

GROUNDWATER MASS TRANSPORT AND HETEROGENEOUS EQUILIBRIUM CHEMICAL REACTION—A KIND OF FREE BOUNDARY PROBLEM

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Abstract

This paper considers another kind of chemical reaction different from [1]. The difference is that the chemical reactions under consideration are assumed to be heterogeneous, fast, reversible and classical. As a typical example, the author reduces this problem to an one phase Stefan problem with noncommon data, and investigates the classical solution as well as the weak solution.

§ 1. Introduction

We consider the transport of reacting solutes in porous media (see [2]). The solution originally present within the porous medium contains a reacting cation M_1 and a reacting anion M_2 , both of which are in equilibrium with a crystalline solid $\overline{M_1M_2}$. The displacing solution contains an inert anion M_4 and the reacting cation M_1 . The solute-transport-affecting reaction is sufficiently fast and reversible. It is represented by the chemical equation



As the displacing solution does not contain M_2 and has M_1 with a concentration smaller than that in the original solution, percolation of the displacing solution through a column will cause a continuous shift of the chemical equilibrium (R4) to the right, bringing about dissolution of $\overline{M_1M_2}$.

It is known that because of such a dissolution process, eventually two zones must develop within the leached column: an upper zone I, from which the solid $\overline{M_1M_2}$ has been entirely leached out and a lower zone II, in which the solid is apresent. It can be proved by means of elementary chemical equilibrium considerations that the dissolution occurs at, and only at, the interface between zone I and

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II and the interface must move gradually and continuously downward (see Fig. 1).

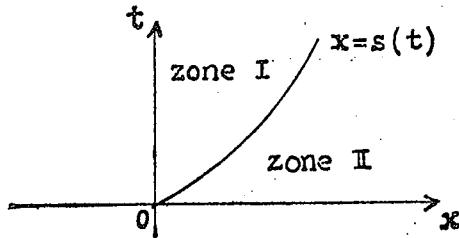


Fig. 1

We reduce this problem to an one phase Stefan problem with noncommon data. In section 2, we give the mathematical model and its reduction. The classical solution and the weak solution are investigated in section 3 and 4 respectively.

§ 2. Mathematical Model and Its Reduction

Because of the differing nature of the chemical processes in two zones, the basic solute transport equations for the present case must be formulated for each zone separately^[2]. Before doing this, we define

$$\text{zone I: } \Omega_1 = \{x \in (0, s(t)), t \in (0, T)\};$$

$$\text{zone II: } \Omega_2 = \{x \in (s(t), l), t \in (0, T)\},$$

$$\Omega = \{x \in (0, l), t \in (0, T)\};$$

$$\Gamma_1 = \{0\} \times (0, T); \quad \Gamma_2 = \{l\} \times (0, T); \quad \Gamma_s = \{s(t)\} \times (0, T);$$

$$\Gamma_0 = (0, l) \times \{0\}; \quad L = D \frac{\partial^2}{\partial x^2} - Q \frac{\partial}{\partial x}; \quad q = -D \frac{\partial}{\partial x} + Q,$$

where l and T are positive constants, D and Q are positive constants representing the coefficients of longitudinal dispersion and x direction volume flux of water respectively, $s(t)$ is the interface with $s(0) = 0$. Then we have following system^[2]

$$\theta \frac{\partial c_4}{\partial t} = Lc_4 \quad \text{in } \Omega, \quad (2.1)$$

$$c_4 = c_{4B} = 0 \quad \text{on } \Gamma_0. \quad (2.2)$$

$$qc_4 = Qc_{4F} \quad \text{on } \Gamma_1, \quad (2.3)$$

$$\frac{\partial c_4}{\partial x} = 0 \quad \text{on } \Gamma_2, \quad (2.4)$$

zone I:

$$\theta \frac{\partial c_i^I}{\partial t} = Lc_i^I \quad \text{in } \Omega_1, \quad (2.5)$$

$$qc_i^I = \theta c_{iF}^I \quad \text{on } \Gamma_1, \quad (2.6)$$

$$c_{i2}^I = 0 \quad \text{in } \Omega_1, \quad (2.7)$$

zone II:

$$\theta \frac{\partial c_i^{II}}{\partial t} + \rho \frac{\partial c_{i2}^{II}}{\partial t} = Lc_i^{II} \quad \text{in } \Omega_2, \quad (2.8)$$

