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## **MATHEMATICAL ANALYSIS AND OPTIMIZATION OF INFILTRATION PROCESSES**

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# Mathematical Analysis and Optimization of Infiltration Processes \*

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## Abstract

A variety of infiltration techniques can be used to fabricate solid materials, particularly composites. In general these processes can be described with at least one time dependent partial differential equation describing the evolution of the solid phase, coupled to one or more partial differential equations describing mass transport through a porous structure. This paper presents a detailed mathematical analysis of a relatively simple set of equations which is used to describe chemical vapor infiltration. The results demonstrate that the process is controlled by only two parameters,  $\alpha$  and  $\beta$ . The optimization problem associated with minimizing the infiltration time is also considered. Allowing  $\alpha$  and  $\beta$  to vary with time leads to significant reductions in the infiltration time, compared with the conventional case where  $\alpha$  and  $\beta$  are treated as constants.

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# 1 Introduction

A variety of materials are produced by infiltration processes. In these techniques a fluid phase (i.e., a gas or a liquid) is transported into a porous structure, where it then reacts to form a solid product. These methods are particularly important for producing composite materials, where the initial porous preform is composed of the reinforcement phase (i.e., fibers, whiskers, or particles) and infiltration produces the matrix. ([1],[2]). A detailed assessment of the relevant reaction and mass transport rates during infiltration requires mathematical modeling, using a minimum of two coupled partial differential equations which describe changes in the reactant concentration and the solid structure as a function of both position and time. This type of modeling can also be extended to analyze the optimization and control of infiltration processes.

The research presented here specifically considers optimization for a set of two equations which describe chemical vapor infiltration (CVI). In this process a vapor-phase precursor is transported into the porous preform, and a combination of gas and surface reactions leads to the deposition of the solid matrix phase. In recent years a number of researchers have developed mathematical descriptions of CVI. While these models do not provide complete, detailed representations of CVI, they provide an excellent starting point for mathematical and computational research on the equations which describe infiltration processes in general. During infiltration the formation of the solid product phase eventually closes off porosity at the external surface of the body, blocking the flow of reactants and effectively ending the process. This is a key feature of most infiltration processes. It is usually desirable to maximize the amount of solid formation that occurs before this endpoint is reached. This optimization goal is often linked to another objective. For example, CVI often requires extremely long times, so it is also important to minimize the total processing times.

The paper is organized as follows: In Section 2 we derive a simple set of two equations that models the infiltration processes, and we show how to get these equations as a subcase of the general system. These are nonlinear partial differential equations. We also derive initial and boundary conditions for the model equations. In Section 3 we present a detailed mathematical analysis concerning the behavior of the solutions in space and time. This analysis provides insights into the behavior of the process. In Section 4 we define the concept of a successful process and get conditions on the parameters of the problem for a process to be successful. In particular we formulate an optimization problem for the minimum time it takes for the process to settle. In Section 5 we present numerical experiments to validate the theory. We also discuss how to design the experimental parameters to get faster successful processes.

## 2 Formulation

A mathematical description of infiltration requires one or more partial differential equations which describe the evolution of the matrix (i.e., the solid phase), and one additional partial differential equation for each chemical species in the fluid phase. For a simple pore

structure, the continuity equation for species  $i$  is

$$\frac{\partial(\varepsilon C_i)}{\partial t} + \nabla \cdot N_i = \sum_r^{n_r} \nu_{ir} R_r \quad (1)$$

where  $t$  is time,  $\varepsilon$  is the void fraction of the media,  $C_i$  is the concentration of species  $i$ ,  $n_r$  is the number of the gaseous species,  $\nu_{ir}$  is the stoichiometric coefficients for the  $i$ th gaseous species in the  $r$ th reaction, and  $R_r$  represents the volumetric reaction rate of reaction  $r$ .

The basic partial differential equation(s) which describe reaction and mass-transport in porous media (i.e., the fluid phase) are well-established [6, 8]. The Dusty-Gas model [9] describes multicomponent diffusion and convection. Neglecting thermal diffusion, the relationship between the molar fluxes,  $N_i$ , is given by [10]:

$$\frac{N_i}{D_{K_i}} + \frac{RT}{P} \sum_{j \neq i} \frac{C_j N_i - C_i N_j}{\mathcal{D}_{M_{ij}}} = -\nabla C_i - \frac{C_i B_e}{\mu D_{K_i}} \nabla P \quad (2)$$

where  $B_e$  is the permeability of the porous media,  $\mu$  is the viscosity of the mixture, and  $P$  is the total pressure.  $\mathcal{D}_{M_{ij}}$  and  $D_{K_i}$  are the effective binary diffusivity for species  $i$  and  $j$  and the effective Knudsen diffusivity of species  $i$ , respectively.

