation properties and hydraulic properties of biofilm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aquifer permeability</td>
<td>$50 \times 10^{-15}$ m$^2$</td>
<td></td>
</tr>
<tr>
<td>Aquifer porosity</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>Aquifer thickness</td>
<td>10 m</td>
<td></td>
</tr>
<tr>
<td>Caprock permeability</td>
<td>$1 \times 10^{-18}$ m$^2$</td>
<td></td>
</tr>
<tr>
<td>Caprock porosity</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>Caprock thickness</td>
<td>10 m</td>
<td></td>
</tr>
<tr>
<td>Permeability of damaged zone</td>
<td>$20 \times 10^{-15}$ m$^2$</td>
<td></td>
</tr>
<tr>
<td>Porosity of damaged zone</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>Radius of damaged zone</td>
<td>0.5 m</td>
<td></td>
</tr>
<tr>
<td>Permeability parameter $\phi_{p,c}/\phi_0$</td>
<td>0.35</td>
<td>from Table 7</td>
</tr>
<tr>
<td>Permeability parameter $n_k$</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Minimum permeability $K_{\text{min}}$</td>
<td>$0.01 \cdot K_0$</td>
<td></td>
</tr>
<tr>
<td>Biofilm porosity $\varepsilon$</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>Depth at bottom of aquifer</td>
<td>1000 m</td>
<td></td>
</tr>
<tr>
<td>Injection well radius</td>
<td>0.2 m</td>
<td></td>
</tr>
<tr>
<td>Domain radius</td>
<td>100 m</td>
<td></td>
</tr>
<tr>
<td>Temperature $T$</td>
<td>40 $^\circ$C</td>
<td>isothermal</td>
</tr>
<tr>
<td>Fluid properties</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brine salinity</td>
<td>0.15 kg/kg</td>
<td></td>
</tr>
<tr>
<td>Brine density $\rho_w$</td>
<td>1102 kg/m$^{3a}$</td>
<td></td>
</tr>
<tr>
<td>Brine viscosity $\mu_w$</td>
<td>$9.63 \times 10^{-4}$ Pa·s$^a$</td>
<td></td>
</tr>
<tr>
<td>CO$_2$ density $\rho_n$</td>
<td>$f(p, T)^b$</td>
<td></td>
</tr>
<tr>
<td>CO$_2$ viscosity $\mu_n$</td>
<td>$f(p, T)^b$</td>
<td></td>
</tr>
<tr>
<td>Biological parameters</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maximum substrate utilisation rate $k_\mu$</td>
<td>$8.91 \times 10^{-5}$ s$^{-1}$</td>
<td>from Table 7</td>
</tr>
<tr>
<td>Monod half-saturation coefficient $K_s$</td>
<td>$7.99 \times 10^{-4}$ kg/m$^3$</td>
<td>from Table 7</td>
</tr>
<tr>
<td>Yield coefficient $Y$</td>
<td>0.0975 kg/kg</td>
<td>Table 3</td>
</tr>
<tr>
<td>Endogenous decay rate $b_0$</td>
<td>$3.18 \times 10^{-7}$ s$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Decay rate parameter $c_c$</td>
<td>$8.7 \times 10^{-3}$ s$^{-1}$</td>
<td>from Table 7</td>
</tr>
<tr>
<td>Decay rate parameter $n_c$</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Biofilm density $\rho_b$</td>
<td>15 kg/m$^3$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Batzle and Wang (1992)
$^b$ Span and Wagner (1996)
$^c$ Fenghour et al. (1998)
especially pressure, on the system. In vertical direction, the mesh is uniform with a size of 0.5 m, whereas in the horizontal direction, the element size varies between 0.2 m at the injection well and 42 m at the outer boundary.

