

Periodic Aggregation Patterns of Oxide Particles on Corroding Metal: Chemical waves due to solution feedback processes

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SUPPORTING INFORMATION

A. Computational Simulation of the Early Stages of Oxide Wave Propagation in Gelatin

The mechanism of metal hydroxide wave propagation involving more than one reaction-diffusion front was explored by computational simulation using COMSOL Multiphysics® software.^[1] Numerical simulations were performed using the *transport of diluted species* and *chemistry* modules in COMSOL Multiphysics® v5.0. Time-dependent diffusion of a droplet of 2 M NaOH into a gel consisting of 0.03 M FeSO₄ was simulated with Fick's second law of diffusion, as implemented in COMSOL Multiphysics®. A one-dimensional, axisymmetric geometry was employed to simulate the spherical symmetry in the gel experiment. The droplet was drawn as an interval extending from 0 to 2.5 mm. The total geometry was 50 mm long. Radial symmetry was implemented at radius 0, while a no flux boundary was enforced at the edge of the simulation length.

Solution-phase diffusion and reactions of all species were formulated as follows with rate constants listed in **Table A.1**.

Diffusion and reaction of hydroxide and ferrous ion respectively:

$$\frac{\partial[OH^-]}{\partial t} = D_{OH^-}^{app} \frac{\partial^2[OH^-]}{\partial x^2} - k_1[OH^-]^2[Fe^{2+}] \quad (A.1)$$

$$\frac{\partial[Fe^{2+}]}{\partial t} = D_{Fe^{2+}}^{app} \frac{\partial^2[Fe^{2+}]}{\partial x^2} - k_1[OH^-]^2[Fe^{2+}] \quad (A.2)$$

Production of ferrous hydroxide and subsequent conversion to ferric hydroxide:

$$\frac{\partial[Fe(OH)_2]}{\partial t} = k_1[OH^-]^2[Fe^{2+}] - k_2[Fe(OH)_2] \quad (A.3)$$

$$\frac{\partial[Fe(OH)_3]}{\partial t} = k_2[Fe(OH)_2] \quad (\text{A.4})$$

where D^{app} is defined by **Eq. A.5** or **Eq. A.6** below and D_{OH^-} , $D_{Fe^{2+}}$, k_1 , and k_2 are given in **Table A.1**. For **Eq. A.4**, the oxygen content and its transport are assumed to be fast enough to minimize concentration gradients. At the top of the reaction mixture, oxygen concentration is in equilibrium with the gas phase, the concentration of which is described by Henry's law.^[2] Due to this quasi-equilibrium, the oxygen concentration along the entire length of the simulation space can be assumed to be constant, such that the rate equation can be simplified to k_2 .

As the experiments were performed in gelatin, apparent diffusion coefficients were implemented in the model. Considering the gelatin content in the experiment was 1.5 wt.%, we assumed an approximate permeability ($\epsilon_{gelatin}$) of 0.9 allowing for the calculation of an apparent diffusion coefficient from the aqueous diffusion coefficient for each species.

$$D^{app} = D * \epsilon_{gelatin} \quad (\text{A.5})$$

In the case where we describe systemic feedback, we replace the diffusion coefficient of OH^- and Fe^{2+} with apparent diffusion coefficients, which are further reduced based on the permeability ($\epsilon([Fe_x(OH)_y])$) of gelatinous ferrous and ferric hydroxides.

$$D^{app} = D * \epsilon_{gelatin} * \epsilon([Fe_x(OH)_y]) \quad (\text{A.6})$$

Using similar concentrations as employed in the gel diffusion experiment, synthesized $Fe(OH)_3/FeOOH$ xerogels were found to possess a porosity (P) in the range of 0.3.^[3] Based on such literature porosity values, we then assumed a linear dependence of porosity on gel concentration ranging from 1 to 0.3 as the total concentration of ferrous and ferric hydroxides increased from 0 to 30 mM. The permeability was then calculated using the Bruggeman equation (**Eq. A.7**).^[4]

$$\epsilon = P^{1.5} \quad (\text{A.7})$$

Table A.1. Constants used in numerical model of diffusion of OH^- into Fe^{2+} -containing gelatin

Symbol	Description	Value
$D_{Fe^{2+}}$	Diffusion coefficient of Fe^{2+}	$7.19 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ [5]
D_{OH^-}	Diffusion coefficient of OH^-	$5.27 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ [5]
k_1	Rate constant for $Fe(OH)_2$ formation	$10^{-4} \text{ m}^6 \cdot \text{s} \cdot \text{mol}^{-2}$
k_2	Rate constant for $Fe(OH)_3$ formation	10^{-3} s^{-1}

$\epsilon_{gelatin}$	Permeability of gelatin	0.9
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B. References

- [1] COMSOL Multiphysics® v.5.0. www.comsol.com. COMSOL AB, Stockholm, Sweden.
- [2] J. H. Noggle, *Physical chemistry*, HarperCollins College Publishers, New York, 3rd ed., 1996.
- [3] S. I. Pechenyuk, Y. V. Ivanov, Y. P. Semushina, Porosity of some iron(III), chromium(III), and zirconium(IV) hydroxide oxide xerogels. *Russ. J. Inorg. Chem.* 2006, **51**, 189–193.
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