$$c_i^{II} = c_{iB} \text{ and } c_{i2}^{II} = c_B \quad \text{on } \Gamma_0, \quad (2.9)$$

$$\frac{\partial c_i^{II}}{\partial x} = 0 \quad \text{on } \Gamma_2, \quad (2.10)$$

$$K_{12} = c_1^{\text{II}} c_2^{\text{II}} \quad \text{in } \Omega_2, \quad (2.11)$$

where the superscripts I and II indicate the zones involved. For $i=1$ and $i=2$, the functions $c_i^{\text{I}}(x, t)$ and $c_i^{\text{II}}(x, t)$ are solutions of two different sets of equations and hence they are two different functions.

c_i 's and \bar{c}_{12} are the concentrations (moles per unit volume of water) of the species M_i ($i=1, 2, 4$) and $\overline{M_1 M_2}$ respectively.

ρ is the porous medium's bulk density.

θ is the volumetric water content.

\bar{c}_B , ρ , θ , K_{12} , c_{iB} and c_{iF}^{I} ($i=1, 2, 4$) are positive constants and satisfy

$$c_{1F}^{\text{I}} = c_{4F}, \quad c_{2F}^{\text{I}} = 0, \quad c_{1B}^{\text{II}} = c_{2B}^{\text{II}} = \sqrt{K_{12}}, \quad c_{4B} = 0. \quad (2.12)$$

Clearly, additional boundary information at the moving interface $x=s(t)$ is needed. In the present case, that is

$$c_i^{\text{I}}(s(t)-, t) = c_i^{\text{II}}(s(t)+, t), \quad (2.13)$$

$$(\theta(c_i^{\text{II}} - c_i^{\text{I}}) + \rho \bar{c}_{12}^{\text{II}}) \frac{ds}{dt} = q c_i^{\text{II}} - q c_i^{\text{I}} \quad \text{on } \Gamma_s, \quad (2.13)'$$

(2.13)' is equivalent to the following

$$\rho \bar{c}_{12}^{\text{II}}(s(t)+, t) \frac{ds}{dt} = D \left(\frac{\partial c_i^{\text{I}}(s(t)-, t)}{\partial x} - \frac{\partial c_i^{\text{II}}(s(t)+, t)}{\partial x} \right). \quad (2.14)$$

Thus, the problem (2.5)—(2.14) (called PI) is a kind of free boundary problem, i.e., it can be reduced to a one phase Stefan problem with noncommon data. In fact, setting

$$v = c_1^m - c_2^m, \quad m = \text{I, II},$$

we have

$$\theta \frac{\partial v}{\partial t} = Lv \quad \text{in } \Omega_1 \cup \Omega_2, \quad (2.15)$$

$$v = 0 \quad \text{on } \Gamma_0, \quad (2.16)$$

$$qv = Q c_{1F}^{\text{I}} \quad \text{on } \Gamma_1, \quad (2.17)$$

$$\frac{\partial v}{\partial x} = 0 \quad \text{on } \Gamma_2, \quad (2.18)$$

$$v(s(t)-, t) = v(s(t)+, t), \quad (2.19)$$

$$\frac{\partial v(s(t)-, t)}{\partial x} = \frac{\partial v(s(t)+, t)}{\partial x}. \quad (2.20)$$

Comparing (2.1)—(2.4) with (2.15)—(2.20), we get (see [3])

$$v \equiv c_4 \quad \text{in } \Omega.$$

From this and (2.8), (2.11), we have

$$c_1^{\text{II}} = \frac{1}{2} (c_4 + (c_4^2 + 4K_{12})^{1/2}), \quad (2.21)$$

$$c_2^{\text{II}} = \frac{1}{2} (-c_4 + (c_4^2 + 4K_{12})^{1/2}), \quad (2.22)$$

$$\frac{\partial c_{12}^{\text{II}}}{\partial t} = \frac{2DK}{\rho} \cdot \frac{(\partial c_4 / \partial x)^2}{(c_4^2 + 4K_{12})^{3/2}}. \quad (2.23)$$

We can extend the definitions of c_i^H and c_{12}^H to zone I because of (2.21)–(2.23) and (2.9). Then setting

$$u_i = c_i^H - c_i^I \quad \text{in } \Omega_1,$$

we reduce the original problem to an equivalent one as follows.