4.3. Reference Simulation: Clogging of Damaged Caprock

This simulation shows the injection of bacteria and substrate into the formation and the subsequent injection of CO$_2$. The injected bacteria is expected to attach to the surface of the formation rock. Given the abundance of nutrients near the well, the bacteria can reproduce to form a biofilm occupying pore space and reducing the permeability of the formation rock, thus, preventing the CO$_2$ from leaking out of the formation.
4.3.1. Initial and Boundary Conditions

The formation is assumed to be initially filled with brine under hydrostatic conditions. It is also assumed that there is no biomass or substrate in the system. These conditions are assigned to the top and outer boundaries as constant boundary conditions. The bottom boundary is a no-flow boundary. The boundary conditions are shown in Figure 10. The inner boundary, i.e., the injection well is also a no-flow boundary except at the interval over which water or CO$_2$ is being injected. Initially, water with suspended biomass is injected into the formation. This is followed by the injection of the nutrient medium containing the substrate. This, in turn, is followed by the injection of CO$_2$. The injection strategy is illustrated in Figure 12. Different regions

![Figure 12: Reference simulation: Boundary conditions at the well.](image)

$A, B, C,$ and $D$ have been demarcated, each representing a different set of boundary conditions at the well as listed below. The total simulation time is 400 days.

$A$ ($0 \leq t < 0.167$ days; $989.25 < z < 994.75$ m)
- Water flow: 0.5 kg/s
- CO$_2$ flow: no flow
- Biomass flow: $4.54 \times 10^{-7}$ kg/s.
  This corresponds to a biomass concentration in the injected medium of $10^{-3}$ kg/m$^3$.
- Substrate flow: no flow

$B$ ($0.167 \leq t < 90$ days; $989.25 < z < 994.75$ m)
- Water flow: 0.5 kg/s
4.3.2. Results

The development of the biofilm in the vicinity of the injection well with time can be seen in Figure 13. The figures show the biofilm volume fraction $\phi_f/\varepsilon$ at six different times (10, 40, 90, 100, 140, and 400 days). The biofilm develops in the region into which the bacteria and substrate are injected. At $t = 90$ days, the injection of substrate is stopped and the injection of $\text{CO}_2$ starts, leading to a reduction of attached biomass with time. At the end of the simulation ($t = 400$ days), there is almost no biofilm left in the formation. The reduction of the amount of attached biomass is caused primarily by endogenous decay because the bacteria within the biofilm are protected from the supercritical $\text{CO}_2$. Suspended bacteria, however, are not protected from the biocidal effects of supercritical $\text{CO}_2$. That is why the concentration of suspended biomass in water drops strongly when $\text{CO}_2$ is injected into the formation as can be seen in Figure 14. At $t = 100$ days, most of the suspended biomass has been damaged by $\text{CO}_2$.

Figure 15 shows the total amount of attached and suspended biomass in the formation with respect to time. As substrate is injected, the biomass in the system increases steadily. When the injection of substrate is stopped, the amount of biomass reduces strongly. As mentioned earlier, this is as
Figure 13: Results of reference simulation: Volume fraction of space occupied by biofilm $\phi_f/\varepsilon$. 
Figure 14: Results of reference simulation: Concentration of suspended biomass in water $C_{bw}$.
a result of the combination of endogenous decay and the biocidal effect of supercritical CO$_2$. However, one can see in the figure that the CO$_2$ kills almost all the suspended bacteria in a very short time, whereas the bacteria in the biofilm are – to an extent – protected from the CO$_2$.

![Graph showing the amount of biomass (attached and suspended) in the formation. The dotted vertical line at $t = 90$ days marks the end of substrate injection and the start of CO$_2$ injection. Note that the amount of suspended biomass is about two orders of magnitude less than that of the attached biomass.]

Figure 15: Reference simulation: Amount of biomass (attached and suspended) in the formation. The dotted vertical line at $t = 90$ days marks the end of substrate injection and the start of CO$_2$ injection. Note that the amount of suspended biomass is about two orders of magnitude less than that of the attached biomass.

