# Mathematical modeling of hydrogen diffusion in biphasic steel.

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**Abstract**

## 1 Derivation of bulk equation

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

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

$$
\frac{\partial m}{\partial t}(r,t) = \alpha \mathcal{O}[m](r,t) + c'(t); \quad m(r,t) = m(-R,t) = 0, \tag{2}
$$

with

$$
\mathcal{O}(m) = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial m}{\partial r}\right) \tag{3}
$$

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

$$
T'\varphi = \alpha \mathcal{O}[\varphi] T + c'(t) \tag{4}
$$

We look then at the eigenvalue problem

$$
\mathcal{O}[\varphi] = -\lambda \varphi, \tag{5}
$$

or

$$
r^2 \varphi'' + 2r\varphi' + \lambda r^2 \varphi = 0. \tag{6}
$$

The above equation equals to

$$(r\varphi)'' + \lambda(r\varphi) = 0. \tag{7}$$

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

$$(r\varphi) = R\sin\left(\sqrt{\lambda_k}r\right); \quad \sqrt{\lambda_k} = \frac{\pi k}{R} \tag{8}$$

Hence, the eigenvalue problem is

$$\varphi_k(r) = \pi k j_0(\pi k r/R); \quad \lambda_k = \frac{\pi^2 k^2}{R^2}; \quad k = 1, 2, ... \tag{9}$$

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 $\varphi_k$ forms an base of functions, that has the orthonormality relations

$$\frac{1}{R}\int_{-R}^{R}(r/R)^2\varphi_k(r)\varphi_l(r)dr = \delta_{m,l}. \tag{10}$$

due to

$$\begin{aligned}
&\frac{1}{R}\int_{-R}^{R}(r/R)^2\varphi_k(r)\varphi_l(r)dr = \\
&2\pi^2k^2\int_0^1 u^2 j_o(\varphi k u)j_0(\varphi l u)du = \\
&2\pi^2k^2\frac{\delta_{k,l}}{2}(j_1(\pi k))^2 = \\
&\delta_{k,l}\pi^2k^2\left(\frac{-(-1)^k}{\pi k}\right)^2 = \\
&\delta_{k,l}
\end{aligned}, \tag{11}$$

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

$$\begin{aligned}
f(r) &= \sum_{k=1}^{\infty} f_k\varphi_k \\
f_k(r) &= \frac{1}{R}\int_{-R}^{R}(r/R)^2 f(r)\varphi_k(r)dr.
\end{aligned} \tag{12}$$

. In particular, we use the decomposition

$$Kc'(t) = \sum_{k=1}^{\infty} Kc'_k(t)\varphi_k(t). \tag{13}$$

We have that, using the eigenvalue problem, decomposing

$$m(r,t) = \sum_{k=1}^{\infty} \psi_k(t)\varphi_k(r), \tag{14}$$

we have that

$$\sum_{k=1}^{\infty} \left(\psi_k'(t) + \lambda_k \alpha \psi_t - c_k'(t)\right) \varphi(k) = 0, \tag{15}$$

Hence, we have

$$\psi_k(t) = e^{-\alpha\lambda_k t}\left(\psi_k(0) + \int_0^t e^{\alpha\lambda k\tau} K c_k'(\tau) d\tau\right), \tag{16}$$

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

$$\begin{aligned}\psi_k(t) = K e^{-\alpha\lambda_k t}\int_0^t e^{\alpha\lambda k\tau} c'(\tau) \frac{1}{R}\int_{-R}^{R} (r/R)^2 \varphi_k(r) dr d\tau = \\ = -2K\frac{(-1)^k}{\pi k} e^{-\alpha\lambda_k t}\int_0^t e^{\alpha\lambda_k\tau} c'(\tau) d\tau = \\ -2K\frac{(-1)^k}{\pi k}\left(c(t) + e^{-\alpha\lambda_k t}c(0) - \frac{e^{-\alpha\lambda_k t}}{\lambda_k t}\int_0^t e^{\alpha\lambda_k t} c(\tau) d\tau\right).\end{aligned} \tag{17}$$

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

$$J = \alpha\frac{\partial n}{\partial r}(t,R) = -\alpha\sum_{k=1}^{\infty}\psi_k(t)\frac{\partial\varphi_k}{\partial r}(R). \tag{18}$$

