Mathematical modeling of hydrogen diffusion in biphasic steel.

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Abstract

1 Model

The main model consists of hydrogen diffusion two-phase system, in which there is a bulk phase, with spherical precipitates in it, disperse enough so that we can do homogenization. Moreover, consider that the precipitates have a radius of R, that the bulk diffusivity is D, the precipitate diffusivity is α, and there is Γ precipitates per unit volume (we can get this statistics from the volume fraction, assuming spherical particles).

We denote by $c(x,t)$ the hydrogen concentration at the bulk phase, while we denote by $n(r,t;x)$ the concentration of hydrogen in the precipitate at x, on radius r (of the precipitate) and time t.

The interface between two phases satisfies both the continuity of chemical potential, which translates to

$$\frac{c}{n} = \frac{S_c}{S_n} = \exp\left(\frac{\mu_c - \mu_n}{RT}\right) =: K, \tag{1}$$

and the continuities of fluxes

$$J_c = J_n = J. \tag{2}$$

Now, consider an interface at (x,t). From the point of view of the bulk, we can think of this interface as being a sink for the bulk concentration, at the boundary. Then, *each precipitate* results in a volumetric sink of strength $4\pi R^2 J$. Of course, then we have that the sink per unit volume becomes $4\pi R^2 \Gamma J$. Therefore, we can consider the bulk transport as following a diffusion equation with sink

$$\frac{\partial c}{\partial t}(x,t) = D\frac{\partial^2 c}{\partial x^2}(x,t) - 4\pi R^2 \Gamma J. \tag{3}$$

Now, from the point of view of the precipitate at x, we have that the continuity of chemical potentials makes that, at the interface *from the precipitate* *size*, we can consider a time-varying inlet concentration dependant on $c(x,t)$. That is, at $r = R$ (and $r = -R$), we must have

$$n(R, t; x) = c(x, t). \tag{4}$$

As for the precipitate itself, it follows that it must obey the spherically symmetric form of the diffusion equation

$$\frac{\partial n}{\partial t}(r,t,x) = \alpha \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial n}{\partial r}(r,t,x)\right) \tag{5}$$

And, of course, Fick's first law says that we can calculate the flux J from the precipitate side, given by

$$J = -\alpha \frac{\partial n}{\partial r}(R,t). \tag{6}$$

. Therefore, we end up with the model as in the next section.

2 Derivation of bulk equation

Consider then

$$\begin{aligned}
&\frac{\partial c}{\partial t}(x,t) = D\frac{\partial^2 c}{\partial x^2}(x,t) - 4\pi R^2 \Gamma J; t \geq 0, 0 \leq x \leq L \\
&\frac{\partial n}{\partial t}(r,t,x) = \alpha \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial n}{\partial r}(r,t,x)\right); \quad t \geq 0, -R \leq x \leq R \\
&J = -\alpha \frac{\partial n}{\partial r}(R,t) \\
&n(R,t,x) = n(-R,t,x) = Kc(x,t)
\end{aligned} \tag{7}$$

First: solving n differential equation. Ommiting x, let $m(r,t) := n(r,t) - c(t)$. Hence,

$$\frac{\partial m}{\partial t}(r,t) = \alpha \mathcal{O}[m](r,t) + c'(t); \quad m(r,t) = m(-R,t) = 0, \tag{8}$$

with

$$\mathcal{O}(m) = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial m}{\partial r}\right) \tag{9}$$