The change in the solid structure is equivalent to considering the change in the void fraction,  $\varepsilon$  (i.e., the volume fraction of gas inside of the porous solid). The evolution of  $\varepsilon$  is given by:

$$\frac{\partial \varepsilon}{\partial t} = -u S_v(\varepsilon) \quad (3)$$

where  $u$  is the rate at which the solid product grows (volume/area/time) and  $S_v(\varepsilon)$  is the gas/solid surface area per unit volume of the porous solid.

The simplest formulation for the fluid phase is obtained by considering one reacting species. For highly diluted reactant systems, the Dusty-Gas model can be simplified to give the following approximate expression for the flux:

$$N = -D \frac{\partial C}{\partial Z} \quad (4)$$

where  $C$  is the concentration of diluted species and  $Z$  is the distance into the preform. The effective diffusivity of the diluted species,  $D$ , can be expressed as

$$D = \frac{\varepsilon}{\theta} D_{Mm} [1 + N_k(\varepsilon)]^{-1} \quad (5)$$

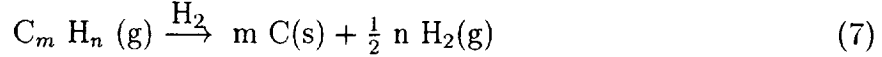
where  $m$  refers to the bulk species,  $D_{Mm}$  is the binary diffusion coefficient for  $M$  in  $m$ ,  $N_k$  is the ratio of the Knudsen diffusion coefficient and  $D_{Mm}$ , and  $\theta$  is the tortuosity factor.

For a diffusion-limited process in one spatial dimension, using Eq. (4), Eq. (1) becomes:

$$\frac{\partial(\varepsilon C_i)}{\partial t} = \frac{\partial}{\partial Z} \left[ D \frac{\partial C}{\partial Z} \right] - \frac{u S_v(\varepsilon)}{V_M} \quad (6)$$

where  $V_M$  is the molar volume of the solid product. The last term in Eq. (6) describes the rate at which the gas-phase precursor is consumed (or created) by chemical reactions inside of the pores, with the assumption that there are no homogeneous gas-phase reactions.

A specific CVI model requires expressions for  $u$ ,  $S_v$ , and  $D$ . Our objective in this work is to use simple formulations for each, as a basis for assessing the general behavior of infiltration problems. As an example, consider the formation of carbon matrix composites using a hydrocarbon in an  $H_2$  carrier gas, where the following net reaction occurs:



The form of Eq. (6) is based on the assumption that the MTS concentration,  $C_r$ , is dilute (i.e., the reactant concentration is much smaller than the carrier gas concentration). If the carbon growth rate is proportional to the precursor concentration, then:

$$u = kC_r \quad (8)$$

where  $k$  is the reaction rate constant.

The preforms used for CVI typically have a complex porous structure. However, a cylindrical pore is often used to formulate simple models. This leads to the following expression for  $S_v$ :

$$S_v(\varepsilon) = \frac{2\sqrt{\varepsilon_o}\sqrt{\varepsilon}}{r_o} \quad (9)$$

where  $r_o$  is the initial pore radius and  $\varepsilon_o$  is the initial concentration of  $\varepsilon$ .

Substituting Eqs. (8) and (9) into Eqs. (3) and (6) gives the following forms:

$$\frac{\partial \eta}{\partial t} = -\frac{1}{2}\beta c \quad (10)$$

$$\frac{\partial}{\partial z} \left[ \frac{\eta^2}{\theta} [1 + N_k(\eta)]^{-1} \frac{\partial c}{\partial z} \right] = \alpha^2 \eta c \quad (11)$$

where:

$$\eta = \sqrt{\varepsilon} \quad (12)$$

$$c = \frac{C_r}{C_o} \quad (13)$$

$$z = \frac{Z}{L} \quad (14)$$

$$\alpha^2 = \frac{2k\sqrt{\varepsilon_o}L^2}{V_M r_o D_{Mm}} \quad (15)$$

$$\beta = \frac{2k\sqrt{\varepsilon_o}C_o}{r_o} = \alpha^2 \frac{V_M C_o D_{Mm}}{L^2} \quad (16)$$

where  $L$  is the half-thickness of the preform,  $C_o$  is the concentration of the reactant species in the bulk gas-phase (i.e., outside of the preform). The expression for  $\alpha$  (15) is based on the assumption that  $u$  is determined by a first order reaction, where  $k$  is the rate constant (i.e.,  $u = kC_r$ ). Note that  $\alpha^2$  is dimensionless and that  $\beta$  has units of inverse time.

