Temperature driven mass transport in concentrated saturated solutions*

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Abstract

We study the phenomenon of thermally induced mass transport in partially saturated solutions under a thermal gradient, accompanied by deposition of the solid segregated phase on the "cold" boundary. We formulate a one-dimensional model including the displacement of all species (solvent, solute and segregated phase) and we analyze a typical case establishing existence and uniqueness.

1 Introduction

It is well known that saturation of a solution of a solute S in a solvent Σ is achieved at some concentration c_S depending on temperature T. Typically c_S is a smooth function of T such that $c'_S(T) > 0$. Therefore, if one excludes supersaturation, it is possible to produce the following facts by acting on the thermal field:

(i) cooling a solution of concentration c^* to a temperature T such that $c^* > c_S(T)$, segregation of the substance S is produced as a solid phase, typically in the form of suspended crystals,

(ii) maintaining a thermal gradient in a saturated solution creates a concentration gradient of the solute inducing diffusion.

These phenomena are believed to be the most important origin of the formation of a deposit of solid wax on the pipe wall during the transportation of mineral oils with a high content of heavy hydrocarbons (waxy crude oils) in the presence of significant heat loss to the surroundings (see the survey paper [1]).

In the paper [2] we have illustrated some general features of the behaviour of non-isothermal saturated solutions in bounded domains, including the appearance of an unsaturated region and the deposition of solid matter at the boundary.

The analysis of [2] was based on the following simplifying assumptions:

(a) the three components of the system, namely the solute, the solvent and the segregated phase, have the same density (supposed constant in the range of temperature considered),

(b) the concentrations of the solute and of the segregated phase are small in comparison with the concentration of the solvent.

The consequences of (a) are that gravity has no effect and that the segregation/dissolution process does not change volume.

The consequences of (b) are that solvent can be considered immobile and that the presence of a growing solid deposit has a negligible effect on the mass transport process.

For the specific application to waxy crude oil assumption (a) is reasonable on the basis of experimental evidence, but assumption (b) may not be realistic. Of course eliminating (b) leads to a much more complex situation.

For this reason we want to formulate a new model in which, differently from [2], the displacement of all the components is taken into account, as well as the influence of the growing deposit on the whole process.

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In order to be able to perform some mathematical analysis of the problem and to obtain some qualitative results we confine our attention to the one-dimensional case, considering a system confined in the slab $0 < x < L$. Of course the results can be adapted with minor changes to a region bounded by coaxial cylinders (the geometry of some laboratory device devoted to the measure of thickness of deposit layers formed under controlled temperature gradients).

The general features of the model are presented in Sect. 2. In Sect. 3 we consider a specific experimental condition in which we pass through three stages: at time $t = 0$ the system is totally saturated with the segregated phase present everywhere, next a desaturation front appears and eventually the saturated zone becomes extinct. The rest of the paper is devoted to the study of the three stages, showing existence and uniqueness and obtaining some qualitative properties.

2 Description of physical system and the governing differential equations

During the evolution of the process we are going to study we can find a saturated and an unsaturated region. Supposing that at any point and at any time the segregated phase is in equilibrium with the solution, there will be no solid component in the unsaturated region. We recall that all the components have the same density ρ, whose dependence on temperature is neglected.

The saturated region is a two-phase system:

- The solid phase is the segregated material. It is made of suspended particles (crystals) having some mobility. We denote its concentration by $\hat{G}(x, t)$
- The liquid phase is a saturated solution. Its concentration in the whole system is $\hat{\Gamma}(x, t)$.

In turn, the solution is a two-component system containing

- the solute with concentration $\hat{c}$ (mass of solute per unit volume of the system)
- the solvent with concentration $\hat{\gamma}$ (mass of solvent per unit volume of the system).

In the sequel we will use the nondimensional quantities

$$G = \hat{G}/\rho, \ \ \Gamma = \hat{\Gamma}/\rho, \ \ c = \hat{c}/\rho, \ \ \gamma = \hat{\gamma}/\rho.$$

Clearly

$$\Gamma = \gamma + c \tag{2.1}$$

$$G + \Gamma = 1 \tag{2.2}$$

We can also introduce the relative nondimensional concentrations (mass of solute and of solvent per unit mass of the solution)

$$c_{rel} = c/\Gamma \quad \gamma_{rel} = \gamma/\Gamma. \tag{2.3}$$

As we pointed out, saturated region is characterized by the fact that $c_{rel} = c_S(T)$ where the latter quantity is the saturation concentration and depends on the local temperature T only.

On $c_S(T)$ we make the following assumption:

$$(H1) \qquad\qquad c_S \in C^3, \ \ c_S' > 0$$

in a temperature interval $[T_1, T_2]$.

Displacement of the various components is generated by spatial dishomogeneity.

Let J_G, J_Γ be the fluxes of segregated solid and of solution, respectively, in a saturated region.

Let Q be the mass passing, per unit time and per unit volume (rescaled by ρ), from segregated to dissolved phase. Then we have the balance equations

$$\frac{\partial G}{\partial t} + \frac{\partial J_G}{\partial x} = -Q, \tag{2.4}$$

$$\frac{\partial \Gamma}{\partial t} + \frac{\partial J_\Gamma}{\partial x} = Q. \tag{2.5}$$

From (2.2) it follows that

$$\frac{\partial}{\partial x}(J_G + J_\Gamma) = 0, \tag{2.6}$$

expressing bulk volume conservation and implying

$$J_G + J_\Gamma = 0 \tag{2.7}$$

if there is no global mass exchange with the exterior, as we suppose.

At this point we do not take the general view point of mixture theory, but we make the assumption that G is transported by diffusion. Thus

$$J_G = -D_G \frac{\partial G}{\partial x}, \tag{2.8}$$

where D_G is the diffusivity coefficient for the segregated phase.

We notice that (2.8) is consistent with the fact that all the components of the system have the same density, so that we may say that suspended particles do not feel internal rearrangements of the solution components.

Next we have to describe the flow of the components in the solution, and denote by J_γ and J_c the flux of solvent and of solute, respectively. Of course

$$J_\Gamma = J_\gamma + J_c. \tag{2.9}$$

Here too we take a simplification supposing that the solute flow J'_c relative to the solution is of Fickian type, i.e.

$$J'_c = -D \frac{\partial c_{rel}}{\partial x}, \tag{2.10}$$

where $D > D_G$ is the solute diffusivity so that in the saturated region J'_c is a given function of the thermal gradient.

