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Wax deposition in crude oils: a new approach

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WAX DEPOSITION IN CRUDE OILS: A NEW APPROACH

To Guido Zappa on the occasion of his 90th birthday

ABSTRACT. — The complex phenomenon of solid wax deposition in wax saturated crude oils subject to thermal gradients has been treated in a number of papers under very specific assumptions (*e.g.* thermodynamical equilibrium between dissolved wax and the wax suspended in the oil as a crystallized phase). Here we want to consider a more general framework in which thermodynamical equilibrium may not exist, the whole system may form a gel-like structure in which the segregated solid wax has no diffusivity, the thermal field may evolve due to a non-negligible difference between the thermal conductivity of the solid wax deposit growing at the cold wall of the container and the conductivity of oil, etc.

KEY WORDS: Free Boundary Problems; Heat and Mass Transfer; Nonisothermal saturated solutions; Wax Deposition in Crude Oils.

1. INTRODUCTION

Crude oils are complex mixtures containing paraffins, aromatics, naphtenics, resins, asphaltenes and other impurities. For the purpose of our analysis, we can consider a solution of a high molecular weight paraffin (referred to as *wax* in this paper) in a solvent (referred to as *oil*).

The solubility of wax in oil decreases very sharply with temperature. At off-shore reservoir temperatures the solubility is sufficiently high to keep wax fully dissolved. But when oil is pumped in subsea pipelines, where the external temperature can be a few degrees centigrades, the decreased solubility causes the formation of wax crystals and at the same time deposition of solid wax on the pipe wall, due to diffusional migration of wax in the saturated solution induced by the radial thermal gradient.

The enormous economic relevance of this phenomenon stimulated several studies, laboratory experiments and field measurements (see, *e.g.*, [1, 2, 7, 15-17]). In the framework of a research contract with Enitecnologie, we have proposed mathematical models [9-11] for the phenomenon and applied them to the interpretation of data form an experimental device called *cold finger* [5-6].

Such models were based on the assumption that the segregated crystals can diffuse (though their diffusivity is much smaller than the one of the dissolved wax) and they are at any time in thermodynamical equilibrium with the solute.

Here, we want to include in our analysis the substantially different case in which wax crystals develop such a strong tendency to aggregate in a gel-like structure, that they can

be considered as immobile and not subject to diffusion (under «reasonable» concentration gradients). This situation occurs when temperature is sufficiently low.

We will also include the case in which the thermal conductivity of the deposit is much smaller than the one of the oil. The main consequence of this circumstance is that the growth of the deposit is accompanied by a quasi-steady evolution of the thermal field.

Let us denote by $c_s(T)$ the *saturation* of the solution, *i.e.* the maximum concentration (mass per unit volume) of wax that can be dissolved in the given oil at temperature T. Let $c_{tot}(\underline{x}, t)$ be the total concentration of wax (either dissolved or crystallized) at each point $\underline{x}$ and time t.

If $G(\underline{x}, t)$ denotes the concentration of wax crystals (often referred to as *segregated wax*), we have the obvious inequality

$$(1) \qquad\qquad G(\underline{x}, t) \geq [c_{tot}(\underline{x}, t) - c_s(T(\underline{x}, t))]_+,$$

where $[\,\cdot\,]_+$ denotes the positive part.

If we assume that thermodynamical equilibrium between dissolved and segregated wax is instantaneously reached, we prescribe that (1) holds with the equality sign. In this circumstance, the concentration $c(\underline{x}, t)$ of the dissolved wax will be given by

$$(2) \qquad\qquad c(\underline{x}, t) = min(c_{tot}(\underline{x}, t), c_s(T(\underline{x}, t)))$$

and, in any case,

$$(3) \qquad\qquad c_{tot}(\underline{x}, t) = c(\underline{x}, t) + G(\underline{x}, t).$$

If we release assumption (2), we have to replace it by imposing that the transition $G \rightarrow c$ occurs according to a given kinetics. A reasonable assumption is

$$(4) \qquad\qquad c(\underline{x}, t) \leq c_s(T(\underline{x}, t)),$$

$$(5) \qquad\qquad Q(\underline{x}, t) = -\beta[c_s(T(\underline{x}, t)) - c(\underline{x}, t)]H(G),$$

where $|Q|$ is the mass of segregated wax dissolving per unit volume and unit time at $\underline{x}, t$,

$$(6) \qquad\qquad H(G) = \begin{cases} 1, & G > 0, \\ 0, & G \leq 0, \end{cases}$$

and β is a positive constant.