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

$$J = \frac{2}{R}\alpha K\sum_{k=1}^{\infty}\left(c(t) + e^{-\alpha\lambda_k t}c(0) - \frac{e^{-\alpha\lambda_k t}}{\lambda_k t}\int_0^t e^{\alpha\lambda_k t}c(\tau)d\tau\right). \tag{19}$$

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

$$\begin{aligned}\frac{\partial c}{\partial t}(x,t) =& D\frac{\partial^2 c}{\partial x^2}(x,t) - \\ & 8\pi R\Gamma\alpha K\sum_{k=1}^{\infty}\left(c(x,t) + e^{-\alpha\lambda_k t}c(x,0) - \frac{e^{-\alpha\lambda_k t}}{\lambda_k t}\int_0^t e^{\alpha\lambda_k t}c(x,\tau)d\tau\right),\end{aligned} \tag{20}$$

or

$$\frac{\partial c}{\partial t}(x,t) = D\frac{\partial^2 c}{\partial x^2}(x,t) - 8\pi R\Gamma\alpha K\sum_{k=1}^{\infty} e^{-\alpha\lambda_k t}\int_0^t e^{\alpha\lambda_k\tau}c'(\tau)d\tau \tag{21}$$

or still

$$\begin{aligned}\frac{\partial c}{\partial t}(x,t) &= D\frac{\partial^2 c}{\partial x^2}(x,t) - 8\pi R\Gamma\alpha K\sum_{k=1}^{\infty}(\omega_k *_t c')(x,t)\\ \omega_k(t) &= \exp\left(-\frac{\alpha\pi^2 k^2 t}{R^2}\right),\end{aligned} \tag{22}$$

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

$$\begin{aligned}\beta &:= 8\pi R\Gamma\alpha K\\ \omega &:= \sum_{k=1}^{\infty}\omega_k = \sum_{k=1}^{\infty}\exp\left(-\frac{\alpha\pi^2 k^2 t}{R^2}\right),\end{aligned} \tag{23}$$

resulting in (22) being written as

$$\frac{\partial c}{\partial t} + \beta\left(\omega *_t \frac{\partial c}{\partial s}\right) = D\frac{\partial^2 c}{\partial x^2}, \tag{24}$$

or, expanding the convolution,

$$\frac{\partial}{\partial t}c(x,t) + \beta\int_0^t \omega(t-s)\frac{\partial}{\partial s}c(x,s)ds = D\frac{\partial^2 c}{\partial x^2}(x,t) \tag{25}$$

# 2 Discretization

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

$$\frac{\partial}{\partial t}c(t) + \beta\int_0^t \omega(t-s)\frac{\partial}{\partial s}c(s)ds. \tag{26}$$

Now, consider a discretization

$$\begin{aligned}&t_0, t_1, \ldots, t_n, t_{n+1}\\ &c_0, c_1, \ldots, c_n, c_{n+1}\\ &h_i := t_i - t_{i-1}\\ &t_{i+1/2} = (t_{i+1} - t_i)/2\end{aligned} \tag{27}$$

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

$$\int_0^t \omega(t-s)\frac{\partial}{\partial s}c(s)ds \approx \sum_{i=0}^{n}\omega(t_{n+1} - t_{i+1/2})(c_{i+1} - c_i). \tag{28}$$

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 $c_{n+1}$

$$\frac{c_{n+1} - c_n}{h_{n+1}} + \beta(c_{n+1} - c_n)\omega^{n+1,n} + \beta\sum_{i=0}^{n-1}(c_{i+1} - c_i)\omega^{n+1,i}, \tag{29}$$

or

$$\left(\frac{1}{h_{n+1}}+\beta\omega^{n+1,n}\right)c_{n+1}-\left(\frac{1}{h_{n+1}}+\beta\omega^{n+1,n}\right)c_n+\beta\sum_{i=0}^{n-1}(c_{i+1}-c_i)\omega^{n+1,i}. \quad (30)$$

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)

$$\begin{aligned}&\left(-A+(h_{n+1}^{-1}+\beta\omega^{n+1,n})I\right)\mathbf{c}_{n+1}=\\&-\beta\sum_{i=0}^{n-1}(\mathbf{c}_{i+1}-\mathbf{c}_i)\omega^{n+1,i}+\left(h_{n+1}^{-1}+\beta\omega^{n+1,n}\right)\mathbf{c}_n,\end{aligned} \quad (31)$$

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

- In practice, $\omega$ 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).