The parameters  $\alpha^2$  and  $\beta$  depend on the three key process variables:  $T$ ,  $P$ , and  $C_o$ .  $T$ ,  $P$  do not appear explicitly in Eqs. 15 and 16, however,  $k$  typically obeys an Arrhenius-type exponential temperature dependence, and  $D_{Mm}$  varies with both temperature and pressure. If the process variables are all held at single fixed values throughout the process, then  $\alpha^2$  and  $\beta$  differ only by a lumped constant. However if one or more of the process variables is changed as infiltration proceeds, then the proportionality between  $\alpha^2$  and  $\beta$  will also vary. As an example of this, we consider a case where  $\alpha^2$  decreases while  $\beta$  is held constant (see Section 5). One way of accomplishing this in practice is to reduce the temperature during the course of the process, such that  $\alpha^2$  decreases (because  $k$  usually decreases faster than  $D_{Mm}$  as  $T$  decreases). To hold  $\beta$  constant,  $C_o$  must be increased in a way which directly offsets the decrease in  $k$ .

The time derivative in Eq. (6) has been removed in Eq. (11). This is permissible because solids are much denser than gases, such that the time-scale for changes in the  $C_r$  profile is much shorter than the time scale associated with changes in the solid structure. For gas-solid reaction processes such as CVI, this is sometimes referred to as the pseudo steady-state approximation [7]. Transforming  $\varepsilon$  to  $\eta$  simplifies equation (10). Basically  $\eta$  is proportional to  $S_v$ , so it is also possible to view  $\eta$  as a dimensionless surface area per volume.

The boundary conditions that are most often used for CVI models are to fix the concentration at the outer surface of the preform at  $C_o$ , and to assume that diffusion occurs in from two opposite sides, such that there is no net flux in the middle of the preform (i.e., at  $Z = L$ ):

$$c(0, t) = 1 \tag{17}$$

$$c_z(1, t) = 0 \tag{18}$$

The initial condition is given by:

$$\varepsilon(z, 0) = \varepsilon_o \tag{19}$$

During CVI, the infiltration kinetics are controlled by diffusion and the deposition reaction. To achieve relatively uniform infiltration, diffusion must be fast relative to the deposition rate. This is typically accomplished by choosing processing conditions that result in a slow deposition rate, which usually leads to long infiltration times. Thus, a key processing objective is to obtain the desired amount of infiltration in the shortest possible time. The total amount of infiltration in the preform is given by integrating over  $z$ :

$$\bar{\varepsilon}(t) = \int_0^1 \varepsilon(z, t) dz \tag{20}$$

It is generally important to obtain the desired density (i.e., void fraction),  $\varepsilon_f$ , in the shortest possible time. Thus, the optimization problem of interest corresponds to determining the shortest time where  $\varepsilon(t) = \varepsilon_f$ , for values of  $\varepsilon_f$  that are significantly smaller than  $\varepsilon_o$ .

### 3 Properties

The following system is obtained from Eqs. (10) and (11):



$$\frac{\partial \eta(z, t)}{\partial t} = -\frac{\beta(t)}{2} c(z, t) \quad (21)$$

$$\frac{\partial}{\partial z} \left( f(\eta(z, t)) \frac{\partial c(z, t)}{\partial z} \right) = \alpha^2(t) \eta(z, t) c(z, t) \quad (22)$$

where  $f(\eta) = \frac{\eta^2}{\theta} [1 + N_k(\eta)]^{-1}$ ,  $\frac{f(\eta)}{\eta} \in C^\infty$  is a monotone increasing function of  $\eta$ ,  $\alpha(t) \neq 0$  and  $\beta(t) \geq 0$  are  $C^\infty$  functions of  $t$ , and  $\eta$  is  $\sqrt{\varepsilon}$ .

The system is subject to initial conditions

$$\eta(z, 0) = \eta_0 > 0 \quad (23)$$

as well as boundary conditions

$$c(0, t) = 1 \quad (24)$$

$$\frac{\partial c}{\partial z}(1, t) = 0 \quad (25)$$

Physically, these correspond to a constant concentration at the outer surface ( $z = 0$ ) and a symmetry plane at  $z = 1$ . We can immediately find the initial value for the concentration function  $c(z, t)$

### **Lemma 1**

The initial distribution of the function  $c(z, t)$  is given by:

$$c(z, 0) = \frac{\cosh \gamma_0 (1 - z)}{\cosh \gamma_0} \quad (26)$$

where

$$\gamma_0 = \sqrt{\frac{\eta_0}{f(\eta_0)}} \alpha(0) \quad (27)$$

### **Proof**

Consider (22) at the initial time  $t = 0$ . Because of the initial condition (23)  $\eta(z, 0) = \eta_0$  is a constant in  $z$ . Equation (22) is, therefore, a second order constant coefficient ODE whose solution is given by (26).

□

### **Lemma 2**

The value of  $\eta(z, t)$  at the boundary point  $z = 0$  is given by

$$\eta(0, t) = \eta_0 - \frac{1}{2} \int_0^t \beta(\tau) d\tau \quad (28)$$

### **Proof**

We read (21) for  $z = 0$  using the boundary condition (24)  $c(0, t) = 1$ . Integration yields (28).