$$Du_{xx} - Qu_x - \theta u_t = g(x, t) \quad \text{in } \Omega_1, \quad (2.24)$$

$$-Du_x + Qu = h(t) \quad \text{on } \Gamma_1, \quad (2.25)$$

$$u(s(t), t) = 0, \quad (2.26)$$

$$-\lambda(s(t), t) \dot{s} = Du_x(s(t), t), \quad (2.27)$$

$$s(0) = 0, \quad (2.28)$$

where

$$g(x, t) = \rho c_{12t}^H = \frac{2DK(\partial c_4 / \partial t)^2}{(c_4^2 + 4K_{12})^{3/2}} \geq 0, \quad (2.29)$$

$$h(t) = \frac{Q}{2} \left(\frac{4K_{12} + c_{1F} c_4(0, t)}{(c_4^2(0, t) + 4K_{12})^{1/2}} - c_{1F} \right), \quad (2.30)$$

$$\lambda(x, t) = \rho c_{12}^H(x, t) = \rho \bar{c}_B + \int_0^t g(x, t) dt \geq \rho \bar{c}_B > 0, \quad (2.31)$$

$$u = u_1 = u_2. \quad (2.32)$$

§ 3. Classical Solution

In this section, we investigate the classical solution of PI.

Definition 3. 1. *The classical solution of PI is a triplet $\{T, u, s\}$ such that $s(t)$ belongs to $C[0, T] \cap C^1(0, T)$, $u_a \in c(\Omega_1 \cup \Gamma_1 \cup \Gamma_s)$, and $u(x, t) \in C(\bar{\Omega}_1) \cap C^{2,1}(\Omega_1)$ satisfying (2.24)–(2.28).*

Assumption A^(*).

$$2\sqrt{K_{12}} - c_{1F} > 0.$$

We have

Theorem 1. *Under Assumption A, there exists a unique solution $(T^*, s(t), u(x, t))$ to PI in $\Omega_{1,T^*} = (0, s(t)) \times (0, T^*)$ and the following cases, only these cases, are possible*

- (a) $T^* = +\infty$,
- (b) $T^* < +\infty$, but $\limsup_{t \rightarrow T^*} u_x(s(t), t) = +\infty$,
- (c) $T^* < +\infty$, but $\liminf_{t \rightarrow T^*} s(t) = 0$ or $\limsup_{t \rightarrow T^*} s(t) = l$.

The proof of this theorem depends on the following lemmas.

Lemma 3. 2. *The PI has a unique solution $c_4(x, t) \in c(\bar{\Omega}) \cap C^{2,1}(\Omega)$ satisfying*

$$0 \leq c_4(x, t) \leq c_{1F}, \quad (3.1)$$

(*) The assumption A seems natural to ensure $s(t) > 0$ as $t > 0$ is small, then it yields that the data $h(t) \geq h(0) > 0$, and $g \geq 0$, hence, are noncommon.

$$-Qc_{1F}/D \leq \frac{\partial c_4(x, t)}{\partial x} \leq 0. \quad (3.2)$$

Proof This is a classical result, and by maximum principle the estimates (3.1) and (3.2) are obtained.

Assumption B. $s(t)$ is nondecreasing and $s(t) \in C^1[0, T]$.

Decomposing

$$u = v + W, \quad (3.3)$$

one can show that v and w satisfy the following systems respectively:

$$Dv_{xx} - Qv_x - \theta v_t = g \quad \text{in } \Omega_1, \quad (3.4)$$

$$-Dv_x + Qv = 0 \quad \text{on } \Gamma_1, \quad (3.5)$$

$$v(s(t), t) = 0 \quad \text{on } \Gamma_s, \quad (3.6)$$

and

$$Dw_{xx} - Qw_x - \theta w_t = 0 \quad \text{in } \Omega_1, \quad (3.7)$$

$$-Dw_x + Qw = h(t) \quad \text{on } \Gamma_1, \quad (3.8)$$

$$w(s(t), t) = 0 \quad \text{on } \Gamma_s. \quad (3.9)$$

Lemma 3.3. Assume A and B. Then the problem (3.7)–(3.9) has a unique solution $w(x, t)$, which and $w_x(x, t)$ are continuous on $\bar{\Omega}_1 = [0, s(t)] \times [0, T]$. Moreover, the following estimates hold:

$$0 \leq w(x, t) \leq P_0(s(t) - x), \quad -P_0 \leq \frac{\partial w(s(t), t)}{\partial x} \leq 0, \quad (3.10)$$

$$|w_x| \leq P, \quad (3.11)$$

$$|w_{xx}| \leq R, \quad (3.12)$$

where P_0 and P depend only on D, Q and $\|h\|_C$, R depends only on $D, Q, \|h\|_C$ and $s(t)$.