In the next section we illustrate the general framework of our analysis, using for simplicity a one-dimensional geometry. The rest of the paper is devoted to the study of various specific situations. For the necessity of being concise most of the proofs will just be sketched.

2. A MODEL PROBLEM

In this paper we will study a one-dimensional problem (confining to the planar symmetry, just to simplify notation). Thus we consider the slab $x \in (0, L)$ whose boundaries are kept at temperatures

$$(7) \qquad\qquad T(0, t) = T_1, \qquad T(L, t) = T_2 > T_1.$$

Since wax diffusivity is much smaller than thermal diffusivity we can assume that thermal equilibrium is instantaneously reached. Therefore, if thermal conductivity is constant, we have the linear profile

(8) $$T_0(x) = T_1 + \frac{x}{L}(T_2 - T_1).$$

We also assume that $c_s(T)$ is a given increasing function and we refer -as it is often done, when the temperature varies on a sufficiently small range (T_1, T_2)- to the case of a linear solubility curve ($c_s'' = 0$), although in Sect. 7 we outline the peculiarities of general $c_s(T)$ and study in some detail a case in which $c_s'' > 0$ in $(T_1, T_2]$, $c_s'(T_1) = 0$, essentially for its mathematical interest.

We suppose that

(9) $$c_{tot}(x, 0) = c^* > c_s(T_2), \quad x \in (0, L),$$

and that we have initially thermodynamical equilibrium, *i.e.*

(10) $$c(x, 0) = c_s(T_0(x)), \quad x \in (0, L),$$

(11) $$G(x, 0) = G_0(x) = c^* - c_s(T_0(x)) > 0, \quad x \in (0, L).$$

We will also assume that the densities of segregated wax, dissolved wax and oil are equal and that the latent heat involved in the transition from crystallized to dissolved wax is negligible (see the discussion in [7]).

The statement of the problem is completed prescribing that the boundaries $x = 0$, $x = L$ are impermeable to wax and oil. The solution is assumed to be *diluted* (even when saturated) in the sense that oil will be considered to be immobile, although wax is displaced by diffusion (this is true in practical cases, for a more general model, see [10]).

The basic idea of our model is that the dissolved wax diffuses towards the cold wall and creates a solid deposit of increasing thickness $\sigma(t)$.

The law of advancement of the interface $x = \sigma(t)$ is given by the mass balance

(12) $$[\rho - G(\sigma(t), t)]\dot\sigma(t) = Dc_x(\sigma(t), t), \quad t > 0$$

where ρ is the density of the solid layer which is supposed to incorporate all the segregated wax present in the region crossed by the interface. The wax diffusivity D will be taken constant for simplicity, although it is likely to depend on G. As a matter of fact, the problem with $D = D(G)$ with $D'(G) < 0$ presents several interesting mathematical aspects. Moreover

(13) $$\rho > maxG_0(x) = G_0(0).$$

REMARK 2.1 (*mass conservation*). In principle, the diffusing wax that deposits on the wall induces the displacement of oil and mass conservation (12) takes into account this additional effect. This would also affect the evolution equation for c and G with the appearance of a convective term. As we pointed out above, the assumption of *diluted* solution allows us to neglect these terms.

REMARK 2.2 (*asymptotics*). Irrespectively of the assumptions on thermodynamical equilibrium (hypotheses (2) or (4)-(5)) and on the diffusivity of c (including or not its

possible dependence on G), the asymptotic situation for $t \to \infty$ is such that $\sigma \to \sigma_\infty$, which is the unique solution of

$$(14) \qquad \rho\sigma_\infty + c_s(T(\sigma_\infty))(L - \sigma_\infty) = c^*L,$$

and $c(x, t) \to c_\infty, \forall x \in (\sigma_\infty, L)$, such that

$$c_\infty = c_s(T(\sigma_\infty)).$$

Note that the same situation is reached irrespectively of the fact that diffusion of G is included or not in the model and for any strictly monotone $c_s(T)$.