# 3 Results

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

- Physical parameters (some taken from Olden)
  - $D$ - 6.0*1e-1 $\mu m^2/s$
  - $\alpha$ - 1.4*1e-4 $\mu m^2/s$
  - $K$ - 32.51/0.033
  - $R = 1\ \mu m$
  - $\Gamma$ - 0.023873241463784306 $\mu m^{-3}$ (from 0.1 of volumetric fraction)
  - $L$ - 100 $\mu m$
- Solver parameters
  - Space discretization points = 21
  - Size of kernel expansion = 10
  - Time step = 0.25
  - Decay limit = 0.1
  - Memory's maximum size = 1000

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

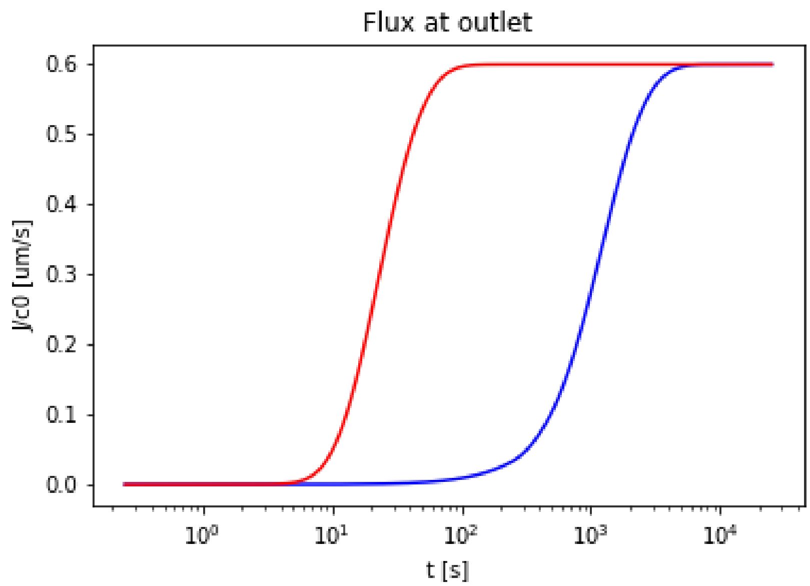


Figure 1

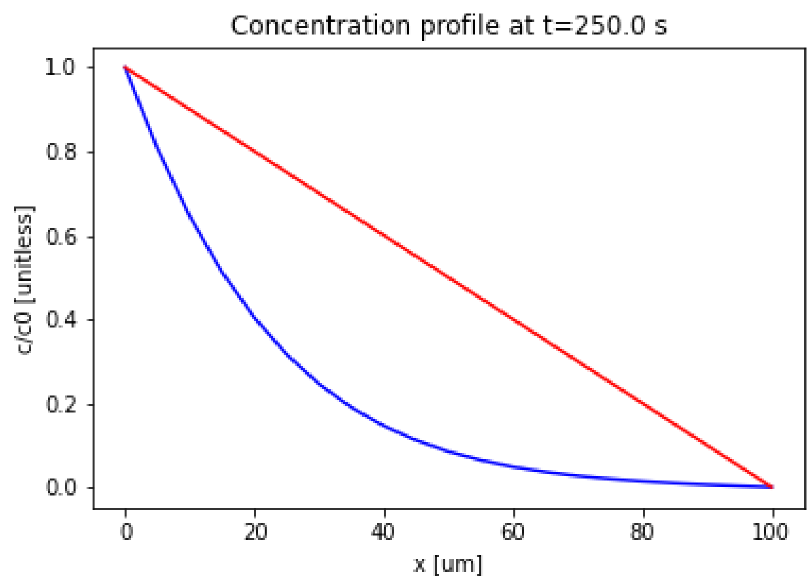


Figure 2

# 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

$$\mathcal{F}_t\left(\frac{\partial}{\partial t}c(x,t)\right)(s) = 2\pi i s C(x,s) \tag{32}$$