Proof It is easy to see that $h(t) \geq h(0) > 0$. Thus the proof is the same as in [4].

Analogously, we have

Lemma 3.4. The estimates (3.10)–(3.12) hold for $-v$ with $\|h\|_C$ replaced by $\|g_x\|_\infty$.

Remark 3.5. Strictly speaking, we need the assumptions: $g \in C^{1,1/2}(\bar{\Omega}_1)$ and $h(t) \in C^1[0, T]$, but these depend on the smoothness of c_4 which is regarded as given functions. We assume that c_4 is sufficiently smooth as we need in this section.

As usual way, we have the integral representation for $s(t)$ and $u(x, t)$:

$$\Lambda(s(t), t) = \int_0^t h(t) dt - \theta \int_0^{s(t)} u(\xi, t) d\xi, \quad (3.13)$$

where

$$\Lambda(s(t), t) = \int_0^{s(t)} \lambda(\xi, t) d\xi. \quad (3.14)$$

We define the operator $F: s(t) \rightarrow b(t)$ as follows

$$\Lambda(b(t), t) = \int_0^t h(t) dt - \theta \int_0^{s(t)} u(\xi, t) d\xi. \quad (3.15)$$

Namely,

$$\dot{b}(t)\lambda(b(t), t) = h(t) - \int_0^{s(t)} (Du_{\xi\xi} - Qu_\xi - g) d\xi - \int_0^{b(t)} \lambda_t(\xi, t) d\xi. \quad (3.16)$$

Hence,

$$\dot{b}(t) \geq \{h(0) - [\|h'(t)\|_\infty + (DR + QP)K]t - \|g\|_\infty(K + b(t))t\}/(\rho c_B). \quad (3.17)$$

That is

$$\dot{b}(t) > 0$$

if $0 \leq s(t) \leq K$ and $t \in [0, \sigma]$ with sufficiently small $\sigma > 0$. For all $t \in [0, \sigma]$, we find that $0 \leq \dot{b}(t) \leq K$, and $F(s(t)) = b(t)$ keeps the monotonicity and the same bound of $s(t)$.

Proof of Theorem 1 For $t \in [0, \sigma]$, we choose the subset

$$E = \{s(t) \in C^1[0, \sigma] \mid s(t) \nearrow, s(0) = 0, 0 \leq s(t) \leq K\}$$

of Banach space $C[0, \sigma]$ and use Schauder fixed point theorem. We can show that F has a fixed point in E . The details of the proof can be found in [4]. According to Theorems 3 and 5 in [5], the solution can be extended to maximal domain $(0, s(t)) \times (0, T^*)$. On the other hand the case (b), maybe, occurs (see [6]), but in our case, if (a) is not true, i.e., $T^* < +\infty$ and (c) do not occur, we have

$$0 < \delta_1 = \liminf_{t \rightarrow T^*} s(t) \leq \limsup_{t \rightarrow T^*} s(t) = \delta_2 < 1 \quad (3.18)$$

for some δ_1 and δ_2 . As done in [7] and [8], we get, for any $0 < T_1 < T < T^*$, the following inequality

$$\int_{T_1}^T dt \int_0^{s(t)} u_{xx}^2(x, t) + \int_0^{s(T)} u(x, T) \leq K_1 + K_2 \int_{T_1}^T u_x^3(s(t), t) dt, \quad (3.19)$$

where K_i 's ($i = 1, 2, 2\dots$) are generic constants depending only on the data and δ_1, δ_2 . If (b) is not true, we conclude that

$$\int_{T_1}^{T^*} dt \int_0^{s(t)} u_{xx}^2(x, t) dx + \int_0^{s(T^*)} u_x^2(x, T^*) dx \leq K_3. \quad (3.20)$$

This means that the solution can be extended to a larger interval $[0, \bar{T}]$ with $\bar{T} > T^*$ (see [8]); the proof is completed.

Theorem 2. If $\|g\|_\infty$ is sufficiently small, then the case (b) is impossible.