We conclude this section by writing the expression for the temperature. With no loss of generality we can rescale length and take $L = 1$. According to the already mentioned assumptions, temperature is a linear function of x in each layer of constant conductivity. We set

$$(15) \qquad \vartheta = k_d/k_0$$

where k_d and k_0 are the thermal conductivities of the deposit and of the solution (the latter being considered to be independent of c and G), and we impose continuity of thermal flux at the interface

$$(16) \qquad k_d T_x(\sigma(t)-, t) = k_0 T_x(\sigma(t)+, t), \quad t > 0.$$

We find:

$$(17) \qquad T(x, t) = T_1 + (T_2 - T_1)\frac{x}{\sigma(t) + \vartheta(1 - \sigma(t))}, \quad x \in (0, \sigma(t)), \quad t > 0,$$

$$(18) \qquad T(x, t) = T_1 + (T_2 - T_1)\frac{\sigma(t) + \vartheta(x - \sigma(t))}{\sigma(t) + \vartheta(1 - \sigma(t))}, \quad x \in (\sigma(t), 1), \quad t > 0.$$

In particular

$$(19) \qquad T(\sigma(t), t) = T_1 + (T_2 - T_1)\frac{\sigma(t)}{\sigma(t) + \vartheta(1 - \sigma(t))}, \quad t > 0.$$

REMARK 2.3. In most practical cases

$$(20) \qquad \sigma(t) \le \sigma_\infty \ll 1.$$

So, if $\vartheta = O(1)$,

$$(21) \qquad T(\sigma(t), t) \simeq T_1,$$

but this is no longer true if $\vartheta \ll 1$, meaning that even a thin deposit can have a relevant influence on the thermal profile. This means that the thermal effect of the deposit can be taken into account, still desregarding the corresponding modification on the geometry of the problem.

In the next two sections we will study in some detail the following cases:

- thermodynamical equilibrium with full saturation (Section 3),
- thermodynamical equilibrium with partial saturation (Section 4).

3. CASE OF THERMODYNAMICAL EQUILIBRIUM: FULL SATURATION

Assume (2) holds and let the initial situation be described by (10), (11). We start by considering the case of non-vanishing diffusivity D_G of wax crystals. Then, there will be a time interval $(0, t_1)$ such that

$$(22) \qquad G(x, t) > 0, \quad c(x, t) = c_s(T(x, t)), \quad x \in (\sigma(t), 1), \quad t \in (0, t_1),$$

where $T(x, t)$ is expressed in terms of $\sigma(t)$ by (18). During this period, dissolved wax migrates towards the cold wall with a flow rate equal to

$$(23) \qquad Dc'_s \frac{T_2 - T_1}{\sigma(t) + \vartheta(1 - \sigma(t))} \equiv \frac{\gamma}{\sigma(t) + \vartheta(1 - \sigma(t))}.$$

Therefore

$$(24) \qquad [\rho - G(\sigma(t), t)]\dot{\sigma}(t) = \frac{\gamma}{\sigma(t) + \vartheta(1 - \sigma(t))}, \quad t \in (0, t_1),$$

$$(25) \qquad \sigma(0) = 0.$$

Dissolution of wax crystals occurs at $x = 1$, where segregated wax has to dissolve to replace the migrating dissolved wax, but also in the bulk because of the increase of saturation concentration.

Hence, owing to thermodynamical equilibrium, G has to be found by solving the problem

$$(26) \quad \begin{cases} D_G G_{xx} - G_t = c'_s T_t = c'_s \dot{\sigma}(t) \dfrac{\vartheta(1 - \vartheta)(1 - x)}{[\sigma(t) + \vartheta(1 - \sigma(t))]^2}, & x \in (\sigma(t), 1), t \in (0, t_1), \\[2mm] D_G G_x(1, t) = -\dfrac{\gamma}{\sigma(t) + \vartheta(1 - \sigma(t))}, & t \in (0, t_1), \\[2mm] G_x(\sigma(t), t) = 0, \quad t \in (0, t_1), \\[2mm] G(x, 0) = G_0(x) = c^* - c_s(T_0(x)), \quad x \in (0, 1), \end{cases}$$

which is coupled with (24), (25).

Problem (24)-(26) is a free boundary problem of a non-standard form for the heat equation. Its solution can be sought *e.g.* by means of successive approximations.