Using separation of variables, let $m(r,t) = T(t)\varphi(r)$. Hence, we have

$$T'\varphi = \alpha \mathcal{O}[\varphi]T + c'(t) \tag{10}$$

We look then at the eigenvalue problem

$$\mathcal{O}[\varphi] = -\lambda\varphi, \tag{11}$$

or

$$r^2\varphi'' + 2r\varphi' + \lambda r^2\varphi = 0. \tag{12}$$

The above equation equals to

$$(r\varphi)'' + \lambda(r\varphi) = 0. \tag{13}$$

Considering $\varphi(R) = \varphi(-R) = 0$, for $\lambda_0 <= 0$, $\varphi(R) = 0$, and, for $\lambda > 0$,

$$(r\varphi) = R\sin\left(\sqrt{\lambda_k}r\right); \quad \sqrt{\lambda_k} = \frac{\pi k}{R} \tag{14}$$

Hence, the eigenvalue problem is

$$\varphi_k(r) = \pi k j_0(\pi k r/R); \quad \lambda_k = \frac{\pi^2 k^2}{R^2}; \quad k = 1, 2, ... \tag{15}$$

with $j_0(x) = \sin(x)/x$ being the zeroth spherical Bessel function of the first kind (who is also the sinc function).

Getting already some things off the table, we have that φ_k forms an base of functions, that has the orthonormality relations

$$\frac{1}{R}\int_{-R}^{R}(r/R)^2\varphi_k(r)\varphi_l(r)dr = \delta_{m,l}. \tag{16}$$

due to

$$\begin{aligned}
&\frac{1}{R}\int_{-R}^{R}(r/R)^2\varphi_k(r)\varphi_l(r)dr = \\
&2\pi^2k^2\int_0^1 u^2 j_o(\varphi k u)j_0(\varphi l u)du = \\
&2\pi^2k^2\frac{\delta_{k,l}}{2}(j_1(\pi k))^2 = \\
&\delta_{k,l}\pi^2k^2\left(\frac{-(-1)^k}{\pi k}\right)^2 = \\
&\delta_{k,l}
\end{aligned}, \tag{17}$$

with $j_1(x)$ being the first spherical Bessel function of the first kind. Hence, for any (suitable) $f(r)$, we can decompose

$$\begin{aligned}
f(r) &= \sum_{k=1}^{\infty} f_k\varphi_k \\
f_k(r) &= \frac{1}{R}\int_{-R}^{R}(r/R)^2 f(r)\varphi_k(r)dr.
\end{aligned} \tag{18}$$

. In particular, we use the decomposition

$$Kc'(t) = \sum_{k=1}^{\infty} Kc_k'(t)\varphi_k(t). \tag{19}$$

We have that, using the eigenvalue problem, decomposing

$$m(r,t) = \sum_{k=1}^{\infty} \psi_k(t)\varphi_k(r), \tag{20}$$

we have that

$$\sum_{k=1}^{\infty} \left(\psi_k'(t) + \lambda_k \alpha \psi_t - c_k'(t)\right) \varphi(k) = 0, \tag{21}$$

Hence, we have

$$\psi_k(t) = e^{-\alpha\lambda_k t} \left(\psi_k(0) + \int_0^t e^{\alpha\lambda k\tau} K c_k'(\tau) d\tau \right), \tag{22}$$

or, assuming $\psi_k(0) = 0$ (because we will consider $n(0,t,x) = 0$ and $c(0,t) = 0$),

$$\begin{aligned}
\psi_k(t) = K e^{-\alpha\lambda_k t} \int_0^t e^{\alpha\lambda k\tau} c'(\tau) \frac{1}{R} \int_{-R}^{R} (r/R)^2 \varphi_k(r) dr d\tau = \\
= -2K \frac{(-1)^k}{\pi k} e^{-\alpha\lambda_k t} \int_0^t e^{\alpha\lambda_k \tau} c'(\tau) d\tau = \\
-2K \frac{(-1)^k}{\pi k} \left(c(t) + e^{-\alpha\lambda_k t} c(0) - \frac{e^{-\alpha\lambda_k t}}{\lambda_k t} \int_0^t e^{\alpha\lambda_k t} c(\tau) d\tau \right).
\end{aligned} \tag{23}$$