Proof We observe that

$$u_x^2 u_t = 2((uu_x u_t)_x - (uu_x^2)_t)/2 - (uu_{xx} u_t)$$

and

$$\begin{aligned} 0 &= \int_{\Omega'} u_x^2 (Du_{xx} - Qu_x - \theta u_t - g) = \int_{T_1}^{T_2} Du_x^3/3 \Big|_0^{s(t)} - \int_{\Omega'} Qu_x^3 + gu_x^2 - \theta u_x^3 u_t \\ &= \int_{T_1}^{T_2} Du_x^3(s(t), t)/3 - \int_{T_1}^{T_2} (Du_x^3/3 - 2\theta uu_x u_t) \Big|_{s=0} + \theta \int_0^{s(t)} u(\xi, t) u_x^2(\xi, t) d\xi \Big|_{T_1}^{T_2} \\ &\quad - \int_{\Omega'} (\theta u_x^3 + gu_x^2) + \int_{\Omega'} uu_{xx} (Du_{xx} - Qu_x - g), \end{aligned} \quad (3.21)$$

where

$$\Omega' = (0, s(t)) \times (T_1, T_2), \quad 0 < T_1 < T_2 < \infty.$$

Hence

$$\int_{T_1}^{T_2} u_x^3(s(t), t) dt \leq \int_{\Omega} -Dv u_{xx}^2 + \varepsilon \int_{\Omega} u_{xx}^2 + K_1. \quad (3.22)$$

Here, we have used

$$\int_{\Omega} u_x^3 = \int_{\varepsilon\Omega} uu_x^2 - \int_{\Omega} 2uu_x u_{xx}, \quad w \geq 0,$$

(2.25), (3.10), (3.11) and Cauchy inequality.

By virtue of (3.19), (3.22) and noting $0 \leq -v \leq K_1 \|g\|_\infty$, we have

$$\int_{T_1}^{T_2} u_x^3(s(t), t) dt \leq K_1. \quad (3.23)$$

So, the case (b) is impossible, because of (3.19) and (3.20).

§ 4. Weak Solution

In this section, we consider the weak solution of PI. First, we introduce the following notations:

$$V = \{v \in H^1(0, l) \mid v=0, \text{ a.e. on } \Gamma_2\},$$

$$W = \{v \in L^2(0, T; V) \cap H^1(0, T; L^2(0, l)) \mid v=0, \text{ a.e. on } (0, l) \times \{T\}\},$$

$$H(\xi) = \begin{cases} 0, & \xi < 0, \\ (0, 1), & \xi = 0, \\ 1, & \xi > 0, \end{cases}$$

$$\tilde{H}(\xi) = \begin{cases} 0, & \xi \leq 0, \\ 1, & \xi > 0, \end{cases} \quad \tilde{\tilde{H}}(\xi) = \begin{cases} 0, & \xi < 0, \\ 1, & \xi \geq 0. \end{cases}$$

Noting $g = \lambda_t$, we naturally assume the following conditions:

(A1) $\lambda \in L^2(\Omega)$, $\lambda_t \in L^2(\Omega)$; $\lambda(x, t) \geq \lambda(x, 0) = \rho c_B > 0$ and $\lambda_t(x, t) \geq 0$ a.e. in Ω ;

(A2) $h \in L^2(0, T)$, $h(t) \geq h(0) > 0$ a.e. in $(0, T)$;

(A3) $h \in H^1(0, T)$, $h(t) \geq h(0) > 0$ a.e. in $(0, T)$.

Definition 4.1. A function $u(x, t)$ defined a.e. in Ω , will be called a weak solution of PI if $u \in L^2(0, T; V)$ satisfies the following identity

$$\iint_{\Omega} (Du_x - Qu) \phi_x - (\theta u + \lambda x) \phi_t = \int_0^T (t) \phi(0, t) \quad (4.1)$$

for all $\phi \in W$, where x is measurable and $\lambda \in H(u)$ a.e. in Ω .

Theorem 3. Under Assumptions (A1) and (A2), there exists a unique weak solution of PI.

Proof In the same way as in [9] we construct an approximating problem of PI as follows.