The flux J_c is the sum of $\Gamma J'_c$ and of the convective flux due to the motion of the solution. Introducing the velocity of the solution

$$V_\Gamma = J_\Gamma / \Gamma \tag{2.11}$$

we have

$$J_c = c V_\Gamma + \Gamma J'_c = c_{rel} J_\Gamma + \Gamma J'_c \tag{2.12}$$

Consequently we have the following expression for J_c for the saturated and unsaturated case (still retaining the basic assumption of absence of bulk mass transfer, (2.7))

$$J_c = c_S D_G \frac{\partial G}{\partial x} - (1-G) D \frac{\partial c_S}{\partial x}, \quad \text{for the saturated case} \tag{2.13}$$

$$J_c = -D \frac{\partial c_{rel}}{\partial x} = -D \frac{\partial c}{\partial x}, \quad \text{for the unsaturated case } (G = 0) \tag{2.14}$$

At this point we can write the balance equation for the solute

$$\frac{\partial c}{\partial t} + \frac{\partial J_c}{\partial x} = Q. \tag{2.15}$$

While for the unsaturated case, (2.15) is nothing but

$$\frac{\partial c}{\partial t} - D \frac{\partial^2 c}{\partial x^2} = 0 \tag{2.16}$$

in the saturated case we have $c = c_S(T)(1-G)$ and hence

$$-c_S \frac{\partial G}{\partial t} + \frac{\partial}{\partial x}\{c_S D_G \frac{\partial G}{\partial x} - (1-G) D \frac{\partial c_S}{\partial x}\} = Q, \tag{2.17}$$

which provides the expression of Q. Thus (2.4) takes the form

$$\frac{\partial G}{\partial t} - D_G \frac{\partial^2 G}{\partial x^2} + \frac{1}{1 - c_S}\{(D_G + D)\frac{\partial c_S}{\partial x}\frac{\partial G}{\partial x} - (1 - G)D\frac{\partial^2 c_S}{\partial x^2}\} = 0 \tag{2.18}$$

It is also convenient to observe that from $\gamma + c + G = 1$ and $c = c_S(1 - G)$ we obtain

$$\gamma = (1 - c_S)(1 - G), \tag{2.19}$$

from which using (2.7), (2.9), (2.13) we deduce the expression

$$J_\gamma = -D_G \frac{\partial \gamma}{\partial x} + (D - D_G)\frac{\gamma}{1 - c_S}\frac{\partial c_S}{\partial x} \tag{2.20}$$

We are interested in the case in which T is a linear function of x independent of time:

$$T = T_1 + (T_2 - T_1)\frac{x}{L} \tag{2.21}$$

where the boundary temperatures T_1, T_2 (with $T_1 < T_2$) are given in such a way that a saturation phase is present, at least for some time.

Remark 1 *The assumption that temperature has the equilibrium profile (2.21) is acceptable if heat diffusivity is much larger than D (which is certainly true), so that thermal equilibrium is achieved before any significant mass transport takes place, and if we may neglect the amount of heat that is released or absorbed during the segregation/dissolution process. In the specific case of waxy crude oils it can be seen that the latter assumption is fulfilled (the influence of latent heat associated to deposition is likewise negligible).*

3 Modelling a specific mass transport process with deposition

We restrict our analysis to the following process, easily reproducible in a laboratory device.

We start with a solution at uniform concentration $\hat{c}^*(< \rho)$ and uniform temperature T^* with $\hat{c}^*$ below saturation. Then we cool the system rapidly to the temperature profile (2.21) in such a way that $c^* = \hat{c}^*/\rho > c_S(T_2)$, so that the whole system becomes saturated with a (nondimensional) concentration

$$G_0(x) = c^* - c_S(T(x))(1 - G_0(x)) \tag{3.1}$$

of segregated phase, with

$$c_0(x) = c_S(T(x))(1 - G_0(x)) \tag{3.2}$$

being the corresponding concentration of the solute.

These will be our initial conditions. Starting from $t = 0$ the system will evolve through the following stages.

STAGE 1. $G > 0$ throughout the system

The mass flow towards the cold wall $x = 0$ produced by the gradient of $c_S(T(x))$ generates various phenomena:

- the solute mass leaving the warm wall $x = L$ has to be replaced by the segregated phase,
- mass exchange occurs between the solid and the liquid phase, as described in the previous section,
- the solute mass liberated at the cold wall has to be segregated: a fraction $\chi \in (0, 1]$ of it is used to build up a deposit layer, while the complementary fraction $1 - \chi$ is released in the form of suspension.

As we shall see, this stage terminates at a finite time t_1.

STAGE 2. The measures of the sets $\{G > 0\}, \{G = 0\}$ are both positive

At time t_1 an unsaturated region appears. This stage is characterized by the simultaneous presence of saturated and unsaturated regions (not necessarily connected for general initial data), separated by one or more free boundaries. Also Stage 2 has to terminate at a finite time t_2, when G becomes zero everywhere.

STAGE 3. The whole system is unsaturated

Deposition goes on as long as $c = c_S$ and $\frac{\partial c}{\partial x} > 0$ on the deposition front.

Remark 2 *The asymptotic equilibrium is characterized by the absence of segregated phase and uniform solute concentration $c_S(\sigma_\infty)$, where σ_∞ denotes the nondimensional asymptotic thickness of the deposit. Therefore we can write the trivial mass balance*

$$\sigma_\infty + (1 - \sigma_\infty) c_S(\sigma_\infty) = c^*$$

Since the l.h.s. is a function of σ_∞ increasing from $c_S(0) < c^*$ for $\sigma_\infty = 0$ to $1 > c^*$ for $\sigma_\infty = 1$, there exists one and only one solution $\sigma_\infty \in (0, 1)$.

We have to write down the boundary conditions for the three stages.

However, before doing that, we introduce the nondimensional variables:

$$\xi = x/L, \;\; \tau = t/t_D, \;\; \delta = D_G/D < 1, \;\; \theta = \frac{T - T_1}{T_2 - T_1}$$

with $t_D = L^2/D$.

For simplicity we keep the symbols $G(\xi,\tau), \Gamma(\xi,\tau), c(\xi,\tau)$ and $c_S(\theta(\xi))$. Note that $\frac{dc_S}{d\xi} = c_S'(\theta), \frac{d^2 c_S}{d\xi^2} = c_S''(\theta)$, since $\theta(\xi) = \xi$.