And, we remember that $m(r,t) = n(0,t) + c(t)$. Finally, we can then find

$$J = \alpha \frac{\partial n}{\partial r}(t,R) = -\alpha \sum_{k=1}^{\infty} \psi_k(t) \frac{\partial \varphi_k}{\partial r}(R). \tag{24}$$

. But, we have that $\frac{\partial \varphi_k}{\partial r}(R) = (-1)^k \pi k / R$. Hence, we can join everything and find that

$$J = \frac{2}{R} \alpha K \sum_{k=1}^{\infty} \left(c(t) + e^{-\alpha\lambda_k t} c(0) - \frac{e^{-\alpha\lambda_k t}}{\lambda_k t} \int_0^t e^{\alpha\lambda_k t} c(\tau) d\tau \right). \tag{25}$$

Therefore, our equation for c becomes (showing again x):

$$\begin{aligned}
\frac{\partial c}{\partial t}(x,t) = & D \frac{\partial^2 c}{\partial x^2}(x,t) - \\
& 8\pi R \Gamma \alpha K \sum_{k=1}^{\infty} \left(c(x,t) + e^{-\alpha\lambda_k t} c(x,0) - \frac{e^{-\alpha\lambda_k t}}{\lambda_k t} \int_0^t e^{\alpha\lambda_k t} c(x,\tau) d\tau \right),
\end{aligned} \tag{26}$$

or

$$\frac{\partial c}{\partial t}(x,t) = D \frac{\partial^2 c}{\partial x^2}(x,t) - 8\pi R \Gamma \alpha K \sum_{k=1}^{\infty} e^{-\alpha\lambda_k t} \int_0^t e^{\alpha\lambda_k \tau} c'(\tau) d\tau \tag{27}$$

or still

$$\begin{aligned}\frac{\partial c}{\partial t}(x,t) &= D\frac{\partial^2 c}{\partial x^2}(x,t) - 8\pi R\Gamma\alpha K\sum_{k=1}^{\infty}(\omega_k *_t c')(x,t) \\ \omega_k(t) &= \exp\left(-\frac{\alpha\pi^2k^2t}{R^2}\right),\end{aligned} \tag{28}$$

with $(f *_t g)(x,t) = \int_0^t f(x,t-\tau)g(x,tau)d\tau$ being the convolution evaluated in the t argument.

Of course, we can simplify things by making

$$\begin{aligned}\beta &:= 8\pi R\Gamma\alpha K \\ \omega &:= \sum_{k=1}^{\infty}\omega_k = \sum_{k=1}^{\infty}\exp\left(-\frac{\alpha\pi^2k^2t}{R^2}\right),\end{aligned} \tag{29}$$

resulting in (28) being written as

$$\frac{\partial c}{\partial t} + \beta\left(\omega *_t \frac{\partial c}{\partial s}\right) = D\frac{\partial^2 c}{\partial x^2}, \tag{30}$$

or, expanding the convolution,

$$\frac{\partial}{\partial t}c(x,t) + \beta\int_0^t \omega(t-s)\frac{\partial}{\partial s}c(x,s)ds = D\frac{\partial^2 c}{\partial x^2}(x,t) \tag{31}$$

2.1 Cylindric precipitates, *mutatis mutandis*

If we consider the approximation by cylindric precipitates, then, defining Γ_c as the amount precipitates per cross-sectional area, we can follow the same arguments above (now using Bessel functions of the first kind), and arrive at almost the same equations, now with

$$\begin{aligned}\beta &= 4\pi\Gamma\alpha K \\ \omega &= \sum_{k=1}^{\infty}\omega_k = \sum_{k=1}^{\infty}\exp\left(-\frac{\alpha u_{0,k}^2 t}{R^2}\right),\end{aligned} \tag{32}$$

with $u_{0,k}$ being the k-th zero of the zeroth Bessel function of the first kind.