Let us sketch the procedure. Let $\Gamma_n(t)$ be a Hölder continuous function such that $\Gamma_n(0) = G_0(1)$ and $0 \le \Gamma(t) \le G(0)$. Compute $\sigma_n(t)$ by integrating

$$(27) \qquad [\sigma_n + \vartheta(1 - \sigma_n)]\dot{\sigma}_n = \frac{\gamma}{\rho - \Gamma_n}, \quad \sigma_n(0) = 0,$$

thus identifying $\sigma_n(t)$ as the positive root of the equation

$$(28) \qquad \frac{1}{2}(1 - \vartheta)\sigma_n^2 + \vartheta\sigma_n = \gamma \int_0^t \frac{d\tau}{\rho - \Gamma_n(\tau)},$$

which possesses a Hölder continuous derivative, positive by definition and a-priori bounded by $\dot{\sigma}_n < \dfrac{\gamma}{\vartheta(\rho - G_0(0))} \equiv \dot{\sigma}_0$.

We fix a time interval $(0, \bar{t})$, such that $\bar{t} < \dfrac{\vartheta(\rho - G_0(0))}{\gamma}$, so that $\sigma_n(\bar{t}) < 1$.

Next we compute $G_n(x, t)$ by solving problem (26) with $\sigma = \sigma_n$ and defining $\Gamma_{n+1}(t) = G_n(\sigma_n(t), t)$. The procedure can be started taking for instance $\Gamma_1(t) = G_0(0)$. It is easy to obtain an a-priori uniform estimate of Γ_{n+1} in a Hölder space.

It is also possible to obtain a uniform estimate of the first vanishing time of $G_n(x, t)$, using the fact that the sink term in the differential equation is dominated by $c'_s \dot{\sigma}_0 \dfrac{1 - \vartheta}{\vartheta}(1 - x)$ and that $D_G G_{nx}(1, t) < -\dfrac{\gamma}{\vartheta}$. Moreover $G_n < G_0(0)$ at all internal points. Thus we possess enough information to say that there exists a subsequence $\{\Gamma_n\}$ converging uniformly to a Hölder continuous limit $\overline{\Gamma}(t)$ taking values in $(0, G_0(0))$ for $t \in (0, \bar{t})$. To this we can associate a pair $(\overline{\sigma}, \overline{G})$ which turns out to be a solution of our free boundary problem, as it can be shown by taking the limit of (σ_n, G_n) along the same subsequence (note that $\dot{\sigma}_n$, G_{nx} are also equibounded).

Uniqueness is not difficult to be proved. Let (σ_1, G_1), (σ_2, G_2) be two solutions. Setting $\delta\sigma = \sigma_1 - \sigma_2$, $\delta G = G_1(\sigma_1(t), t) - G_2(\sigma_2(t), t)$, from (24), (25) we deduce an integral inequality of the type

$$(29) \qquad |\delta\sigma(t)| \leq \int_0^t \{A|\delta\sigma(\tau)| + B|\delta G(\tau)|\}d\tau,$$

for some easily computable positive constants A, B. Since $|\delta G(t)|$ can be estimated in terms of $\sup_{\tau \in (0,t)} |\delta\sigma(\tau)| \equiv |\delta\sigma|_t$ (the proof is lengthy and is omitted), (29) leads to a Gronwall inequality for $|\delta\sigma|_t$ with zero free term, implying $\delta\sigma \equiv 0$. Thus the recursive scheme described above is convergent.

This procedure can be iterated up to the time $t_1 > 0$ such that

$$(30) \qquad G(x, t) > 0, \quad \sigma(t) \leq x < 1, \quad 0 \leq t \leq t_1.$$

The time t_1 is necessarily bounded. Note that if the diffusivity of segregated wax vanishes, t_1 is also zero and a part of the domain will be unsaturated from the very beginning.

4. CASE OF THERMODYNAMICAL EQUILIBRIUM: PARTIAL SATURATION

At time t_1, a new free boundary $x = r(t)$ appears, separating the zone $x \in (\sigma(t), r(t))$ where $c = c_s$ and $G > 0$ from the zone $x \in (r(t), 1)$ where $c < c_s$ and $G = 0$. This stage ends at time t_2 when $r(t_2) = \sigma(t_2)$.