With the new variables equations (2.18), (2.16) take the form

$$\frac{\partial G}{\partial \tau} - \delta \frac{\partial^2 G}{\partial \xi^2} + \frac{1}{1 - c_S} \{(1 + \delta) c_S'(\theta) \frac{\partial G}{\partial \xi} - (1 - G) c_S''(\theta)\} = 0, \tag{3.3}$$

$$\frac{\partial c}{\partial \tau} - \frac{\partial^2 c}{\partial \xi^2} = 0. \tag{3.4}$$

BOUNDARY CONDITIONS FOR STAGE 1

During Stage 1 equation (3.3) must be solved in the domain $D_1 = \{(\xi,\tau) | \sigma(\tau) < \xi < 1, 0 < \tau < \tau_1\}$, where $\xi = \sigma(\tau)$ is the deposition front, with initial conditions

$$\sigma(0) = 0, \;\; G_0(\xi) = \frac{c^* - c_S(\xi)}{1 - c_S(\xi)}, \xi \in (0, 1). \tag{3.5}$$

At the boundary $\xi = 1$ we just have $J_\gamma = 0$, meaning

$$\delta \frac{\partial G}{\partial \xi}|_{\xi=1} = -c_S'(1) \frac{1 - G}{1 - c_S(1)}, 0 < \tau < \tau_1. \tag{3.6}$$

Conditions on the deposition front depend on the way the deposit layer is built. As we said, the primary source of the deposit is a fraction $\chi \in (0, 1]$ of the incoming solute flux. In addition we expect that the advancing front can capture by adhesion a fraction $\eta \in [0,1]$ of the suspension it finds on its way (in [2] we just considered $\eta = 1$).

Therefore, with the adopted rescaling, the speed $\dfrac{d\sigma}{d\tau}$ is the sum of two terms

$$\frac{d\sigma}{d\tau} = \chi(1-G)c_S'(\sigma) + \eta\frac{d\sigma}{d\tau}G,$$

yielding

$$\frac{d\sigma}{d\tau} = \chi\frac{1-G}{1-\eta G}c_S'(\sigma), 0 < \tau < \tau_1. \tag{3.7}$$

The most obvious way of deriving the second condition on the deposition front is to impose that the solvent is displaced precisely with the speed $\dfrac{d\sigma}{d\tau}$.

In the original physical variables the solvent velocity is

$$v_\gamma = \frac{J_\Gamma - J_c}{\gamma} = \frac{D_G\dfrac{\partial G}{\partial x}(1-c_S) + (1-G)D\dfrac{\partial c_S}{\partial x}}{(1-G)(1-c_S)} \tag{3.8}$$

from which we deduce the desired condition

$$\frac{d\sigma}{d\tau} = \frac{1}{(1-G)(1-c_S(\sigma))}[\delta\frac{\partial G}{\partial \xi}(1-c_S) + c_S'(\sigma)(1-G)], 0 < \tau < \tau_1. \tag{3.9}$$

Eliminating $\dfrac{d\sigma}{d\tau}$ between (3.7) and (3.9) we obtain the equivalent equation

$$\frac{\delta}{1-G}\frac{\partial G}{\partial \xi}|_{\xi=\sigma(\tau)} = c_S'[\chi\frac{1-G}{1-\eta G} - \frac{1}{1-c_S}]|_{\xi=\sigma(\tau)} \tag{3.10}$$

For instance, when $\chi = \eta = 1$ (3.10) simply reduces to

$$\frac{\delta}{1-G}\frac{\partial G}{\partial \xi}|_{\xi=\sigma(\tau)} = -\frac{c_S(\sigma)}{1-c_S(\sigma)}c_S'(\sigma), \tag{3.11}$$

while for $\chi = 0$ (no deposition, i.e. $\dfrac{d\sigma}{d\tau} = 0$ from (3.7)) we find

$$\delta\frac{\partial G}{\partial \xi}|_{\xi=\sigma(\tau)} = -(1-G)\frac{c_S'(\sigma)}{1-c_S'(\sigma)}, 0 < \tau < \tau_1. \tag{3.12}$$

(irrespectively of η which cancels out, having no role).

Thus we have now the complete model for Stage 1, which can be summarized as follows:

PROBLEM 1 ($\eta \neq 1$)

Find the pair (σ, G) *satisfying the differential equation (3.3) in* D_1*, with initial conditions (3.5), boundary condition (3.6), and free boundary conditions (3.7), (3.10), all in the classical sense.*

For $\eta = 1$ condition (3.7) reduces to the o.d.e. $\dfrac{d\sigma}{d\tau} = \chi c_S'(\sigma)$ and consequently the motion of the deposition front becomes known. The problem is standard in that case.

BOUNDARY CONDITIONS FOR STAGE 2

Stage 2 differs from Stage 1 because of the simultaneous presence of a saturated and an unsaturated region, separated by a free boundary $\xi = s(\tau)$, which, in the specific case we refer to, is a curve starting from the point $(1, \tau_1)$, where $G(\xi, \tau)$ vanishes for the first time. We shall find sufficient conditions on c_S ensuring that $G(\xi, \tau_1) > 0$ for $\xi \in [\sigma(\tau_1), 1)$ and that the unsaturated region remains connected. We denote by τ_2 the transition time to Stage 3.

In the region $\{s(\tau) < \xi < 1, \tau_1 < \tau < \tau_2\}$, corresponding to concentration below saturation ($G = 0$, and hence $c_{rel} = c < c_S$), the governing equation is (3.4).

The wall $\xi = 1$ is a no-flux boundary, i.e.

$$\frac{\partial c}{\partial \xi}|_{\xi=1} = 0, \tau_1 < \tau < \tau_2, \tag{3.13}$$

implying of course that also $\frac{\partial \gamma}{\partial \xi}|_{\xi=1} = 0$.

On the desaturation front we have

$$G(s(\tau)^-, \tau) = 0 \tag{3.14}$$

which implies that the absolute solute concentration equals $c_S(s(\tau))$ on both sides of the front:

$$c(s(\tau)+, \tau) = c_S(s(\tau)). \tag{3.15}$$

Continuity of (all) concentrations across the front implies in turn that the total solvent flux has to be continuous, or equivalently that

$$(\delta(1 - c_S)\frac{\partial G}{\partial \xi} + \frac{\partial c_S}{\partial \xi})|_{\xi=s(\tau)-} = \frac{\partial c}{\partial \xi}|_{\xi=s(\tau)+}, \tau_1 < \tau < \tau_2. \tag{3.16}$$

The model for Stage 2 is completed by the conditions

$$G(\xi, \tau_{1+}) = G_1(\xi), \sigma(\tau_1) < \xi < 1, \;\; s(\tau_1) = 1 \tag{3.17}$$

where $G_1(\xi) = G(\xi, \tau_1-)$.

Thus we can state

PROBLEM 2

Find the functions (σ, s, G, c) such that σ, G satisfy (3.3), (3.7), (3.10), (3.17), and s, G, c satisfy (3.4), (3.13)-(3.16), all in the classical sense.