3 Discretization

Let's discretize this. Forgetting about x for now, consider only the operator

$$\frac{\partial}{\partial t}c(t) + \beta\int_0^t \omega(t-s)\frac{\partial}{\partial s}c(s)ds. \tag{33}$$

Now, consider a discretization

$$\begin{aligned}
&t_0, t_1, \ldots, t_n, t_{n+1} \\
&c_0, c_1, \ldots, c_n, c_{n+1} \\
&h_i := t_i - t_{i-1} \\
&t_{i+1/2} = (t_{i+1} - t_i)/2
\end{aligned} \tag{34}$$

Then, we can discretize the integral at time t_{n+1} by

$$\int_0^t \omega(t-s)\frac{\partial}{\partial s}c(s)ds \approx \sum_{i=0}^{n} \omega(t_{n+1} - t_{i+1/2})(c_{i+1} - c_i). \tag{35}$$

Separating the c_{n+1} from the rest, and defining $\omega^{n+1,i}$ as $\omega(t_{n+1} - t_{i+1/2})$, we have the discretization as a function of c_{n+1}

$$\frac{c_{n+1} - c_n}{h_{n+1}} + \beta(c_{n+1} - c_n)\omega^{n+1,n} + \beta \sum_{i=0}^{n-1}(c_{i+1} - c_i)\omega^{n+1,i}, \tag{36}$$

or

$$\left(\frac{1}{h_{n+1}} + \beta\omega^{n+1,n}\right)c_{n+1} - \left(\frac{1}{h_{n+1}} + \beta\omega^{n+1,n}\right)c_n + \beta\sum_{i=0}^{n-1}(c_{i+1} - c_i)\omega^{n+1,i}. \tag{37}$$

Now, considering the space discretization [1], let the discretized operator matrix be A letting $\mathbf{c}$ be the space discretization vector, we have that, using the implicit Euler method, the above problem translates to (rewritten so that we guarantee a positive diagonal)

$$\begin{aligned}
&\left(-A + (h_{n+1}^{-1} + \beta\omega^{n+1,n})I\right)\mathbf{c}_{n+1} = \\
&-\beta\sum_{i=0}^{n-1}(\mathbf{c}_{i+1} - \mathbf{c}_i)\omega^{n+1,i} + \left(h_{n+1}^{-1} + \beta\omega^{n+1,n}\right)\mathbf{c}_n,
\end{aligned} \tag{38}$$

which we can then solve at each time step. Some notes here

- In practice, ω decays as $t_{n+1} - t_i$ grows large. Can probably do some cutoff here.
- If we use a constant time step, we can define $\hat{\omega}^j := \omega^{n+1,n-j} = \omega(h(j + 1/2))$. We just calculate beforehand for some values of j and hold the values (remembering the cutoff note above).

4 Results

There are the results of a simulation of this model, with unit concentration at the inlet and zero concentration at the outlet.