The effect of the biofilm on the permeability of the formation can be seen in Figure 16. The right column of figures shows the total permeability, i.e., the sum of the permeabilities of the two continua ($K = K_p + K_f$) at $t = 100, 140,$ and $400$ days, and the left column shows the CO$_2$ saturation $S_{n,p}$ in Continuum $P$. The biofilm causes a considerable reduction of permeability preventing the CO$_2$, which is injected below the biofilm, from leaking through the damaged zone. However, as biomass decay within the biofilm progresses, the permeability increases. At $t = 400$ days, no influence of attached biomass on the permeability can be seen. This would mean that a renewal of the biofilm by the injection of nutrients would be necessary at some point. A more lasting solution would be the use of biofilms which actively precipitate CaCO$_3$ minerals as mentioned in Section 1.2.

In Section 4.4, a renewal of the substrate at regular intervals even during CO$_2$ injection is modelled. Even though the model does not account for mineral precipitation, Section 4.5 studies the implications a biobarrier consisting of biofilm and mineral precipitates would have on the system by using a reduced biofilm decay rate.
Figure 16: Results of reference simulation: $S_{n,p}$ (left) and $K = K_p + K_f$ (right).
4.4. Variation 1: Continued Injection of Substrate Medium

In this simulation, all the parameters, mesh, domain etc. are exactly the same as in the reference simulation. Only the boundary conditions at the injection well differ from those of the reference simulation. These are illustrated in Figure 17a. The injection well is divided into different regions (A, B, C, D, E) in space z and time t. The regions A, B, C, and D are identical to those of the reference simulation. E represents the injection of substrate at intervals and is simultaneous to C (the injection of CO\textsubscript{2}). The boundary conditions in E are defined below.

\[ E \ (90 \leq t \leq 400 \text{ days}; \ 989.25 < z \leq 994.75 \text{ m}) \]

- Water flow: \( f_e(t) \cdot 0.5 \text{ kg/s} \)
- CO\textsubscript{2} flow: no flow
- Biomass flow: no flow
- Substrate flow (Continuum P): \( f_s(t) \cdot 1.13 \times 10^{-4} \text{ kg/s}. \) This corresponds to a substrate concentration in the injected medium of 0.25 kg/m\textsuperscript{3}.
- Substrate flow (Continuum F): no flow
$f_e(t)$ is the positive part of a sine function of time with a period $T$ of 120 days and a unit amplitude as defined in Equation (41).

$$f_e(t) = \max \left(0, -\sin \left(\frac{t - t_0}{T/2\pi}\right)\right),$$  

where $t_0 = 90$ days marks the beginning of region $E$. A plot of the resulting mass flow of water over the boundary of the injection well for the regions $A, B,$ and $E$ is given in Figure 17b.

4.4.1. Results

Figure 18a shows the total amount of biomass in the formation over time. As is the case in the reference simulation, there is a build-up of attached and suspended biomass in the formation during the first 90 days. This is followed by a strong drop when the substrate injection is stopped and CO$_2$ is injected. However, in contrast to the reference simulation, the amount of biomass in the system increases again when the injection of the nutrient medium is resumed. There is a cyclic pattern corresponding to the injection strategy as shown in Figure 17b. One can see that the amount of suspended biomass reduces very quickly when the medium injection is shut down compared to that of the attached biomass.

![Variation 1](image1.png) ![Variation 2](image2.png)

Figure 18: Variations: Amount of biomass (attached and suspended) in the formation.

The CO$_2$ saturation and the total permeability of the formation at three time-steps, i.e., at 180, 270, and 400 days are shown in Figure 19. The magnitude and extent of permeability reduction changes with time. They
are greatest in the middle of an injection phase, e.g., at $t = 180$ days and lowest at the end of a starvation phase, e.g., at $t = 270$ days.

4.5. Variation 2: Reduced Biofilm Decay Rate

One way of increasing the durability of the biobarrier is to use biofilms which mediate the precipitation of CaCO$_3$, thus forming a biobarrier which consists of biofilm and mineral precipitates (Cunningham et al., 2009). This process cannot be modelled explicitly here. But, the potential effect it would have on the system is studied in this variation of the reference simulation. This is done by assuming that a biomineral barrier has been formed in the same places as in the reference simulation, and that this biomineral barrier has a decay rate which is two orders of magnitude less than in the reference case, i.e.,

$$b_f = 0.01 \cdot (3.18 \times 10^{-7} + 8.7 \times 10^{-4} \cdot S_{n,f}^3) \text{ s}^{-1}. \quad (42)$$

This is an arbitrary choice. However, recent experiments on this topic at the Center for Biofilm Engineering, Montana State University, suggest that decay of biomineral deposits is very slow, although an exact quantification is not available yet.