BOUNDARY CONDITIONS FOR STAGE 3

At time τ_2 the saturated region disappears, i.e. $\sigma(\tau_2) = s(\tau_2)$ (we are still referring to the particular case in which the unsaturated region during Stage 2 is connected). From that time on deposition continues as long as $c(\sigma, \tau) = c_S(\sigma), \frac{\partial c}{\partial \xi}|_{\xi=\sigma(\tau)} > 0$ and necessarily all the incoming mass enters the deposit, irrespectively of the value of χ during Stage 2. Therefore the new conditions on the deposition front are

$$c(\sigma(\tau), \tau) = c_S(\sigma(\tau)), \quad \tau > \tau_2 \tag{3.18}$$

$$\frac{d\sigma}{d\tau} = \frac{\partial c}{\partial \xi}|_{\xi=\sigma(\tau)}, \quad \tau > \tau_2 \tag{3.19}$$

Of course $c(\xi, \tau)$ satisfies (3.13) with initial condition

$$c(\xi, \tau_{2+}) = c_2(\xi), \quad \sigma(\tau_2) < \xi < 1, \tag{3.20}$$

with $c_2(\xi) = c(\xi, \tau_2-)$.

Thus during this stage we have to solve

PROBLEM 3

Find (σ, c) satisfying (3.4), (3.13), (3.18)-(3.20) in the classical sense.

4 Analysis of Stage 1

The overall mass balance during Stage 1 can be expressed by imposing that the solvent mass is conserved, starting from the equation

$$\frac{\partial \gamma}{\partial t} + \frac{\partial J_\gamma}{\partial x} = 0 \tag{4.1}$$

and remembering that $J_\gamma = J_\Gamma - J_c = D_G(1-c_S)\frac{\partial G}{\partial x} + D(1-G)\frac{\partial c_S}{\partial x}$, so that in nondimensional variables we have

$$\frac{\partial \gamma}{\partial \tau} + \frac{\partial}{\partial \xi}\{\delta(1-c_S)\frac{\partial G}{\partial \xi} + (1-G)c_S'(\theta)\} = 0. \tag{4.2}$$

Since $G = 1 - \frac{\gamma}{1-c_s}$, it is easily seen that the equation above is equivalent to

$$\frac{\partial \gamma}{\partial \tau} - \delta\frac{\partial^2 \gamma}{\partial \xi^2} + (1-\delta)\frac{\partial}{\partial \xi}(\frac{\gamma c_S'}{1-c_S}) = 0 \tag{4.3}$$

Integrating (4.2) over any domain $D_\tau = \{(\xi,\tau')|\sigma(\tau') < \xi < 1, 0 < \tau' < \tau\}$, with $\tau \le \tau_1$, we get

$$\oint_{\partial D\tau}\{\gamma d\xi - [\delta(1-c_S)\frac{\partial G}{\partial \xi} + (1-G)c_S'(\theta)]d\tau'\} = 0, \tag{4.4}$$

simply expressing $\oint_{\partial D\tau}\{\gamma d\xi - J_\gamma d\tau\} = 0$.

Since $J_\gamma = 0$ on $\xi = 1$, $J_\gamma = \gamma\dot{\sigma}$ on $\xi = \sigma(\tau)$, we obtain

$$\int_{\sigma(\tau)}^1 \gamma(\xi,\tau)d\xi = \int_0^1 (1-c_s)(1-G_0)d\xi,$$

as expected, which can also be written as

$$\int_{\sigma(\tau)}^1 [G(\xi,\tau) + c(\xi,\tau)]d\xi = c^* - \sigma(\tau) \tag{4.5}$$

having an evident physical meaning.

Remark 3 *For $\eta = 1$ (complete inclusion of the suspended phase) (3.7) simplifies to*

$$\frac{d\sigma}{dc} = \chi c_S'(\theta(\sigma)) \tag{4.6}$$

which can be integrated. In this case the deposition front becomes a known function $\sigma^{(1)}(t)$. If we can establish an a priori upper bound $G_{max} < 1$ for G, the factor $\frac{1-G}{1-\eta G}$ takes values in $[\frac{1-G_{max}}{1-\eta G_{max}}, 1]$. Denoting by $\sigma^{(\eta)}$ the integral of $\frac{d\sigma}{d\tau} = \chi\frac{1-G_{max}}{1-\eta G_{max}}c_S'(\theta(\sigma))$ with zero initial value, we have the a-priori bounds

$$\sigma^{(\eta)}(\tau) \le \sigma(\tau) \le \sigma^{(1)}(\tau) \text{ for } \tau \in (0,\tau_1). \tag{4.7}$$

Proposition 1 *The extinction time τ_1 of Stage 1 is finite. An upper estimate is given by the solution τ^* of*

$$\sigma^{(\eta)}(\tau^*) = \sigma_\infty \tag{4.8}$$

Proof. Simply use the inequality (4.7) and Remark 2.

□

Let us show that G never reaches 1, thus preventing the formation of a solid layer inside the system. To assumption (H1) on c_S we add

$$(H2) \qquad c_S'' \le 0.$$

Proposition 2 *Under assumptions (H1), (H2) during Stage 1 we have* $G < 1$ *in* D_1.

Proof. We know that $0 < G_0 < 1$, so it will be $G < 1$ at least for some time. Moreover $G > 0$ by definition. Moving the term $(1 - G)c''_S(\theta)/(1 - c_S)$ to the r.h.s. of (3.3) we see that it is nonpositive, thanks to (H2). Thus G has to take its maximum on the parabolic boundary of D_1. From (3.6) we see that, still for $G < 1$, we have $\frac{\partial G}{\partial \xi} < 0$ on $\xi = 1$.

On the boundary $\xi = \sigma(\tau)$ (as long as $G < 1$) we see that for $\eta = 1$

$$\frac{\delta}{1-G}\frac{\partial G}{\partial \xi} = -c'_S(\frac{1}{1-c_S} - \chi) < 0, \ \ \forall \chi \in [0, 1].$$

Thus $\frac{\partial G}{\partial \xi} < 0$ for $\eta \in (0, 1)$ too because the r.h.s. of (3.10) is monotone in η.

We conclude that the maximum of G can be taken on $\xi = \sigma(\tau)$. However, if G tends to 1 there, $\frac{\partial G}{\partial \xi}$ tends to zero contradicting the boundary point principle for equation (3.3).

□

Since in our case we start with $G'_0 < 0$, we can have G monotone in ξ if we add the assumption

$$(H3) \ \ (\frac{c''_s}{1-c_S})' \leq 0.$$

Proposition 3 *Under assumptions (H1)-(H3) we have* $\frac{\partial G}{\partial \xi} < 0$ *during Stage 1.*

Proof. Set $\omega = \frac{\partial G}{\partial \xi}$. In the previous proposition we have seen that $\frac{\partial G}{\partial \xi} < 0$ on the lateral boundaries. Moreover

$$G'_0 = -c'_S\frac{1-c^*}{(1-c_S)^2} < 0 \tag{4.9}$$

Differentiating (3.3) w.r.t. ξ we obtain

$$\frac{\partial \omega}{\partial \tau} - \delta\frac{\partial^2 \omega}{\partial \xi^2} + \frac{1+\delta}{1-c_S}c'_S\frac{\partial \omega}{\partial \xi} + \omega\{\frac{c''_S}{1-c_S}(2+\delta) + \frac{1+\delta}{(1-c_S)^2}c'^2_S\} = (1-G)(\frac{c''_S}{1-c_S})', \tag{4.10}$$

from which the thesis follows easily using the maximum principle and assumption (H3).