□

Examining the boundary value for  $\eta(0, t)$  given in (28), it is clear that a positive solution does not exist if

$$\frac{1}{2} \int_0^t \beta(\tau) d\tau = \eta_0 \quad (29)$$

for some  $t$ . We define the first time that (29) is satisfied as *the terminal time*  $t_\beta$ . If (29) is never satisfied we define the terminal time  $t_\beta$  as  $\infty$ .

We assume now that before the terminal time,  $\eta(z, t)$  exists and is positive, to be precise

**Assumption 1**

There exists a unique positive solution  $\eta(z, t)$  for any  $0 \leq t < t_\beta$ ,  $0 \leq z \leq 1$ . This solution is  $C^\infty$  in both  $z$  and  $t$ .

□

**Comment:**

From Assumption 1, it follows that there exists a solution  $c(z, t)$  in the same time and space intervals.

In the rest of this section we will derive properties of the solutions  $c(z, t)$  and  $\eta(z, t)$ . Study of these properties is important not only for the understanding of the behavior of the infiltration process, but also to find ways to speed up the process, in particular it will help us to define a successful process.

In the following Lemma we will consider the behavior of the concentration function  $c(z, t)$

**Lemma 3**

The concentration function  $c(z, t)$  is a positive function for  $0 \leq z \leq 1$  for any  $0 \leq t < t_\beta$ . Moreover,  $c(z, t)$  decreases as a function of  $z$ .

**Proof**

We multiply (22) by  $c(z, t)$  for every  $0 \leq t < t_\beta$  and integrate from some point  $z$  to the point  $z = 1$  taking into account that the spatial derivative of  $c(z, t)$  vanishes at  $z = 1$ . For convenience we drop the dependence on  $t$ . We then get

$$\begin{aligned} -c(z)f(\eta(z))\frac{dc(z)}{dz} &= \int_z^1 f(\eta(\xi)) \left( \frac{dc(\xi)}{d\xi} \right)^2 d\xi \\ &\quad + \alpha^2 \int_z^1 \eta(\xi)c(\xi)^2 d\xi \quad , \end{aligned} \quad (30)$$

thus  $c(z)\frac{dc(z)}{dz}$  is negative. It can never vanish, since, if  $c(z)$  vanishes at a point  $z_0$  then the right hand side of (30) has to vanish and thus both  $c$  and  $\frac{dc}{dz}$  vanish in the interval  $[z_0, 1]$ . By the standard theory of linear differential equations the solution  $c(z, t)$  must vanish everywhere. So that  $c(z)\frac{dc(z)}{dz}$  is strictly negative. Since  $c(0, t) = 1$ , it follows that  $c(z)$  is positive and  $\frac{dc(z)}{dz}$  is negative. Thus the lemma is proven.

□

We turn now to the behavior of  $\eta(z, t)$  as a function of the spatial variable  $z$ , for any fixed  $t$ .

**Lemma 4**

The function  $\eta(z, t)$  increases as a function of  $z$ . In particular

$$\eta(0, t) \leq \eta(z, t) < \eta_0 \quad (31)$$

where  $\eta(0, t)$  is given in (28).

**Proof**

Consider equation (21) and integrate with respect to  $t$  to get

$$\eta(z, t) = \eta_0 - \frac{1}{2} \int_0^t \beta(\tau) c(z, \tau) d\tau \quad (32)$$

By Lemma 3,  $c(z, t)$  is monotonically decreasing (in  $z$ ), therefore  $\eta(z, t)$  is monotonically increasing (in  $z$ ).

The lower bound in (31) is a consequence of the monotonicity of  $\eta$ , the upper bound is a result of (32) and the fact that  $c(z, t)$  is positive.

□

We can also establish an upper bound on the concentration function  $c(z, t)$ :

**Lemma 5**

The concentration function  $c(z, t)$  is bounded by

$$c(z, t) \leq \frac{\cosh \gamma_1 (1 - z)}{\cosh(\gamma_1)} \quad (33)$$

where

$$\gamma_1 = \sqrt{\frac{\eta_0}{f(\eta_0)}} \alpha(t) \quad (34)$$

In particular if  $\alpha(t) = \alpha(0)$ , is independent of time, then

$$c(z, t) \leq c(z, 0) \quad (35)$$

**Proof**

Denote first by  $F(z, t)$  the solution of

$$\frac{\partial^2}{\partial z^2} F(z, t) - \gamma_1^2 F(z, t) = 0 \quad (36)$$

with the boundary conditions

$$F(0, t) = 1 \quad , \quad \frac{\partial F}{\partial z}(1, t) = 0. \quad (37)$$