The simulation starts at $t = 90$ days, and the initial conditions here are the conditions in the reference simulation at $t = 90$ days. The boundary conditions and all other parameters remain unchanged.

4.5.1. Results

The results in Figure 18b, i.e., the total biomass in the system over time, show that the amount of suspended biomass is the same as in the reference simulation. The amount of attached “biomass” (which is composed of biofilm and biominerals) does not drop as quickly as in the reference case. This is obviously due to the reduced biofilm decay rate. There is a slight increase in attached biomass at about $t = 190$ days. This occurs when biofilm growth, which still occurs as long as the injected substrate has not been fully consumed, exceeds biofilm decay in total.

4.6. Remarks

The simulations show that the presented model is capable of qualitatively modelling the accumulation of biomass in a geological formation in the presence of water and CO$_2$ as well as the effects of the accumulated biomass on the hydraulic properties of the formation. In the simulations, the bacterial
Figure 19: Results of Variation 1: $S_{n,p}$ (left) and $K = K_p + K_f$ (right).
cells embedded in the biofilm are protected from supercritical CO$_2$, and thus the biofilm persists longer than the suspended cells. The biofilm can even grow in the presence of CO$_2$ when nutrients are injected. These are important prerequisites for the use of biofilms to increase storage safety. However, in the presence of supercritical CO$_2$, an important process which enhances the spreading of the biofilm is strongly inhibited, i.e., the transport of detached cells and subsequent reattachment at new sites. Since detached cells leave the protective environment of the biofilm, the presence of a biocide in the bulk fluid prevents them from successfully colonising new surfaces.

5. Summary and Conclusions

This article deals primarily with the development of a numerical model capable of describing the accumulation of biomass in the subsurface and its application to the plugging of damaged caprock in a subsurface CO$_2$ storage reservoir. This involves the description of fluid flow and microbial activity in porous media. On the one hand, the accumulation of biomass in a porous medium changes the hydraulic properties of the medium which affects flow. Flow processes, on the other hand, determine the transport of nutrients to the microbes, and thus directly influence the rate and distribution of biomass growth. Thus, the proper description of the interaction between flow and microbial processes is an essential challenge for such a model.

Two sets of experiments with particular relevance to the processes of interest were chosen for the validation of the model. By comparison of simulation results to the results of one of the experiments, which considers one-phase flow through a sand column, it could be shown that the model can qualitatively reproduce and predict the relevant processes for the given conditions. However, quantitative validation was not possible. Due to lack of information and the complexity of the system, the second set of experiments could not be used for validation purposes. Rather, it served as a source of calibration for the model.

Finally, the model was applied to a fictitious test scenario in which the caprock of a CO$_2$ storage reservoir is damaged at the injection well. Bacterial cells and nutrients are injected into the formation just below the caprock until a biofilm is formed within the damaged zone. CO$_2$ is then injected into the formation. For the given example, it is possible to plug the damaged caprock with biofilm. However, the biofilm is temporary and requires regular feeding. This problem could be solved by the use of biofilms which serve as
catalysts for the precipitation of minerals, leading to longer-lasting clogging. The described model does not account for geochemical processes, and such scenarios cannot be modelled yet. Thus, in future work, an extension of the model to account for such processes is important. If it is possible to transport the chemical species necessary for biomineralisation to the biofilm, the use of this technology to plug leakage pathways can be a very useful method of mitigating leakage and increasing storage safety.

6. Outlook

The capabilities of the model allow the simulation of biofilm formation in the subsurface. However, there is very much room for improvement. Further work on this topic should include the following points.