□

Remark 4 *An important consequence of the proposition above is that*

$$G(\xi, \tau_1) > 0 \ \text{ for } \ \xi \in [\sigma(\tau_1), 1), \tag{4.11}$$

in other words the desaturation front starts from the point $(1, \tau_1)$.

We conclude this section by proving existence and uniqueness of the solution to Problem 1.

Theorem 1 *Problem 1 has one unique solution under the assumptions (H1), (H2).*

Proof. We start by noting that from (3.7) we have the obvious a priori estimate

$$0 \leq \frac{d\sigma}{d\tau} \leq \chi||c'_s|| =: A, \tag{4.12}$$

$||c'_s||$ denoting the sup-norm (of course we recall that $0 < G < 1$).

□

Now, if we introduce the set

$$\Sigma = \{\sigma \in C^1([0,\tilde{\tau}]) | \sigma(0) = 0, 0 \le \dot{\sigma} \le A, \frac{|\dot{\sigma}(\tau) - \dot{\sigma}(\tau'')|}{|\tau' - \tau''|^{\alpha}} \le B\} \tag{4.13}$$

for some $B > 0$ and $\alpha \in (0, \frac{1}{2})$, and we take any $\sigma \in \Sigma$, we may formulate the problem consisting of equation (3.3), initial condition (3.5) and boundary conditions (3.6), (3.10). For the corresponding solution G of such a problem, whose existence and uniqueness can be proved by means of standard methods, it is not difficult to find $\tilde{\tau}$ such that $G > 0$ for $\tau \in (0, \tilde{\tau})$ irrespectively of the choice of σ in Σ. The inequality $G < 1$ can be established like in Prop. 2. Finally, working on the problem satisfied by $\omega = \frac{\partial G}{\partial \xi}$ we can easily find the bound

$$|\frac{\partial G}{\partial \xi}| \le B \tag{4.14}$$

with B independent of σ in Σ.

At this point existence can be proved using the following fixed point argument.

Taken $\sigma \in \Sigma$ and computing G we can define $\tilde{\sigma}$ via

$$\frac{d\tilde{\sigma}}{d\tau} = \chi \frac{1-G}{1-\eta G} c_s'(\sigma), \ \ \tilde{\sigma}(0) = 0, \tag{4.15}$$

which automatically satisfies $0 \le \frac{d\tilde{\sigma}}{d\tau} \le A$.

Noting that $|\frac{d}{dG}\frac{1-G}{1-\eta G}| \le \frac{1}{1-\eta}$ for $\eta < 1$ (while it just vanishes for $\eta = 1$, which however is not the interesting case) for a pair (σ_1, σ_2) of functions in Σ, we have the easy estimate

$$|\frac{d\tilde{\sigma}_1}{d\tau} - \frac{d\tilde{\sigma}_2}{d\tau}| \le \frac{A}{1-\eta} |G_1(\sigma_1(\tau), \tau) - G_2(\sigma_2(\tau), \tau)| + \chi ||c_s''|| \ |\sigma_1 - \sigma_2| \tag{4.16}$$

with obvious meaning of the symbols.

Therefore at this point we only need to show that $G(\sigma(t), t)$ depends in a Lipschitz continuous way on σ in the topology of Σ . More precisely, we want to show that

$$||G_1 - G_2||_{\tau} \le K_1 ||\sigma_1 - \sigma_2||_{\tau} + K_2 \int_0^{\tau} ||\dot{\sigma}_1 - \dot{\sigma}_2||_{\tau'} (\tau - \tau')^{-1/2} d\tau' \tag{4.17}$$

for some positive constants K_1, K_2, with $|| \cdot ||_{\tau}$ denoting the sup-norm restricted to the time interval $(0, \tau)$.

Now, $G(\xi, \tau)$ corresponding to a given $\sigma \in \Sigma$ has the representation

$$\begin{aligned} G(\xi,\tau) = & \int_0^{\tau} \phi(\tau')\Gamma(\xi,\tau;\sigma(\tau'),\tau')d\tau' + \\ & + \int_0^1 G_0(\xi')\Gamma(\xi,\tau;\xi',0)d\xi' + \int_0^{\tau} \psi(\tau')\Gamma(\xi,\tau;1,\tau')d\tau' + \\ & + \int_0^{\tau}\int_{\sigma(\tau')}^1 \Gamma(\xi,\tau;\xi',\tau')\frac{c_s''(\xi')}{1-c_s(\xi')}d\xi' d\tau', \end{aligned} \tag{4.18}$$

with $\Gamma(\xi, \tau; \xi', \tau')$ fundamental solution of the parabolic operator $L = \frac{\partial}{\partial \tau} - \delta \frac{\partial^2}{\partial \xi^2} + \frac{1+\delta}{1-c_s} c_s' \frac{\partial}{\partial \xi} + \frac{c_s''}{1-c_s'}$, with $\tau' < \tau$ and $(\xi, \tau), (\xi', \tau')$ varying in $[0,1] \times [0, \tilde{\tau}]$. The densities $\phi(\tau), \psi(\tau)$, together with a third unknown $G_{\sigma}(\tau)$, representing the value of G over $\xi = \sigma(\tau)$, satisfy the system

$$\frac{1}{2}\phi(\tau) = \int_0^{\tau} \phi(\tau')\Gamma_{\xi}(\sigma(\tau), \tau; \sigma(\tau'), \tau')d\tau' + \tag{4.19}$$

$$+\int_0^\tau \psi(\tau')\Gamma(\sigma(\tau),\tau;\,1,\tau')d\tau' + \int_0^1 G_0(\xi')\Gamma_\xi(\sigma(\tau),\tau,\xi',0)d\xi' +$$

$$+\int_0^\tau \int_{\sigma(\tau')}^1 \Gamma_\xi(\sigma(\tau),\tau;\xi',\tau')\frac{c_s''(\xi')}{1-c_s(\xi')}d\xi' d\tau' - \frac{1-G_\sigma(\tau)}{\delta}c_s'(\sigma)[\chi\frac{1-G_\sigma}{1-\eta G_\sigma} - \frac{1}{1-c_s(\sigma)}]$$