The solution of (36) is clearly

$$F(z, t) = \frac{\cosh \gamma_1(1 - z)}{\cosh(\gamma_1)} \quad (38)$$

We rewrite now equation (22) as

$$\frac{\partial^2 c(z, t)}{\partial z^2} + \frac{f_z}{f} \frac{\partial c(z, t)}{\partial z} = \gamma^2 c(z, t) \quad (39)$$

where

$$\gamma = \sqrt{\frac{\eta(z, t)}{f(\eta(z, t))}} \alpha(t) \quad (40)$$

We multiply now (36) by  $c(z, t)$ , (39) by  $F(z, t)$  and integrate between some  $z$  and 1, taking into account that the spatial derivatives of both  $c(z, t)$  and  $F(z, t)$  vanish at  $z = 1$ , to get:

$$- \left( F \frac{\partial c}{\partial z} - c \frac{\partial F}{\partial z} \right) = - \int_z^1 \frac{f_z}{f} \frac{\partial c}{\partial z} F d\xi + \int_z^1 (\gamma^2 - \gamma_1^2) F c d\xi \quad (41)$$

Now  $f_z > 0$  since  $f$  is monotone in  $\eta$  and  $\eta$  is monotone in  $z$ . By Lemma 3,  $\frac{\partial c(z, t)}{\partial z}$  is negative and so while  $F$  is positive. Also we have assumed that  $\frac{f(\eta)}{\eta}$  is monotone so that  $\gamma^2 - \gamma_1^2$  is positive. We conclude that the RHS of (41) is positive. Thus

$$F \frac{\partial c}{\partial z} - c \frac{\partial F}{\partial z} \leq 0 \quad (42)$$

Leading to

$$\frac{\partial}{\partial z} \frac{c(z, t)}{F(z, t)} \leq 0 \quad (43)$$

Since at  $z = 0$ ,  $c(z, t) = F(z, t) = 1$  we can conclude

$$c(z, t) \leq \frac{\cosh \gamma_1(1 - z)}{\cosh(\gamma_1)} \quad (44)$$

We note that if  $\alpha(t)$  is constant in time then  $\gamma_1$  defined in (34) is exactly  $\gamma_0$  defined in (27) and thus  $F(z, t) = c(z, 0)$  proving (35).

□

With Lemma 5 proven we can find a better lower bound on the pore function  $\eta(z, t)$  than the one given in Lemma 4.

**Lemma 6**

The pore function  $\eta(z, t)$  is bounded from below by

$$\eta(z, t) \geq \eta_0 - \int_0^t \frac{1}{2} \beta(\tau) F(z, \tau) d\tau \quad (45)$$

where  $F(z, t)$  is given in (38).

**Proof**

By Lemma 5,  $c(z, t) \leq F(z, t)$ . Substituting in (32) we get (45).

□

The above lemmas provide us with an insight into the behavior of the solution. We summarize the main points as follows:

- For any fixed time  $t$ , the pore function  $\eta(z, t)$  is a monotonically increasing function (in  $z$ ), achieving the value  $\eta(0, t)$  (defined in (28)) at  $z = 0$ . The function  $\eta(z, t)$  for any time is bounded from above by the initial value  $\eta_0$ , and from below by (45).
- At the time  $t_\beta$  the solution becomes discontinuous. In fact integrating (22) between  $z = 0$  and  $z = 1$  we get

$$-f(\eta(0, t)) \frac{\partial c(z, t)}{\partial z} \Big|_{z=0} = \int_0^1 \alpha^2(t) \eta(\xi, t) c(\xi, t) d\xi \quad (46)$$

Since the RHS is positive  $\frac{\partial c(z, t)}{\partial z} \Big|_{z=0}$  must tend to infinity!!

- The concentration function  $c(z, t)$  is bounded from above by (44) and is *monotonically decreasing* as a function of  $z$  for any  $t$ . The derivative at  $z = 0$  is becoming more and more negative.
- The function  $\eta(z, t)$  is a decreasing function in time.

## 4 Optimization

After establishing the properties of the solutions, we turn to discuss the concept of a successful process. In CVI, it is generally desirable to produce a solid with a relatively uniform porosity distribution.

The process obviously terminates if  $\eta(0, t)$  is small, and we would like  $\eta(z, t)$  to be *uniformly* small, i.e. we do not want  $\eta(z, t)$  to have a large variation in space. Consider therefore the average of  $\epsilon$ :

**Definition:**

$$\bar{c}(t) = \int_0^1 \eta^2(\xi, t) d\xi \quad (47)$$

By a *successful process* we mean a process such that  $\bar{c}(t) \leq \bar{c}_f$  for a given target value  $\bar{c}_f$  for some  $t_f \leq t_\beta$ . We will show that for each target value  $\bar{c}_f$  there are functions  $\alpha(t), \beta(t)$  such that the process is successful. The question is how to pick  $\alpha(t), \beta(t)$  such that the final time  $t_f$  is minimal.