[1] can be finite differences, elements, or whatever

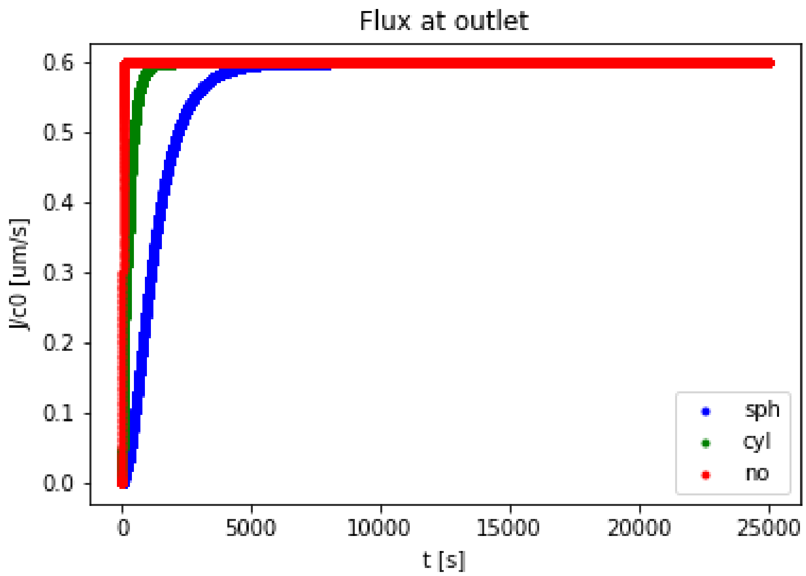

Figure 1

- Physical parameters (some taken from Olden)
  - D - 6.0*1e-1 $\mu m^2/s$
  - α - 1.4*1e-4 $\mu m^2/s$
  - K - 32.51/0.033
  - $R = 5\ \mu m$
  - Γ - 0.0007639437268410977 μm^{-3} (from 0.1 of volumetric fraction)
  - L - 100 μm
- Solver parameters
  - Space discretization points = 21
  - Size of kernel expansion = 10
  - Time step = 0.25
  - Decay limit = 0.1
  - Memory's maximum size = 1000

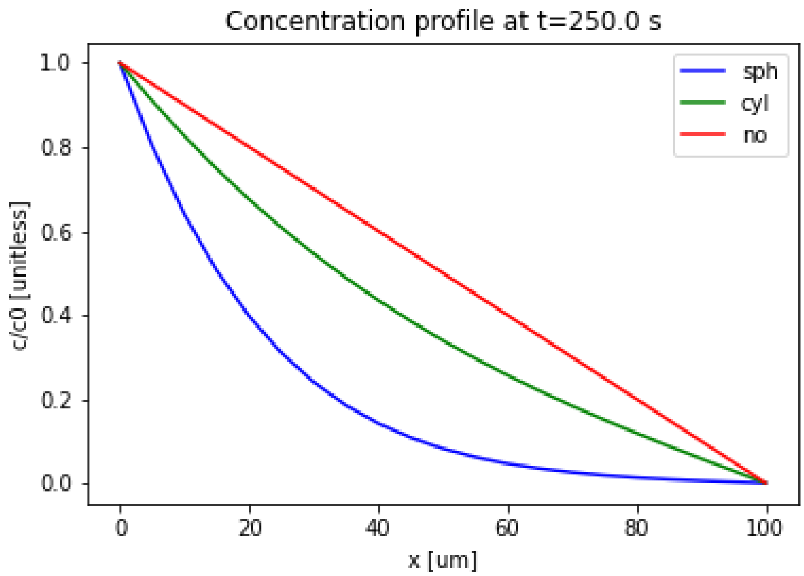

Figure 2

A Transform approaches

A.1 Fourier transforming bulk equation

We can do other things. Let's try to Fourier transform this (in t). Let $C(x,s) = \mathcal{F}_t(c(x,t))(s)$. Hence, we have that

$$\mathcal{F}_t\left(\frac{\partial}{\partial t}c(x,t)\right)(s) = 2\pi i s C(x,s) \tag{39}$$

$$\mathcal{F}_t\left(\sum_{k=1}^{\infty}(\omega_k *_t c')(x,t)\right) = C(x,s)\sum_{k=1}^{\infty}\frac{1}{1 - i\frac{\alpha\pi^2 k^2}{2R^2\pi s}}, \tag{40}$$

or

$$\mathcal{F}_t\left(\sum_{k=1}^{\infty}(\omega_k *_t c')(x,t)\right) = C(x,s)\sum_{k=1}^{\infty}\frac{1}{1+\left(\frac{\alpha\pi^2k^2}{2R^2\pi s}\right)^2}\left(1 + i\frac{\alpha\pi^2 k^2}{2R^2\pi s}\right), \tag{41}$$

and the diffusive term stays the same. Hence, joining everything

$$C(x,s)\zeta(s) = D\frac{\partial^2 C}{\partial x^2}(x,s), \tag{42}$$

with

$$\zeta(s) = 2\pi i s + 8\pi R\Gamma\alpha K\sum_{k=1}^{\infty}\frac{1}{1 - i\frac{Ak^2}{s}}; \quad A = \frac{\alpha\pi}{2R^2} \tag{43}$$