$$\frac{1}{2}\psi(\tau) = -\int_0^\tau \phi(\tau')\Gamma_\xi(1,\tau;\sigma(\tau'),\tau')d\tau' - \int_0^\tau \psi(\tau')\Gamma_\xi(1,\tau;1,\tau')d\tau' - \tag{4.20}$$

$$-\int_0^1 G_0(\xi')\Gamma_\xi(1,\tau;\xi',0)d\xi' - \int_0^\tau \int_{\sigma(\tau')}^1 \Gamma_\xi(1,\tau;\xi',\tau')\frac{c_s''(\xi')}{1-c_s(\xi')}d\xi' d\tau' - \frac{1}{\delta}\frac{c_s'(1)}{1-c_s(1)}G(1,\tau)$$

$$G_\sigma(\tau) = \int_0^\tau \phi(\tau')\Gamma(\sigma(\tau),\tau;\sigma(\tau'),\tau')d\tau' + \tag{4.21}$$

$$+\int_0^1 G_0(\xi')\Gamma(\sigma(\tau),\tau;\xi',0)d\xi' + \int_0^\tau \psi(\tau')\Gamma(\sigma(\tau),\tau;1,\tau')d\tau' +$$

$$+\int_0^\tau \int_{\sigma(\tau')}^1 \Gamma(\sigma(\tau),\tau;\xi',\tau')\frac{c_s''(\xi')}{1-c_s(\xi')}d\xi' d\tau',$$

where $G(1,\tau)$ in (4.20) must be replaced with expression obtained from (4.18).

Note that G_σ appears nonlinearly in (4.19) if $\eta < 1$, as we are supposing.

Eliminating G_σ leads to a nonlinear system of Volterra equations with weakly singular kernels. Existence and uniqueness can anyway be proved by standard methods, thanks to the fact that the dependence on G_σ in (4.19) is Lipschitz. Functions ϕ, ψ, G_σ are bounded uniformly for $\sigma \in \Sigma$ and as a consequence of (4.19)-(4.21) they are at least Hölder continuous of order $\frac{1}{2}$ with a Hölder norm uniformly bounded in Σ. In turn this implies that $\frac{\partial G}{\partial \xi}|_{\xi=\sigma(\tau)}$ has the same type of regularity.

Our task now is to estimate $|G_{\sigma_1} - G_{\sigma_2}|$. Introducing the functions ϕ_i, ψ_i corresponding to $\sigma_i, i = 1, 2$, from (4.21) we see that

$$|G_{\sigma_1}(\tau) - G_{\sigma_2}(\tau)| \le \int_0^\tau |\phi_1(\tau') - \phi_2(\tau')||\Gamma(\sigma_1(\tau),\tau;\sigma_1(\tau'),\tau')|d\tau' + \tag{4.22}$$

$$+\int_0^\tau |\psi_1(\tau') - \psi_2(\tau')||\Gamma(\sigma_1(\tau),\tau;\sigma_1(\tau');\tau')|d\tau' +$$

$$+M\int_0^\tau |\Gamma(\sigma_1(\tau),\tau;\sigma_1(\tau'),\tau') - \Gamma(\sigma_2(\tau),\tau;\sigma_2(\tau'),\tau')|d\tau' +$$

$$+N\{\int_0^\tau |\int_{\sigma_1(\tau)}^{\sigma_2(\tau')} \Gamma(\sigma_1(\tau),\tau;\xi',\tau')d\xi'|d\tau' +$$

$$+\int_0^\tau \int_{\sigma_2(\tau')}^1 |\Gamma(\sigma_1(\tau),\tau;\xi',\tau') - \Gamma(\sigma_2(\tau),\tau;\xi',\tau')|d\xi' d\tau'\}.$$

which has to be coupled with similar inequalities for $|\phi_1(\tau) - \phi_2(\tau)|$ and $|\psi_1(\tau) - \psi_2(\tau)|$.

According to the parametrix method [3] the function $\Gamma(\xi,\tau,\xi',\tau')$ is constructed as follows

$$\Gamma(\xi,\tau;\xi',\tau') = Z(\xi,\tau;\xi',\tau') + \int_{\tau'}^\tau \int_0^1 Z(\xi,\tau,\eta,\theta)\Phi(\eta,\theta;\xi',\tau')d\eta d\theta \tag{4.23}$$

where

$$Z(\xi,\tau;\xi',\tau') = \frac{1}{2\sqrt{\pi\delta(\tau-\tau')}}\exp[-\frac{(\xi-\xi')^2}{4\delta(\tau-\tau')}] \tag{4.24}$$

is the fundamental solution of the heat operator $\frac{\partial}{\partial\tau} - \delta\frac{\partial^2}{\partial\xi^2}$, and $\Phi(\xi,\tau;\xi',\tau')$ is the solution of the integral equation

$$\Phi(\xi,\tau;\xi',\tau') = LZ(\xi,\tau;\xi',\tau') + \int_{\tau'}^{\tau} LZ(\xi,\tau;\eta,\theta)\Phi(\eta,\theta;\xi',\tau')d\eta d\theta. \tag{4.25}$$

Since the operator L is particularly simple, we can calculate LZ explicitly:

$$LZ(\xi,\tau;\xi',\tau') = \{-\frac{1+\delta}{1-c_s}c_s'\frac{\xi-\xi'}{2\delta(\tau-\tau')} + \frac{c_s''}{1-c_s}\}Z(\xi,\tau;\xi',\tau'), \tag{4.26}$$

so that the development of the parametrix method is largely simplified.

In particular

$$|LZ(\xi,\tau;\xi',\tau')| \le \frac{const.}{(\tau-\tau')^{\mu}}\frac{1}{|\xi-\xi'|^{1-\mu}}, \quad \mu\in(\frac{1}{2},1) \tag{4.27}$$

so that the kernel in (4.26) is integrable. Moreover Φ is continuous, Hölder continuous w.r.t. the first argument, for $\tau' < \tau$.