For $x \in (\sigma(t), r(t))$ dissolved wax diffuses with a flow rate still given by (23) and the differential equation for the function $\sigma(t)$ representing the thickness of the deposit is still (24) with *initial* condition

$$(31) \qquad \sigma(t_1) = \sigma_1,$$

where σ_1 is calculated from the previous stage, if $t_1 > 0$ (*i.e.* if $D_G \neq 0$).

a) We start by considering the case $D_G \neq 0$.
Now we have in the saturated zone:

(32)
$$\begin{cases} D_G G_{xx} - G_t = c'_s T_t = c'_s \dot{\sigma}(t) \dfrac{\vartheta(1-\vartheta)(1-x)}{[\sigma(t) + \vartheta(1-\sigma(t))]^2}, & x \in (\sigma(t), 1), t \in (0, t_1), \\[2mm] G(r(t), t) = 0, & t \in (t_1, t_2), \\[2mm] G_x(\sigma(t), t) = 0, & t \in (t_1, t_2), \\[2mm] G(x, t_1) = G_1(x), & x \in (\sigma(t_1), 1), \end{cases}$$

where $G_1 \geq 0$ ($G_1 > 0$ in $[\sigma(t), 1)$) has been found in the previous stage (remember (31)).

On the other hand, $c(x, t)$ solves the following problem in the unsaturated zone $x \in (r(t), 1)$:

(33)
$$\begin{cases} D c_{xx} - c_t = 0, & x \in (r(t), 1), \quad t \in (t_1, t_2), \\[2mm] c(r(t), t) = c_s(r(t), t), & t \in (t_1, t_2), \\[2mm] c_x(1, t) = 0, & t \in (t_1, t_2), \end{cases}$$

and on the new free boundary we have the following condition expressing mass balance

(34)
$$\frac{\gamma}{\sigma(t) + \vartheta(1 - \sigma(t))} + D_G G_x(r(t)-, t) = D c_x(r(t)+, t)$$

for $t \in (t_1, t_2)$ with condition

(35)
$$r(t_1) = 1.$$

Problem (24), (31)-(35) is a problem with two free boundaries of explicit/implicit type.

For the necessity of being concise, we confine ourselves to sketch a possible way of proving existence, leaving a more precise analysis of the well-posedness of the problem to a future paper.

For every given σ in a ball of $C_1(t_1, t_2)$ satisfying (31), problem (32)-(35) can be seen as a *diffraction* problem for the function

$$u(x, t) = c_{tot}(x, t) - c_s(x, t),$$

noting that the diffusivity for u has a jump for $u = 0$.

This class of problems has been investigated in the context of fast chemical reactions (see [3, 4]) and those techniques can be adapted to fit the present situation. Then a compactness argument can be used to find $\sigma(t)$ and conclude the proof of the existence theorem: taken σ in a convenient convex set Σ of Lipschitz continuous increasing functions, solve the free boundary problem for u and compute $\tilde{\sigma}$ by means of (24), (25), this time using the formula

$$\tilde{\sigma}(t) = \gamma \int_0^t [\sigma(\tau) + \vartheta(1 - \sigma(\tau))]^{-1} [\rho - u(\sigma(\tau), \tau)]^{-1} d\tau,$$

and show that if Σ is selected properly, then $\tilde{\sigma} \in \Sigma$ and that the mapping $\sigma \to \tilde{\sigma}$ is compact w.r.t. the sup-norm.

b) The case of $D_G = 0$ is simpler. We have already noted that $t_1 = 0$, so that the initial conditions for the two free boundaries are

$$(36) \qquad\qquad\qquad \sigma(0) = 0, \quad r(0) = 1.$$

Up to time t_2 when the whole solution becomes unsaturated we have that the deposit grows according to equation (24).

In the saturated layer $x \in (\sigma(t), r(t))$ we have

$$(37) \quad G(x,t) = G_0(x) - [c_s(T(x,t)) - c_s(T_0(x))] =$$

$$= G_0(x) - c_s'(T_2 - T_1)(1 - \vartheta)\frac{\sigma}{\sigma + \vartheta(1 - \sigma)}(1 - x),$$

for $x \in (\sigma(t), r(t))$ and $t \in (0, t_2)$.

In the unsaturated region $x \in (r(t), 1)$ $c(x,t)$ solves (33), and the condition on $x = r(t)$ is the following

$$(38) \qquad\qquad \frac{\gamma}{\sigma(t) + \vartheta(1 - \sigma(t))} - \dot{r}(t)G(r(t)-, t) = Dc_x(r(t)+, t),$$

for $t \in (0, t_2)$, with

$$G(r(t)-, t) = G_0(r) - c_s'(T_2 - T_1)(1 - \vartheta)\frac{\sigma(1 - r)}{\sigma + \vartheta(1 - \sigma)} > 0.$$

Note that in this scheme G is discontinuous across the free boundary.