We start by observing

**Lemma 7**

Let  $\bar{c}(t)$  defined in (47). Then  $\bar{c}(t)$  is a monotonically decreasing function of  $t$ . Moreover

$$\frac{d\bar{c}(t)}{dt} = \frac{\beta(t)}{\alpha^2(t)} f(\eta(0, t)) \frac{\partial c(z, t)}{\partial z} \Big|_{z=0} \quad (48)$$

**Proof**

Upon differentiating  $\bar{c}(t)$  we get

$$\frac{d\bar{c}(t)}{dt} = 2 \int_0^1 \eta(\xi, t) \eta_t(\xi, t) \quad (49)$$

$$= -\beta(t) \int_0^1 \eta(\xi, t) c(\xi, t) d\xi \quad (50)$$

$$= -\frac{\beta(t)}{\alpha^2(t)} \int_0^1 \frac{\partial}{\partial z} \left( f(\eta(\xi, t)) \frac{\partial c(\xi, t)}{\partial z} \right) d\xi \quad (51)$$

$$= \frac{\beta(t)}{\alpha^2(t)} f(\eta(0, t)) \frac{\partial c(z, t)}{\partial z} \Big|_{z=0} \quad (52)$$

$$\leq 0 \quad (53)$$

For the first two steps we used the differential equations (21) and (22), the last step used the fact that  $c \frac{\partial c(z, t)}{\partial z}$  is negative (see Lemma 3 (31)).

□

Lemma 7 implies that the average concentration  $\bar{c}$  is decreasing in time for any parameters  $\alpha(t), \beta(t)$ . This however does not necessarily yield that the process is successful and that there is a time  $t_f \leq t_\beta$  in which  $\bar{c} \leq \bar{c}_f$ . We need a better estimate of  $\bar{c}$ . This is given in the next lemma.

**Lemma 8**

Let  $\bar{c}(t)$  be the concentration average defined in (47). The following estimation holds

$$\bar{\epsilon}(t) \leq \epsilon_0 - \int_0^t \frac{\beta(\tau)}{\alpha(\tau)} \sqrt{\eta(0, \tau) f(\eta(0, \tau))} \tanh \alpha(\tau) \sqrt{\frac{\eta(0, \tau)}{f(\eta(0, \tau))}} d\tau \quad (54)$$

where  $\eta(0, t)$  is given in (28).

**Proof**

Let

$$d(z, t) = \frac{\cosh \gamma_2 (1 - z)}{\cosh \gamma_2} \quad (55)$$

$$\gamma_2 = \sqrt{\frac{\eta(0, t)}{f(\eta(0, t))}} \alpha(t)$$

Clearly the function  $d(z, t)$  satisfies

$$\frac{\partial}{\partial z} \left( f(\eta(0, t)) \frac{\partial d(z, t)}{\partial z} \right) = \alpha^2(t) \eta(0, t) d(z, t) \quad (56)$$

$$d(0, t) = 1 \quad , \quad \frac{\partial d}{\partial z}(1, t) = 0 \quad (57)$$

We multiply now (22) by  $d(z, t)$ , (56) by  $c(z, t)$ , subtract and integrate between  $z = 0$  and  $z = 1$ . Taking the boundary conditions for  $c(z, t)$ ,  $d(z, t)$  into consideration we get:

$$\begin{aligned} -f(\eta(0, t)) \frac{\partial c(z, t)}{\partial z} \Big|_{z=0} + f(\eta(0, t)) \frac{\partial d(z, t)}{\partial z} \Big|_{z=0} &= \quad (58) \\ & \alpha^2(t) \int_0^1 (\eta(\xi, t) - \eta(0, t)) c(\xi, t) d(\xi, t) d\xi \\ & + \int_0^1 (f(\eta(\xi, t)) - f(\eta(0, t))) \frac{\partial c(\xi, t)}{\partial \xi} \frac{\partial d(\xi, t)}{\partial \xi} d\xi \end{aligned}$$

The right hand side of (58) is positive leading to

$$\frac{\partial c(z, t)}{\partial z} \Big|_{z=0} \leq \frac{\partial d(z, t)}{\partial z} \Big|_{z=0} \quad (59)$$

$$= -\gamma_2 \tanh(\gamma_2) \quad (60)$$

We turn now to (48) and integrate (in respect to the time  $t$ ) to get

$$\bar{\epsilon}(t) = \bar{\epsilon}_0 + \int_0^t \frac{\beta(\tau)}{\alpha^2(\tau)} f(\eta(0, \tau)) \frac{\partial c(z, \tau)}{\partial z} \Big|_{z=0} d\tau \quad (61)$$

Substituting (59) into (61) yields (54).

□

We will show now that for any target value  $\bar{\epsilon}_f$  there are functions  $\alpha(t)$  and  $\beta(t)$  such that the process is successful. In fact we will show that a successful process can be obtained by choosing time independent  $\alpha(t) = \alpha$  and  $\beta(t) = \beta$ . In this case (28) reads

$$\eta(0, t) = \eta_0 - \frac{1}{2}\beta t \quad (62)$$

and the terminal time is given by

$$t_\beta = \frac{2\eta_0}{\beta} \quad (63)$$

In the following Lemma we show that we can always choose  $\alpha$  small enough to have a successful process.