When calculating the differences $\phi_1 - \phi_2$ or $\Gamma(\sigma_1(\tau),\tau;\sigma_1(\tau'),\tau') - \Gamma(\sigma_2(\tau),\tau;\sigma_2(\tau'),\tau')$ the main term which comes into play is

$$\Gamma_\xi(\sigma_1(\tau),\tau;\sigma_1(\tau'),\tau') - \Gamma_\xi(\sigma_2(\tau),\tau;\sigma_2(\tau'),\tau')$$

which in turn requires the computation of

$$\Omega(\tau,\tau') = Z_\xi(\sigma_1(\tau),\tau;\sigma_1(\tau'),\tau') - Z_\xi(\sigma_2(\tau),\tau;\sigma_2(\tau'),\tau') =$$

$$-\frac{\sigma_1(\tau)-\sigma_1(\tau')-[\sigma_2(\tau)-\sigma_2(\tau')]}{4\sqrt{\pi}[\delta(\tau-\tau')]^{3/2}}\exp[-\frac{(\sigma_1(\tau)-\sigma_1(\tau'))^2}{4\delta(\tau-\tau')}]$$

$$-\frac{\sigma_2(\tau)-\sigma_2(\tau')}{4\sqrt{\pi}[\delta(\tau-\tau')]^{3/2}}\{\exp[-\frac{(\sigma_1(\tau)-\sigma_1(\tau'))^2}{4\delta(\tau-\tau')}] - \exp[-\frac{(\sigma_2(\tau)-\sigma_2(\tau'))^2}{4\delta(\tau-\tau')}]\}$$

.

Writing

$$|\sigma_1(\tau)-\sigma_1(\tau')-[\sigma_2(\tau)-\sigma_2(\tau')]| = |\dot\sigma_1(\bar\tau)-\dot\sigma_2(\hat\tau)|(\tau-\tau')$$

with $\bar\tau,\hat\tau\in(\tau',\tau)$, and

$$|\exp[-\frac{(\sigma_1(\tau)-\sigma_1(\tau'))^2}{4\delta(\tau-\tau')}] - \exp[-\frac{(\sigma_2(\tau)-\sigma_2(\tau'))^2}{4\delta(\tau-\tau')}]| \le \frac{A}{2\delta}|\dot\sigma_1(\bar\tau)-\dot\sigma_2(\hat\tau)|(\tau-\tau'),$$

we obtain the estimate

$$|\Omega(\tau,\tau')| \le K\frac{||\dot\sigma_1-\dot\sigma_2||_\tau}{\sqrt{\tau-\tau'}} \tag{4.28}$$

where K is a constant independent of the choice of σ_1,σ_2 in Σ.

Similar computations can be performed for the other terms involved, leading to the desired estimate (4.17). Coupling (4.16) and (4.17) leads to the conclusion that the mapping $\sigma\to\tilde\sigma$ is contractive for $\tilde\tau$ sufficiently small in the selected topology.

By means of standard arguments we can infer existence and uniqueness (any solution has to belong to Σ) up to the first time G vanishes.

5 Analysis of Stage 2: a priori results

First we prove that mass balance is expressed by an equation similar to (4.5)

Proposition 4 *For all $\tau \in (\tau_1, \tau_2)$ we have*

$$\sigma(\tau) + \int_{\sigma(\tau)}^{s(\tau)} [G(\xi,\tau) + c(\xi,\tau)]d\xi + \int_{s(\tau)}^{1} c(\xi,\tau)d\xi = c^*, \text{ where } c = c_S(1-G). \tag{5.1}$$

Proof. Take the mass balance of the solvent separately in the domains $\sigma(\tau') < \xi < s(\tau')$, $\tau_1 < \tau' < \tau$; $s(\tau') < \xi < 1$, $\tau_1 < \tau' < \tau$, with $\tau \in (\tau_1, \tau_2)$.

Remembering that in the nondimensional form J_γ is expressed by $J_\gamma = \delta(1-c_s)G_\xi + (1-G)c_s'$ in the first domain and simply by $J_\gamma = \frac{\partial c}{\partial \xi}$ in the second domain, and using $J_\gamma = \gamma\dot{\sigma}$ on the deposition front, $J_\gamma = 0$ on $\xi = 1$, $G = 0$, $[\gamma] = [J_\gamma] = 0$ on the desaturation front, (5.1) easily follows by integration of $\frac{\partial \gamma}{\partial r} + \frac{\partial J_\gamma}{\partial \xi} = 0$.

□

Since Stage 2 is characterized by the presence of a saturated region, the same argument used in the proof of Prop. 1 leads to an analogous conclusion, i.e.

Proposition 5 *The extinction time τ_2 of Stage 2 is finite. Moreover $\tau_2 < \tau^*$ defined by (4.8).*

Likewise we can say that Prop. 2 ($G < 1$) is still valid. It is enough to recall that $G(\xi, \tau_1) < 1$ and that $\frac{\partial G}{\partial \xi} \leq 0$ on the desaturation front, owing to (3.17).

Clearly we can also extend Prop. 3 ($\frac{\partial G}{\partial \xi} < 0$), implying that the saturated region remains connected during Stage 2.

A peculiar feature of Stage 2 is that there cannot be the analog of a "mushy region", in the following sense

Proposition 6 *During Stage 2 the complement of the set $\{G > 0\}$ cannot contain an open set where $c \equiv c_s$.*

Proof. The differential equation to be satisfied in such a set should be (3.4), with $\frac{\partial c}{\partial \tau} = 0$. Thus the presence of such a region is compatible only with $c_s'' = 0$. Because of the analyticity with respect to ξ of the solution of (3.4), the unique continuation of c up to $\xi = 1$ is a function constant in time, linear and increasing in ξ, thus contradicting the boundary condition $\frac{\partial c}{\partial \xi} = 0$.

□

6 Analysis of Stage 2: weak formulation and existence

Clearly the nature of the free boundary conditions on the desaturation front, namely (3.14), (3.15), (3.16), is quite different from the conditions on the deposition front, which involve the free boundary velocity in an explicit way.

In order to prove existence the most convenient approach is to introduce a weak formulation, in which the desaturation front plays the role of a level set (the set of discontinuity of some coefficients).

The natural approach to a weak formulation seems to re-write the problem in terms of the solvent concentration γ.

We can identify the desaturation front with the level curve $\gamma = 1 - c_s(s)$.

We know that in nondimensional variables the current density of the solvent has the expression

$$j_\gamma = -\delta \frac{\partial \gamma}{\partial \xi} + (1-\delta)\frac{\gamma c_s'}{1-c_s}, \text{ for } \gamma < 1 - c_s \tag{6.1}$$

$$j_\gamma = -\frac{\partial \gamma}{\partial \xi} \;\; for \;\; \gamma > 1 - c_s \tag{6.2}$$

If we set

$$v = 1 - c_s - \gamma \tag{6.3}$$

and we define

$$A(v) = \{^{\delta \;\; for v>0 \;\; (where \;\; v \equiv G(1-c_s))}_{1 \;\; for v<0 \;\; (where \;\; v \equiv c - c_s)} \tag{6.4}$$

then the balance equation

$$\frac{\partial \gamma}{\partial \tau} + \frac{\partial j_\gamma}{\partial \xi} = 0 \tag{6.5}$$

can be written in the distributional sense in the whole domain $D_\sigma = \{(\xi, r) : \sigma(\tau) < \xi < 1, \;\; \tau_1 < \tau < \bar{\tau}\}$:

$$\frac{\partial v}{\partial r} - \frac{\partial}{\partial \xi}\{A(v)\frac{\partial v}{\partial \xi} - [1 - A(v)]v\frac{c_s'}{1 - c_s}\} = c_s'' \tag{6.6}$$

Here $\bar{\tau}$ is a time instant sufficiently close to τ_1, still to be specified.