For a given increasing $\sigma \in C^1$, problem (33), (38) is a problem of generalized Stefan type for which we have proved a well-posedness result in [13]. Again, the completion of the proof is achieved via a compactness argument. In order to follow this procedure it is important to be sure that the region $r(t) < x < 1$ remains desaturated. Since

$$\frac{\partial c_s}{\partial t} = c_s'(T_2 - T_1)(1 - \vartheta)\vartheta\frac{1 - x}{[\sigma + \vartheta(1 - \sigma)]^2}\dot{\sigma} > 0,$$

it is easy to check that the function $u = c - c_s$ is negative in the domain considered, just applying the maximum principle ($u_t - Du_{xx} < 0$, $u(r(t), t) = 0$, $u_x(1, t) < 0$).

5. FULLY UNSATURATED SLAB

Of course, once we know that the solution has a wax concentration under saturation and $G = 0$, the mathematical model becomes insensitive of whatever assumption we have made on the behaviour of the segregated phase.

To be specific, we assume we have gone through the previous stages and we start from time t_2, knowing the following *initial* data:

$$(39) \qquad\qquad\qquad\qquad \sigma(t_2) = \sigma_2$$

$$(40) \qquad\qquad\qquad G(x, t_2) = 0, \quad x \in (\sigma_2, 1),$$

$$(41) \qquad\qquad\qquad c(x, t_2) = c_2(x), \quad x \in (\sigma_2, 1),$$

where

(42) $$c_2(x) < c_s(T(x)), \quad x \in (\sigma_2, 1),$$

and $c_s(T(x))$ is found from (19).

We have the following diffusion problem for $c(x, t)$ with one free boundary:

(43) $$Dc_{xx} - c_t = 0, \quad x \in (\sigma(t), 1), \quad t > t_2,$$

(44) $$c(x, t_2) = c_2(x), \quad x \in (\sigma_2, 1),$$

(45) $$c_x(1, t) = 0, \quad t > t_2,$$

(46) $$c(\sigma(t), t) = c_s(T(\sigma(t), t)), \quad t > t_2,$$

(47) $$\rho\dot{\sigma}(t) = -Dc_x(\sigma(t), t), \quad t > t_2,$$

(48) $$\sigma(t_2) = \sigma_2 \in (0, 1).$$

The fact that $c(x, t)$ remains below $c_s(T(x, t))$ can be proved as follows. First replace (47) by

$$\rho\dot{\sigma} = -D[c_x(\sigma(t), t)]_+,$$

(no dissolution of the deposit) so that $\dot{\sigma} \geq 0$ by definition. Then we apply the same argument we have used at the end of the previous section, showing that $u = c - c_s < 0$. Moreover, as an easy consequence of the maximum principle, we can prove that we have $c_x(x, t) > 0$ as long as $c_x(\sigma, t) > 0$. Now, if for some time interval (t', t'') we have $\dot{\sigma} = 0$, we can easily see that c takes its minimum for $x = \sigma$, implying that $c_x(\sigma(t), t) > 0$ in (t', t''), thus contradicting the assumption $\dot{\sigma} = 0$. Hence we may say that $\dot{\sigma}(t) > 0$ for all $t > t_2$.

At this point global existence and uniqueness for (43)-(48) is a well known result (see [13]).

6. Case of nonequilibrium

In this section we will assume (4)-(6) and we suppose that the same initial conditions (9)-(11) are prescribed.

With respect to previous sections, we have a basic difference, that is a consequence of the fact that (excluding the trivial case $\vartheta = 1$) the deposition causes $c_s(x, t)$ to be an increasing function of time at any point x: in the present case immediate desaturation takes place. Indeed, since we are assuming $c_s'' = 0$, the solution has to be unsaturated throughout, because to keep $c = c_s$ one should have $Q < 0$, thus contradicting (5).