A.2 Laplace transforming bulk equation

In a similar manner, we try Laplace transform then. Let $\mathcal{C}(x,s) = \mathcal{L}_t(c(x,t))(s)$. He have that

$$\mathcal{L}_t\left(\frac{\partial}{\partial t}c(x,t)\right)(s) = s\mathcal{C}(x,s) - c(x,0), \tag{44}$$

and

$$\mathcal{L}_t\left(\sum_{k=1}^{\infty}(\omega_k *_t c')(x,t)\right) = (s\mathcal{C}(x,s) - c(x,0))\sum_{k=1}^{\infty}\frac{1}{1+\frac{\alpha\pi^2k^2}{R^2}s} \tag{45}$$

$$\sum_{k=1}^{\infty}\frac{1}{1+\frac{\alpha\pi^2k^2}{R^2}s} = \frac{1}{2}\left(\sqrt{\frac{R}{\alpha}}s^{-1/2}\coth\left(\sqrt{\frac{R}{\alpha}}s^{-1/2}\right) - 1\right). \tag{46}$$

Since we assumed $c(x,0) = 0$, the equation for $\mathcal{C}$ becomes

$$\begin{aligned} \mathcal{C}(x,s)\xi(s) &= \frac{\partial^2\mathcal{C}}{\partial x^2}(x,s) \\ \xi(s) &= \frac{s}{D}\left(1+\frac{\beta}{2}\left(\sqrt{\frac{R}{\alpha s}}\coth\left(\sqrt{\frac{R}{\alpha s}}\right)-1\right)\right) \end{aligned}. \tag{47}$$

We must have

$$\mathcal{C}(x,s) = A(s)e^{\sqrt{\xi(s)}x} + B(s)e^{-\sqrt{\xi(s)}x} \tag{48}$$

Using Dirichlet conditions $c(0,s) = c_0$, $c(L,s) = 0$, we have that $\mathcal{C}(0,s) = c_0/s$, $\mathcal{C}(L,0) = 0$, and we find $A(s), B(s)$ solving the system

$$\begin{bmatrix} 1 & 1 \\ e^{\sqrt{\xi(s)}L} & e^{-\sqrt{\xi(s)}L} \end{bmatrix}\begin{bmatrix} A(s) \\ B(s) \end{bmatrix} = \begin{bmatrix} c_0/s \\ 0 \end{bmatrix}, \tag{49}$$

We have that

$$\begin{aligned} A(s) &= \frac{e^{-\sqrt{\xi(s)}L}}{e^{-\sqrt{\xi(s)}L} - e^{\sqrt{\xi(s)}L}}\frac{c_0}{s} \\ B(s) &= -\frac{e^{\sqrt{\xi(s)}L}}{e^{-\sqrt{\xi(s)}L} - e^{\sqrt{\xi(s)}L}}\frac{c_0}{s} \end{aligned} \tag{50}$$

Then, we have that

$$\mathcal{C}(x,s) = \frac{c_0}{s\left(e^{-\sqrt{\xi(s)}L} - e^{\sqrt{\xi(s)}L}\right)}\left(e^{-\sqrt{\xi(s)}(L-x)} - e^{\sqrt{\xi(s)}(L-x)}\right) \tag{51}$$

Or, simplifying

$$\frac{c_0}{s}\frac{\sinh\left(\sqrt{\xi(s)}(L-x)\right)}{\sinh\left(\sqrt{\xi(s)}L\right)} \tag{52}$$

For each x, Laplace-invert $\mathcal{C}(x,s)$. Have no idea how tough this is numerically.