- Some of the simplifications made in the development of the model are restrictive and need to be revisited. A good example is the assumption that both continua have the same pressure. This way, the advective exchange of solutes between the two continua cannot be accounted for. Instead, both pressures could be solved for independently and linked only with the exchange term. The exchange of solutes would then be driven by a combination of solute and pressure gradients.

- Dissolved CO$_2$ plays an important role in the inactivation of bacterial cells (Zhang et al., 2006). Thus, an extension of the model to account for the dissolution of CO$_2$ in water and its subsequent transport within the water phase is necessary and would improve the capability of the model to capture the biocidal effect of CO$_2$ on the microorganisms, especially the suspended cells.

- The model assumes that there is only one growth-limiting substrate and that all other nutrients necessary for growth are abundantly available. This is a strong restriction. An injection strategy could involve the injection of a substrate and the delayed injection of an electron acceptor with the aim of growing a biofilm at some distance from the injection. This cannot be simulated with the model. Thus, an electron acceptor needs to be accounted for by the model.

- The model makes use of many empirical parameters and relationships. Sensitivity studies are necessary to determine the parameters which
have the strongest influence on the system. Values for these parameters need to be determined in experimental investigations. Experiments are also necessary to gain a better understanding of the relevant mechanisms involved.

- All the equations, correlations, and parameters used in the model are defined on the macroscale. However, it is often easier to understand and describe processes on the microscale. Well-understood microscale phenomena should be properly depicted on the macroscale. This is not always easy. Therefore, research on the upscaling of microscale processes relevant to biofilms in porous media to the macroscale (e.g., van Noorden et al., 2010; Golfier et al., 2009) is absolutely necessary.

- The conservation equations of the different components (water, CO₂, biomass, and substrate) are solved simultaneously. This is computationally expensive. Future work could focus on decoupling processes of different time scales. For example, the simulation of flow processes, involving water and CO₂, could be partly decoupled from transport and biological processes, involving biomass and substrate.

- Under starvation conditions, the biobarrier slowly loses its efficiency. A more enduring option is the use of mineral-precipitating biofilms. In further work, it could be of interest to extend the model to account for the transport of the chemical species necessary for such mineralisation.

A. Acknowledgement

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B. Notation
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon$</td>
<td>biofilm porosity</td>
<td>[-]</td>
</tr>
<tr>
<td>$\phi$</td>
<td>porosity</td>
<td>[-]</td>
</tr>
<tr>
<td>$\phi_0$</td>
<td>porosity of porous medium unaffected by biofilm</td>
<td>[-]</td>
</tr>
<tr>
<td>$\phi_{p,c}, \phi'_{p,c}$</td>
<td>parameters for the calculation of $K_p$ and $K_f$</td>
<td></td>
</tr>
<tr>
<td>$\lambda$</td>
<td>pore-size distribution index</td>
<td>[-]</td>
</tr>
<tr>
<td>$\mu_\alpha$</td>
<td>dynamic fluid viscosity of the phase $\alpha$</td>
<td>[kg/(m s)]</td>
</tr>
<tr>
<td>$\mu_\kappa$</td>
<td>growth rate of biomass in Continuum $\kappa$</td>
<td>[1/s]</td>
</tr>
<tr>
<td>$\varrho_\alpha$</td>
<td>fluid density of the phase $\alpha$</td>
<td>[kg/m$^3$]</td>
</tr>
<tr>
<td>$\varrho_b$</td>
<td>biofilm density</td>
<td>[kg/m$^3$]</td>
</tr>
<tr>
<td>$C^b_w$</td>
<td>concentration of biomass in water</td>
<td>[kg/m$^3$]</td>
</tr>
<tr>
<td>$C^s_w$</td>
<td>concentration of substrate in water</td>
<td>[kg/m$^3$]</td>
</tr>
<tr>
<td>$D$</td>
<td>diffusion coefficient</td>
<td>[m$^2$/s]</td>
</tr>
<tr>
<td>$F$</td>
<td>continuum accounting for fluid flow in biofilm</td>
<td></td>
</tr>
<tr>
<td>$P$</td>
<td>continuum accounting for fluid flow in porous matrix</td>
<td></td>
</tr>
<tr>
<td>$K$</td>
<td>isotropic intrinsic permeability</td>
<td>[m$^2$]</td>
</tr>
<tr>
<td>$K_0$</td>
<td>permeability of biofilm-free porous medium</td>
<td>[m$^2$]</td>
</tr>
<tr>
<td>$K_{\text{min}}$</td>
<td>permeability of biofilm-filled porous medium</td>
<td>[m$^2$]</td>
</tr>
<tr>
<td>$K_s$</td>
<td>Monod half-saturation coefficient</td>
<td>[kg/m$^3$]</td>
</tr>
<tr>
<td>$M$</td>
<td>specific surface</td>
<td>[m$^2$/m$^3$]</td>
</tr>
<tr>
<td>$S$</td>
<td>saturation</td>
<td>[-]</td>
</tr>
<tr>
<td>$S_r$</td>
<td>residual saturation</td>
<td>[-]</td>
</tr>
<tr>
<td>$S_e$</td>
<td>effective saturation</td>
<td>[-]</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
<td>[$^\circ$ C]</td>
</tr>
<tr>
<td>$Y$</td>
<td>yield coefficient</td>
<td></td>
</tr>
<tr>
<td>$a$</td>
<td>exchange parameter</td>
<td>[s/m$^2$]</td>
</tr>
<tr>
<td>$b$</td>
<td>biomass decay rate</td>
<td>[1/s]</td>
</tr>
</tbody>
</table>
\( b_0 \) endogenous biomass decay rate \( [1/\text{s}] \)