Let s be a positive infinitesimal sequence such that

$$\{H_s \in C^\infty(\mathbf{R})\}, \{\lambda_s \in C^\infty(\bar{\Omega})\}, \{h_s \in C^\infty(0, T)\}$$

and $\{u_{0s} \in C^\infty[0, l]\}$ satisfy

$$\begin{aligned} H_s(\xi) &= 0 \quad \text{if } \xi \leq 0, \\ H_s(\xi) &= 1 \quad \text{if } \xi > s, \\ 0 &\leq H'_s(\xi) \leq 2/s, \end{aligned} \tag{4.2}$$

$$\forall \xi \in \mathbb{R}, \lim_{s \rightarrow 0} H_s(\xi) = \tilde{H}(\xi);$$

$$\lambda_s \geq \rho c_B, \lambda_{st} \geq 0, \lambda_s \rightarrow \lambda \text{ and } \lambda_{st} \rightarrow \lambda_t \text{ in } L^2(\Omega) \text{ strong}; \tag{4.3}$$

$$h_s(t) \geq h(0) > 0, h_s \rightarrow h \text{ in } L^2(0, T) \text{ strong}; \tag{4.4}$$

$$u_{0s}=0 \text{ and if } x>s, -K \leq u'_{0s} \leq 0, -Du_{0s}(0)+Qu_{0s}(0)=h_s(0). \tag{4.5}$$

We introduce the following approximating problem:

P_s : to find $u_s \in C^1(\Omega \cap \Gamma_1) \cap C^2(\Omega)$ such that

$$Du_{sx} - Qu_{sx} - (\theta u_s + \lambda_s H_s(u_s))_t = 0 \quad \text{in } \Omega, \tag{4.6}$$

$$u_s = u_{0s} \quad \text{on } \Gamma_0, \tag{4.7}$$

$$-Du_{sx} + Qu_s = h_s \quad \text{on } \Gamma_1, \tag{4.8}$$

$$u_s = 0 \quad \text{on } \Gamma_2. \tag{4.9}$$

For P_s , there exists uniquely one classical solution u_s , and equation (4.7) yields

$$\int_0^1 \int_0^t (Du_{sx} - Qu_s) \phi_x + (\theta u_s + \lambda_s H_s(u_s))_t \phi = \int_0^t h_s(\tau) \phi(0, \tau) \tag{4.10}$$

for all $\phi \in L^2(0, T; V)$.

After taking $\phi = u_s$ in (4.10), we obtain

$$\int_0^1 \int_0^t u_{sx}^2 + \int_0^1 u_s^2(x, t) dx + \int_0^1 \lambda_{st}(x, t) \int_0^{u_s(x, t)} H'_s(\xi) \xi d\xi dx + \int_0^t u_s^2(0, t) dt \leq K, \tag{4.11}$$

where K depends only on $\|h(t)\|_{L^2(0, T)}$, $\|\lambda_t\|_{L^2(\Omega)}$, $\|\lambda\|_{L^2(\Omega)}$.

Hence

$$\|u_s\|_{L^\infty(0, T; L^2(0, 1)) \cap L^2(0, T; H^1(0, 1))} \leq K \tag{4.12}$$

and

$$0 \leq H_s(u_s) \leq 1, \quad \int_0^1 \int_0^T H_s(u_s) dx dt \leq K. \tag{4.12}'$$

By (4.11) and (4.12), there exist u and ω , such that, passing to subsequences if necessary, as $s \rightarrow 0$,

$u_s \rightarrow u$ in $L^\infty(0, T; L^2(0, 1))$ weak star and in $L^2(0, T; H^1(0, 1))$ weak,

$$(4.13)$$

$H_s(u_s) \rightarrow \omega$ in $L^\infty(\Omega)$ weak star and in $L^2(\Omega)$ weak, (4.14)

From (4.10), one finds^[9]

$$\iint_{\Omega} (Du_x - Qu) \phi_x - (Du + \lambda \omega) \phi_t = \int_0^T h(t) \phi(0, t) dt, \quad \forall \phi \in H^1(\Omega). \tag{4.15}$$

In order to complete the proof of existence, it thus remains to show that $\omega \in H(u)$. This is done in [9], i.e.,

$$\tilde{H}(u) \leq \omega \leq \tilde{\tilde{H}}(u) \quad \text{a. e. in } \Omega. \tag{4.16}$$

Concerning the uniqueness, we suppose that u_1, κ_1 and u_2, κ_2 are two weak solutions. Set $w = u_1 - u_2$ and

$$\phi = \begin{cases} \text{Exp}\left(-\frac{Q}{D}x\right) \int_{t_1}^t w(x, \tau) d\tau, & 0 \leq t \leq t_1, \\ 0, & t_1 \leq t \leq T. \end{cases}$$