**Lemma 9**

Let  $\eta(z, t)$  be the solution of (21),(22) with fixed  $\alpha$  and  $\beta$ . Let  $\bar{\epsilon}$  be defined in (47). Then

$$\lim_{\alpha \rightarrow 0} \bar{\epsilon}\left(\frac{2\eta_0}{\beta}\right) = 0 \quad (64)$$

**Proof**

We start by using (54) for fixed  $\alpha$  and  $\beta$  and the expression (62) for  $\eta(0, t)$  to get

$$\bar{\epsilon}\left(\frac{2\eta_0}{\beta}\right) \leq \bar{\epsilon}_0 - \int_0^{\frac{2\eta_0}{\beta}} \beta \eta(0, \tau) \frac{\tanh(g(\tau, \alpha))}{g(\tau, \alpha)} d\tau \quad (65)$$

Where

$$g(t, \alpha) = \alpha(t) \sqrt{\frac{\eta(0, t)}{f(\eta(0, t))}} \quad (66)$$

We introduce now a change of variables

$$\xi = \frac{\beta \tau}{2\eta_0}$$

To get

$$\bar{\epsilon}\left(\frac{2\eta_0}{\beta}\right) \leq \bar{\epsilon}_0 - 2\eta_0^2 \int_0^1 (1 - \xi) \frac{\tanh(G(\xi, \alpha))}{G(\xi, \alpha)} d\xi \quad (67)$$

We use now the Lebesgue theorem and the fact that  $G(\xi, \alpha)$  tends to zero as  $\alpha$  tend to zero to conclude that

$$\lim_{\alpha \rightarrow 0} \bar{\epsilon}\left(\frac{2\eta_0}{\beta}\right) \leq \bar{\epsilon}_0 - 2\bar{\epsilon}_0 \int_0^1 (1 - \xi) d\xi = 0 \quad (68)$$

This proves the Lemma.



□

The parameters  $\alpha$  and  $\beta$  are not independent. In fact  $\beta$  is proportional to  $\alpha^2$  see (16). Thus if we choose these parameters as constants as in Lemma 9, the time needed for the completion of a successful process is very long. We would like to minimize that time. We therefore formulate the following minimization problem.

**Problem:**

Let  $\eta(z, t), c(z, t)$  be the solution of (21-25) for some  $\alpha(t), \beta(t)$ . Let the average concentration be defined in (47). Given a target concentration value  $\bar{\epsilon}_f$  we define the final time  $t_f(\alpha, \beta)$  as the first time such that

$$\bar{\epsilon}(t_f) \leq \bar{\epsilon}_f$$

**find**  $\min_{\alpha(t), \beta(t)} t_f(\alpha, \beta)$ .

We did not solve this optimization problem, however Lemma 9 provides us with some insight to the minimization process. In fact it is easier to treat the upper bound on the average concentration given in (54).

In the following we will show an example in which some savings in the time needed to reach the target value  $\bar{\epsilon}(t_f)$  is realized by choosing  $\alpha$  and  $\beta$  that are time dependent.

Consider the special case

$$\beta(t) = 2\alpha^2(t)$$

and

$$f(\eta) = \eta^3$$

This expression for  $f(\eta)$  corresponds to the case were  $N_k \ll 1$  and  $\theta = \eta^{-1}$ . Physically, the small value of  $N_k$  means that Knudsen diffusion contributions are not significant. As the porosity is filled by the matrix phase this assumption will invariably break down, however, with relatively large pressure and/or pore sizes,  $N_k$  will only become significant at the end of the process. In this case, the analysis presented below (i.e., where  $N_k$  was ignored) will be reasonably accurate.

In this case we may rewrite the estimate (54) for the average concentration in the form

$$\bar{\epsilon}(t) \leq \eta_0^2 - \int_0^t \beta(\tau) \eta(0, \tau) \frac{\tanh \gamma_2}{\gamma_2} d\tau \quad (69)$$

where

$$\gamma_2(t) = \frac{\alpha(t)}{\eta(0, t)}$$

and the pore function  $\eta(0, t)$  is given in Lemma 2. From this Lemma we can deduce that

$$\beta = -2 \frac{d}{dt} \eta(0, t) \quad (70)$$

We will look now for a design function  $\alpha(t)$  such that  $\gamma_2$  is independent of time. This leads to an explicit expression for  $\alpha(t)$ , in fact solving

$$\frac{\alpha^2(t)}{\eta(0, t)^2} = R^2$$

and taking into account that

$$\alpha^2(t) = -\frac{d}{dt} \eta(0, t)$$

we get

$$\eta(0, t) = \frac{\eta_0}{1 + \eta_0 R^2 t} \quad (71)$$

$$\alpha(t) = \frac{|R| \eta_0}{1 + \eta_0 R^2 t} \quad (72)$$

We can now substitute the result in (69) to get

$$\bar{\epsilon}(t) \leq \eta_0^2 - \frac{\tanh \gamma_2}{\gamma_2} \left( \frac{|R| \eta_0^2}{(1 + \eta_0 R^2 t)^2} - \eta_0^2 \right) \quad (73)$$

The parameter  $R$  can be chosen to minimize the time needed for  $\bar{\epsilon}(t)$  to be less than the target value. This approach leads to some savings, as described below.