\( b_c \) biomass decay rate due to lysis \( [1/\text{s}] \)

\( c_c \) parameter for the calculation of \( b_c \)

\( c_{a,1}, c_{a,2} \) parameters for the calculation of \( k_a \)

\( c_{d,1}, c_{d,2}, \tilde{c}_{d,2} \) parameters for the calculation of \( k_d \)

\( d_r \) characteristic pore diameter \( [\text{m}] \)

\( e \) exchange term \( [\text{kg/(m}^3\text{s})] \)

\( g \) vector of gravitational acceleration \( (0, 0, -g)^T \)

\( g \) (scalar) gravitational acceleration \( [\text{m/s}^2] \)

\( k_{\mu} \) maximum substrate utilisation rate \( [1/\text{s}] \)

\( k_a \) attachment function \( [1/\text{s}] \)

\( k_d \) detachment function \( [1/\text{s}] \)

\( k_d^s \) detachment due to shear \( [1/\text{s}] \)

\( k_d^b \) detachment due to biological factors \( [1/\text{s}] \)

\( k_r \) relative permeability \( [-] \)

\( n_c \) parameter for the calculation of \( b_c \)

\( n_k \) parameters for the calculation of \( K_p \)

\( p \) pressure \( [\text{N/m}^2] \)

\( p_d \) entry pressure \( [\text{N/m}^2] \)

\( p_c \) capillary pressure \( [\text{N/m}^2] \)

\( q \) source/sink \( [\text{kg/(m}^3\text{s})] \)

\( r_g \) biomass growth \( [\text{kg/(m}^3\text{s})] \)

\( r_b \) biomass decay \( [\text{kg/(m}^3\text{s})] \)

\( r_a \) biomass attachment rate \( [\text{kg/(m}^3\text{s})] \)

\( r_d \) biomass detachment rate \( [\text{kg/(m}^3\text{s})] \)

\( v \) Darcy flux/velocity \( [\text{m/s}] \)

**Subscripts:**

\( \alpha \) phase, either \( w \) or \( n \)

\( n \) non-wetting phase

\( w \) wetting phase

\( \kappa \) continuum, either \( p \) or \( f \)

\( p \) Continuum \( P \)

\( f \) Continuum \( F \)

**Superscripts:**

\( b \) biomass

\( s \) substrate/solute
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