Equation (6.6) includes the free boundary conditions, that in the classical statements are

$$v = 0 \;\; on \;\; both \;\; sides \;\; of \;\; x = s(t) \tag{6.7}$$

$$[j_\gamma] = 0. \tag{6.8}$$

The latter condition, taking into account (6.7), reduces to

$$[A(v)\frac{\partial v}{\partial \xi}] = 0. \tag{6.9}$$

Thus, regarding the boundary $\xi = \sigma(\tau)$ as known, which is true for $\eta = 1$, the weak formulation of the problem for v is: find $v \in V^{1,0}(D_\sigma)$ such that

$$\begin{aligned} &\int_{D_\sigma} \{[A(v)\frac{\partial v}{\partial \xi} - (1 - A(v))v\frac{c_s'}{1 - c_s} + c_s']\frac{\partial \phi}{\partial \xi} - v\frac{\partial \phi}{\partial \tau}\}d\xi d\tau - \\ &- \int_0^{\prime} v(\xi, \tau_1)\phi(\xi, \tau_1)d\xi + \int_{\tau_1}^{\bar{\tau}} \phi(\sigma(\tau), \tau)\chi c_s' \frac{1 - v}{1 - \eta v}(1 - c_s)|_{\xi = \sigma(\tau)} dr \end{aligned} \tag{6.10}$$

$\forall \phi \in W_2^{1,1}(D_\sigma)$ such that $\phi = 0$ for $\tau = \bar{\tau}$. The notation of functional spaces is taken from [4].

(For the formulation of a similar problem in a cylindrical domain see [4], Chap. 3, Sect. 5). Existence and uniqueness can be established as in Theorem 5.1, p. 170 of [4].

At this point we can use Theorem 10.1, p. 204, of [4], ensuring that v is Hölder continuous, uniformly with respect to σ in the same class Σ used in the fixed point argument of Sect. 4, in a closed domain separated from σ and including an interval $[\xi_0, \xi_1] \subset (0, 1)$ for $\tau = \tau_1$, where we know that v is separated from zero.

Let $\Xi \in (\xi_0, \xi_1)$. On the basis of the above Hölder estimate we can find $\tilde{\tau}$ such that $v(\Xi, \tau) \geq \frac{1}{2} v(\Xi, \tau_1)$ for $\tau \in [\tau_1, \tilde{\tau}]$, for all $\sigma \in \Sigma$.

Thus, for a given σ we can solve the problem for $G(\xi, \tau)$ in the classical way in the domain $D_{\sigma,\Xi} = \{\sigma(\tau) < \xi < \Xi, \;\; \tau_1 < \tau < \tilde{\tau}\}$ with the boundary condition $G(\Xi, \tau) = \frac{v(\Xi, \tau)}{1 - c_s(\Xi)}$.

The function $v = G(1 - c_s)$ will necessarily be the restriction of the weak solution (i.e. the solution of (6.10)) to $D_{\sigma,\Xi}$.

Therefore, for each σ we know a domain $D_{\sigma,\Xi}$, such that $\Xi - \sigma(\tilde{\tau})$ remains positive for $\sigma \in \Sigma$, in which $A(v) = \delta$.

This is enough to apply the machinery of Sect. 4 to obtain a similar existence and uniqueness result in the interval $(\tau_1, \tilde{\tau})$. An additional information we have to provide is the continuous dependence of $v(\Xi, \tilde{\tau})$ on σ. Using the stability theorem on p. 166 of [4] in connection with the already quoted th. 10.1,

p. 204, we can see that if $\sigma_1, \sigma_2 \to 0$ in the C^1 norm, then the corresponding difference $v_1(\Xi, \tau) - v_2(\Xi, \tau)$ tends to zero in the Hölder norm. What mainly matters, however, is the dependence of G_σ on σ. It is well known that $\dfrac{\partial G}{\partial \xi}$ can be estimated uniformly w.r.t. $\sigma \in \Sigma$ in a domain $D_{\sigma,\Xi'}$, for some $\Xi' < \Xi$. In practice it is possible to identify Ξ' with Ξ, by possibly reducing $\tilde{\tau}$, thanks to the arbitrariness of Ξ. In turn, writing the equation for the difference $G_1 - G_2$ after having performed the transformation which maps $D_{\sigma_i,\Xi}$ into the rectangle $(0, \Xi) \times (0, \tilde{\tau})$, it is easy to realize that $|G_{\sigma_1}(\tau) - G_{\sigma_2}(\tau)|$ can be estimated by a linear combination of $\sup_{\tau' \in (\tau_1, \tau)} |\sigma_1(\tau') - \sigma_2(\tau')|$ and $\int_{\tau_1}^{\tau} \dfrac{|\dot{\sigma}_1(\tau') - \dot{\sigma}_2(\tau')|}{\sqrt{\tau' - \tau}} d\tau'$.

This is the basic estimate in the fixed point argument already used in Stage 1 to obtain existence and uniqueness.

Precisely the same argument can be iterated (thanks to the a priori properties illustrated in the previous section) up to the extinction of the saturated zone.

We summarize the above results in the following statement

Theorem 2 *During Stage 2 the weak formulation of Problem 2 has one unique solution (σ, v) with $\sigma \in C^1$ and $v \in V^{1,0}$. The functions G and c can be easily deduced from v in the sets $\{v > 0\}, \{v < 0\}$, where they satisfy their respective differential equations in the classical sense. The set $\{v = 0\}$ must have zero measure.*

We conclude the paper by just remarking that the analysis of Stage 3 follows the pattern of the analysis of Stage 1 and the problem of existence and uniqueness Theorem for Problem 3 is in fact a simplification of the parallel result for Problem 1.

References

[1] A. Fasano, L. Fusi, S. Correra, *Mathematical models for waxy crude oils.* To appear on MECCANICA (2004).

[2] A. Fasano, M. Primicerio, *Heat and mass transport in non-isothermal partially saturated oil-wax solutions.* To appear on New Trends in Mathematical Physics, P. fergola et al. editors (2004).

[3] A. Friedman, *Partial differential equations of parabolic type.* Prentice-Hall, Englewood Cliffd, N.J. (1964).

[4] O.A. Ladyzenskaya, V.A. Solonnikov, N.N. Uralceva, *Linear and quasilinear equations of parabolic type.* AMS Translations of Mathematical Monographs 27, Providence R.I. (1968).