$$\mathcal{F}_t\left(\sum_{k=1}^{\infty}(\omega_k *_t c')(x,t)\right) = C(x,s)\sum_{k=1}^{\infty}\frac{1}{1-i\frac{\alpha\pi^2k^2}{2R^2\pi s}}, \tag{33}$$

or

$$\mathcal{F}_t\left(\sum_{k=1}^{\infty}(\omega_k *_t c')(x,t)\right) = C(x,s)\sum_{k=1}^{\infty}\frac{1}{1+\left(\frac{\alpha\pi^2k^2}{2R^2\pi s}\right)^2}\left(1+i\frac{\alpha\pi^2k^2}{2R^2\pi s}\right), \tag{34}$$

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

$$C(x,s)\zeta(s) = D\frac{\partial^2 C}{\partial x^2}(x,s), \tag{35}$$

with

$$\zeta(s) = 2\pi i s + 8\pi R\Gamma\alpha K\sum_{k=1}^{\infty}\frac{1}{1-i\frac{Ak^2}{s}}; \quad A = \frac{\alpha\pi}{2R^2} \tag{36}$$

## 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

$$\mathcal{L}_t\left(\frac{\partial}{\partial t}c(x,t)\right)(s) = s\mathcal{C}(x,s) - c(x,0), \tag{37}$$

and

$$\mathcal{L}_t\left(\sum_{k=1}^{\infty}(\omega_k *_t c')(x,t)\right) = (s\mathcal{C}(x,s)-c(x,0))\sum_{k=1}^{\infty}\frac{1}{1+\frac{\alpha\pi^2k^2}{R^2}s} \tag{38}$$

$$\sum_{k=1}^{\infty}\frac{1}{1+\frac{\alpha\pi^2k^2}{R^2}s} = \frac{1}{2}\left(\sqrt{\frac{R}{\alpha}}s^{-1/2}\coth\left(\sqrt{\frac{R}{\alpha}}s^{-1/2}\right)-1\right). \tag{39}$$

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

$$\begin{aligned}\mathcal{C}(x,s)\xi(s) &= \frac{\partial^2\mathcal{C}}{\partial x^2}(x,s)\\ \xi(s) &= \frac{s}{D}\left(1+\frac{\beta}{2}\left(\sqrt{\frac{R}{\alpha s}}\coth\left(\sqrt{\frac{R}{\alpha s}}\right)-1\right)\right)\end{aligned}. \tag{40}$$

We must have

$$\mathcal{C}(x,s) = A(s)e^{\sqrt{\xi(s)}x} + B(s)e^{-\sqrt{\xi(s)}x} \tag{41}$$

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

$$\begin{bmatrix} 1 & 1 \\ e^{\sqrt{\xi(s)}L} & e^{-\sqrt{\xi(s)}L} \end{bmatrix} \begin{bmatrix} A(s) \\ B(s) \end{bmatrix} = \begin{bmatrix} c_0/s \\ 0 \end{bmatrix}, \tag{42}$$

We have that

$$\begin{aligned} A(s) &= \frac{e^{-\sqrt{\xi(s)}L}}{e^{-\sqrt{\xi(s)}L} - e^{\sqrt{\xi(s)}L}} \frac{c_0}{s} \\ B(s) &= -\frac{e^{\sqrt{\xi(s)}L}}{e^{-\sqrt{\xi(s)}L} - e^{\sqrt{\xi(s)}L}} \frac{c_0}{s} \end{aligned} \tag{43}$$

Then, we have that

$$\mathcal{C}(x,s) = \frac{c_0}{s\left(e^{-\sqrt{\xi(s)}L} - e^{\sqrt{\xi(s)}L}\right)} \left(e^{-\sqrt{\xi(s)}(L-x)} - e^{\sqrt{\xi(s)}(L-x)}\right) \tag{44}$$

Or, simplifying

$$\frac{c_0}{s} \frac{\sinh\left(\sqrt{\xi(s)}(L-x)\right)}{\sinh\left(\sqrt{\xi(s)}L\right)} \tag{45}$$

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