We start by considering the case $D_G = 0$ and we study the following problem

(49) $$G_t(x, t) = -\beta[c_s(T(x, t)) - c(x, t)]H(G), \quad x \in (\sigma(t), 1), \quad t > 0,$$

(50) $$G(x, 0) = G_0(x) = c^* - c_s(T_0(x)), \quad x \in (0, 1),$$

(51) $$Dc_{xx} - c_t = -\beta[c_s(T(x, t)) - c(x, t)]H(G), \quad x \in (\sigma(t), 1), \quad t > 0,$$

(52) $$c(x, 0) = c_s(T_0(x)), \quad x \in (0, 1),$$

(53) $c_x(1,t) = 0, \quad t > 0,$

(54) $c(\sigma(t), t) = c_s(T(\sigma(t), t)), \quad t > 0,$

with the free boundary conditions

(55) $[\rho - G(\sigma(t), t)]\dot{\sigma}(t) = Dc_x(\sigma(t), t),$

(56) $\sigma(0) = 0.$

From (49) we find a formal expression for G

(57) $$G(x,t) = G_0(x) - \beta \int_0^t [c_s(T(x,\tau)) - c(x,\tau)]d\tau,$$

holding for $x > \sigma(t)$ and $t \leq t_G(x)$ which is the unknown time of extinction of G at the location x, if $\sigma(t_G) < x$, and is $\sigma^{-1}(x)$ otherwise.

For the sake of brevity we just sketch the procedure to prove the well-posedness of problem (49)-(56). We use again a fixed point argument. We prescribe $\sigma(t)$ in a Lipschitz class Σ of monotone functions so that $T(x,t)$ is given by (18) and thus (57) expresses function G as a functional of $c(x,t)$.

Then, the r.h.s. of (51) is also a functional of c, through $H(G)$. Problems of this kind are non-standard, but the existence of one unique classical solution can be proved by the methods of [14] and we note that the argument works also if we allow D to depend on G, provided that suitable conditions are satisfied.

The resulting function $c(x,t)$ is easily shown to be such that $c_x(\sigma(t), t)$ is Hölder continuous and that its Hölder norm depends on the Lipschitz constant of σ.

So, a mapping $\sigma \to \tilde{\sigma}$ can be defined using (55), (56). It is not difficult to show that this mapping is contractive in Σ with respect to the sup-norm in a sufficiently small time interval. Hence, a unique fixed point is found, providing a solution to our problem, which is actually C^1.

Extension to arbitrary time intervals is then obtained by means of standard arguments.

Finally, let us just see how the arguments change when $D_G \neq 0$. Now (50) is replaced by

(58) $D_G G_{xx} - G_t = \beta[c_s(T(x,t)) - c(x,t)]H(G),$

and no flux conditions are to be assigned on the boundaries

(59) $G_x(1,t) = 0, \quad G_x(\sigma(t), t) = 0, \quad t > 0.$

Of course, for each given σ in the Lipschitz class, the two parabolic problems for G and for c are strictly coupled and hence the existence of c and G has to be proved beforehand. However this task is not particularly difficult. Once this is accomplished, the proof follows the same pattern as in the previous case.

7. MASS TRANSFER WITH NO DEPOSITION

In this section we give some ideas on the behaviour of the system when linearity of $c_s(T)$ is no longer assumed. As a general remark, we note that if we start from initial conditions (10)-(11) and we have $c_s''(T) < 0$ in some interval (x_1, x_2), then a zone of desaturation will immediately appear in case (4)-(5) (even if T remains constant in time).

On the contrary, saturated layers, bound to become extinct in a finite time, are present in correspondence of intervals in which $c_s'' > 0$. Intervals in which $c_s'' = 0$ confining on the r.h.s. with an interval where $c_s'' > 0$, remain saturated provided temperature does not change in time. Desaturation occurs immediately at $x = 1$, irrespectively of the sign of $c_s''(T_2)$, if $D_G = 0$.

Assuming thermodynamical equilibrium leads to a very similar scenario, unless temperature is time independent. In the latter case saturation persists locally for some time (with the exception of $x = 1$ if $D_G = 0$), and points where $c_s'' < 0$ may become desaturated before they are reached by the desaturation front coming from the warm wall. Thus the general problem is considerably complicated.

We will consider in more detail a situation in which we assume time-independent temperature

(60) $$T(x, t) = T_0(x) = T_1 + (T_2 - T_1)x$$

and this assumption is justified by the absence of solid deposit. Indeed, we assume

(61) $$c_s'(T_1) = 0, \quad c_s''(T) \geq 0 \quad \text{in } (T_1, T_2).$$

For the sake of brevity we confine to the case $D_G = 0$ and to the absence of thermodynamical equilibrium.