## 5 Numerical Results

We have solved numerically the following set of equations

$$\left( \eta^3 c_z \right)_z + \alpha^2 \eta c = 0 \quad (74)$$

$$\eta_t = -\beta c \quad (75)$$

subject to the initial condition

$$\eta(z, 0) = 1 \quad (76)$$

and boundary conditions

$$c(0, t) = 1 \quad c_z(1, t) = 0 \quad (77)$$

To discretize (74) we used the pseudospectral Chebyshev method. In this method we choose the grid points to be

$$x_j = \frac{1 + \cos\left(\frac{\pi j}{N}\right)}{2} \quad 0 \leq j \leq N \quad (78)$$

$N$  is the total number of grid points.

The spectral differentiation matrix takes the value of a given function at the gridpoints  $x_j$  and yields the values of the derivative of the interpolation polynomial at these points. The points  $x_j$  are the nodes of the Gauss Lobatto Chebyshev quadrature formula. The matrix can be written explicitly:

$$\begin{aligned} D_{jk} &= \frac{1}{2} \frac{c_j}{c_k} \frac{(-1)^{j+k}}{\sin \frac{\pi}{2N}(j+k) \sin \frac{\pi}{2N}(-j+k)} & j \neq k, \\ D_{jj} &= -\frac{1}{2} \frac{x_j}{\sin^2(\frac{\pi}{N}j)} & j \neq 0, N, \\ D_{00} &= -D_{NN} = \frac{2N^2+1}{6} \end{aligned} \quad (79)$$

We apply the matrix  $D_{jk}$  twice, once for the vector  $c$  taking into account the boundary condition  $c(0, t) = 1$  and then to  $\eta^3 c_z$  now taking into account that  $c_z(1, t) = 0$ . This yields a linear system for the values of  $c(x_j, t)$ .

In the next stage we update  $\eta$  by the standard fourth order Runge-Kutta scheme.

- We first ran the scheme with constant  $\alpha$  ( $\beta = \alpha^2$ ) with the requirements that the process stops when  $\bar{\epsilon}$  is less than 5% of the original value, and also that  $\epsilon(1, t)$  will be less than 8%. The largest  $\alpha$  (and therefore the shortest time to reach the end of the process) that satisfied the conditions was  $\alpha = .235$ . The total time needed for the process to settle was

$$t_{f1} = \frac{2.458}{\beta(0)}$$

- We then used formula (72) to choose  $\alpha(t)$  where  $\alpha(0) = .3$ . Again  $\beta(t) = \alpha^2(t)$ . The process terminated successfully at time

$$t_{f2} = .963t_{f1}$$

- A better strategy was to use (72) until  $\alpha$  became smaller than .25 and then to raise it to .27 and reapply (72). Here too  $\beta(t) = \alpha^2(t)$ . The process terminated here at

$$t_{f3} = .935t_{f1}$$

Whereas the savings do not seem extremely significant, they indicate that one can get better results by varying the design parameters  $\alpha$  and  $\beta$  with time.

- Another possibility is to change the relationship between  $\alpha$  and  $\beta$  in time. This is motivated by Lemma 9. It is clear from this Lemma that for the process to converge we need  $\alpha$  small. It is also clear that the time for the process to settle is proportional to  $(\beta)^{-1}$ , thus one wants to minimize  $\alpha$  to get a successful process and to maximize  $\beta$

to reduce time. We ran our problem with  $\alpha(0) = .4$  and  $\beta(0) = \alpha^2(0)$ . We then varied  $\alpha$  in time according to (72) while holding  $\beta$  fixed. We got convergence at

$$t_{f4} = .397t_{f1}!!!$$

(the final  $\alpha$  was .2). This result indicates that great savings can be obtained by choosing appropriate values for the design functions  $\alpha(t)$  and  $\beta(t)$ .

## 6 Conclusions

In summary, the mathematical results presented here are potentially important in several ways. First they provide detailed information on the solutions in space and in time, as well as upper and lower bounds. The formulation and general analysis provide a basis for understanding the infiltration process in terms of only two parameters:  $\alpha$  and  $\beta$ . The treatment of the optimization problem makes it possible to assess optimal (i.e. minimal) infiltration times concisely. The observation that the minimum time can be dramatically decreased by varying  $\alpha$  with time is particularly important because of the long times that are typically associated with CVI. Varying  $\alpha$  while  $\beta$  is constant requires varying one or more of the relevant processing conditions (e.g.,  $T$ ,  $Cr$ , or  $P$ ) in a controlled way. A detailed analysis of these possibilities will be presented elsewhere ([12]).

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