Then

$$\iint (Dw_\alpha - Qw) \phi_\alpha - \theta w \phi_t - \lambda(\kappa_1(u_1) - \kappa_2(u_2)) \phi_t = 0. \quad (4.17)$$

Applying (A1) and $(\kappa_1(u_1) - \kappa_2(u_2))(u_1 - u_2) \geq 0$, we get

$$0 = \frac{D}{2} \int_0^1 \text{Exp}\left(\frac{Qx}{D}\right) \phi_x^2(x, 0) dx + \theta \int_0^1 \int_0^{t_1} \text{Exp}\left(-\frac{Q}{D}x\right) \cdot w^2(x, t) dx dt \\ + \int_0^1 \int_0^{t_1} \lambda(\kappa_1(u_1) - \kappa_2(u_2))(u_1 - u_2) \text{Exp}\left(-\frac{Q}{D}x\right) dx dt.$$

Hence, $w = 0$ a. e. in Ω .

We proceed to consider the regularity and properties of the weak solution.

Theorem 4. Under the assumptions (A1) and (A3), the weak solution u of PI belongs to $L^\infty(0, T; H(0, 1)) \cap H^1(0, T; L^2(0, 1)) \cap C^{1/2, 1/4}(\bar{\Omega})$, and $u \geq 0$ in Ω .

Proof The proof follows from (4.10) by taking $\phi = u_{st}$, the maximum principle and imbedding theorem.

Lemma 4. 2. The set $S = \{t \in [0, T] \mid u(0, t) > 0\}$ is dense in $[0, T]$.

Proof For any $t = t_0 > 0$, in (4.10) taking

$$\phi(x, t) = \begin{cases} (\delta - x)^2(t - t_0)^2(t_1 - t)^2 & \text{in } (0, \delta) \times (t_0, t_1), \\ 0, & \text{otherwise,} \end{cases}$$

we have

$$\begin{aligned} & \int_{t_0}^{t_1} Du(0, t) \delta(t - t_0)^2(t_1 - t)^2 - \int_0^\delta \int_{t_0}^{t_1} (Du - 2Qu(\delta - x))(t - t_0)^2(t_1 - t)^2 \\ & - \int_0^\delta \int_{t_0}^{t_1} (\theta u + \lambda \kappa) 2(\delta - x)^2(t - t_0)(t_0 + t_1 - 2t)(t_1 - t) \\ & = \int_{t_0}^{t_1} h(t) \delta^2(t_1 - t)^2(t - t_0)^2. \end{aligned} \quad (4.18)$$

Then let $\delta = \eta(t_1 - t_0)$ ($0 < \eta \ll 1$), (4.18) gives

$$\begin{aligned} & \int_0^1 u(0, t_0 + \alpha(t_1 - t_0)) \alpha^2(1 - \alpha)^2 d\alpha \\ & \geq \eta(t_1 - t_0) \int_0^1 h(t_0 + \alpha(t_1 - t_0)) \alpha^2(1 - \alpha)^2 d\alpha - K \int_0^1 \eta^2(1 - \alpha)\alpha|2\alpha - 1| d\alpha \cdot (t_1 - t_0) \\ & \geq h(0)(t_1 - t_0)^2 \eta/2 > 0. \end{aligned} \quad (4.19)$$

So, there exists $\xi \in [t_0, t_1]$, such that $u(0, \xi) > 0$. Here we have used the fact that η is sufficiently small and the continuity of $u \geq 0$ from Theorem 4. In sequel, we also assume (A1) and (A3) hold.

Theorem 5. If $h(0) \geq Ml$ ($M = \max_i \lambda_i$), then the weak solution $u(0, t) > 0$, $\forall t \in (0, T)$.