Once more we take D independent of G. It can be seen that if $D = D(G)$ with $D' \leq 0$ the problem presents an interesting mathematical structure, however too complicated to be treated here.

It is clear that the situation described by (60), (61) is rather artificial from the physical point of view, also because the corresponding asymptotic limit of $G(x)$ would be a point mass located in $x = 0$. Nevertheless we will investigate it briefly because of its mathematical interest.

We have

(62) $$G_t = -\beta H(G)[c_s(T_0(x)) - c(x, t)] + \widehat{H}(c(x, t) - c_s(T_0(x)))Dc_s''(T_0')^2$$

where

(63) $$\widehat{H}(z) = \begin{cases} 1, & z \geq 0 \\ 0, & z < 0. \end{cases}$$

Since $c \leq c_s$ either the positive or the negative term is active.

Now we have to solve a free boundary problem in the unsaturated layer $x \in (s(t), 1)$:

(64) $\qquad c_t - Dc_{xx} = H(G)\beta(c_s - c), \quad x \in (s(t), 1), \quad t \in (0, \bar{t}),$

(65) $\qquad\qquad\qquad\qquad s(0) = 1,$

(66) $\qquad\qquad\qquad c_x(1, t) = 0, \quad t \in (0, \bar{t}),$

(67) $\qquad\qquad\qquad c(s(t), t) = c_s(T_0(s(t))), \quad t \in (0, \bar{t}),$

(68) $\qquad\qquad\qquad c_x(s(t), t) = c_s'(T_0(s(t)))T_0', \quad t \in (0, \bar{t}).$

Condition (68) expresses the continuity of solute flux and follows from the continuity of G at the interface.

Indeed, $G(s(t)-, t) > 0$ can be evaluated from (62)

(69) $\qquad\qquad G_t(x, t) = Dc_s''(T_0(x))T_0'^2, \quad x \in (0, s(t)), \quad t \in (0, \bar{t}),$

(70) $\qquad\qquad\qquad G(x, 0) = G_0(x), \quad x \in (0, 1),$

while, in the unsaturated zone G is decreasing according to the kinetics

(71) $\qquad\qquad\qquad G_t(x, t) = -\beta(c_s - c)H(G)$

and (71) has to be integrated starting from $x = s(t)$.

Following the technique of [8] it can be shown that (64)-(68) can be reduced to a Stefan-type problem, although of a singular kind. For instance, as long as $G > 0$ in the unsaturated zone setting $c_t = w$, performing formal differentiations on (64), (66), (67), (68) one arrives at the scheme

(72) $\qquad\qquad w_t - Dw_{xx} = -w, \quad x \in (s(t), 1), \quad t \in (0, \bar{t}),$

(73) $\qquad\qquad\qquad w_x(1, t) = 0, \quad t \in (0, \bar{t}),$

(74) $\qquad\qquad\qquad w(s(t), t) = 0, \quad t \in (0, \bar{t}),$

(75) $\qquad\qquad w_x(s(t), t) = c_s''(T_0(s(t)))T_0'^2 \dot{s}(t), \quad t \in (0, \bar{t}).$

To this system one has to add the information that the limit of w in the corner point $(0, 1)$ along directions marked by a unit vector pointing inside the domain is $-\infty$. The solution can be obtained as the limit as $n \to \infty$ of regularized problems in which the initial condition is

(76) $\qquad\qquad\qquad\qquad s^{(n)}(0) = 1 - \dfrac{1}{n},$

(77) $\qquad\qquad\qquad\qquad w^{(n)}(x, 0) = f^{(n)}(x),$

where $f^{(n)}(x) = -nc_s'(T_0s^{(n)}(0))T_0'^2$ for $1 - \dfrac{1}{n} + \dfrac{1}{n^2} < x < 1$, $f_n(s^{(n)}(0)) = 0$ while in $\left(1 - \dfrac{1}{n}, 1 - \dfrac{1}{n} + \dfrac{1}{n^2}\right)$ it is any decreasing function such that $f^{(n)}$ is smooth in $[s^{(n)}(0), 1]$.

The feasibility of this procedure can be proved using a technique similar to the one employed in [12] for obtaining existence for a singular diffusion-consumption problem.

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