Proof Let.

$$z = u_s + w, \quad (4.20)$$

where

$$w = -M(l-x-D(1-\text{EXP}(-Q(l-x)/D)/Q)/Q. \quad (4.21)$$

For any $t_0 \in (0, T)$, a quick calculation in $\Omega \cap \{t > t_0\}$ gives

$$Dz_{xx} - Qz_x - (\theta + \lambda H'_s(u_s))z_t = \lambda_t H_s(u_s) - M \leq 0,$$

$$z(1, t) = 0,$$

$$-Dz_x + Qz|_{x=0} = h(t) - Ml \geq h(0) - Ml \geq 0.$$

By maximum principle, the negative minimum value of z can not be reached in $\bar{\Omega} \cap \{t > t_0\}$, and there exists a point (x_s, t_0) satisfying

$$\min_{\Omega \cap \{t > t_0\}} z = z(x_s, t_0) < 0, \quad (4.22)$$

i. e.,

$$z(x, t) \geq u_s(x_s, t_0) + w(x_s, t_0), \quad \forall t \in [t_0, T].$$

Hence,

$$\begin{aligned} u_s(0, t) &\geq u_s(x_s, t_0) + M(x_s - (\text{EXP}(\alpha(1-x_s)) - \text{EXP}(-l\alpha))/\alpha)/Q \\ &\quad \left(\alpha = \frac{Q}{D} \right). \end{aligned} \quad (4.23)$$

Since $0 < x_s < 1$, there exists x^* such that, passing to subsequences if necessary, as $s \rightarrow 0$,

$$x_s \rightarrow x^*.$$

If $x^* = 0$, then $u(0, t) \geq u(0, t_0)$, and if $x^* \neq 0$, then

$$u(0, t) \geq M(x^* - (\text{EXP}(-\alpha(1-x^*)) - \text{EXP}(-\alpha l))/\alpha)/(\alpha D) > 0. \quad (4.24)$$

Applying lemma 4.2, we can choose $t_0 \in (0, T)$ with $u(0, t_0) > 0$. (4.24) then implies $u(0, t) > 0 \quad \forall t \in (0, T)$.

We conclude this paper by proving the following important property of weak solution.

Theorem 6. If $\text{mes}\{x \in (0, 1) | \lambda(x, 0) > 0\} > 0$, then

$$\text{mes}\{(x, t) \in \Omega | u(x, t) = 0\} > 0. \quad (4.25)$$

Proof Suppose $u(x, t) > 0$ a. e. in Ω . Then u satisfies (4.7)–(4.9) and (4.6) with $H_s(u_s) = 1$. Thus

$$\begin{aligned} \iint_{\Omega} (Du_x - Qu) \phi_x - (\theta u + \lambda) \phi_t - \int_0^t \lambda(x, 0) \phi(x, 0) \\ = \int_0^T h(t) \phi(0, t) dt, \quad \forall \phi \in W. \end{aligned} \quad (4.26)$$

Comparing (4.26) with (4.15) ($n=1$), we obtain

$$\int_0^1 \lambda(x, 0) \phi(x, 0) dx = 0, \quad (4.27)$$

and it yields

$$\lambda(x, 0) = 0 \quad \text{a. e. in } (0, 1). \quad (4.27)$$

This contradiction leads to the completion of the proof.

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References

- [1] Guan Zhicheng Groundwater Mass Transport and Homogeneous Equilibrium Chemistry in the Presence of Flux Boundary Conditions (to appear).
- [2] Rubin, J., Transport of Reacting Solution in Porous Media: Relation Mathematical Nature of Problem Formulation and Chemical Nature of Reactions, *Water Resources Research*, **19**: 5(1983), 1231—1252.
- [3] Ladyzenskaja, O. A., Solonnikov, V. A. & Ural'ceva, N. N., Linear and Quasilinear Equations of Parabolic Type, American Mathematical Society, Providence, 1968.
- [4] Jiang Lishang, The Proper Posing of Free Boundary Problems for Nonlinear Parabolic Differential Equation, *Acta Math. Sinica*, **12**: 4(1962), 369—388.
- [5] Fasano, A. & Primicerio, M., General Free Boundary Problems for Heat Equation I, *J. Math. Anal. Appl.*, **57**: 3(1977), 694—723.
- [6] Primicerio, M., The Occurrence of Pathologies in Some Stefan-Like Problem, *Int. Ser. Num. Math.*, **58** (1982), 233—244.
- [7] Evans, L. C., A Free Boundary Problem. The Flow of Two Immiscible Fluids in a One-Dimensional Porous Medium II., *Ind. Univ. Math. J.*, **28**(1978), 93—111.
- [8] Knabner, P., Global Existence in a General Stefan-Like Problem, (Preprint).
- [9] Visintin, A., General Free Boundary Evolution Problems in Several Space Dimensions, *J. Math. Anal. Appl.*, **95**: 1(1983), 117—143.