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#### **Key Points:**

- Time-lapse microphotography captures a lively long-term pore filling history
- The rate of pore filling is diffusion-controlled for a given interfacial configuration, that is, pinned or free interfaces
- Various concurrent phenomena include condensation, corner flow, capillary-induced flow, instabilities, and changes in wettability

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# **Time-Dependent Pore Filling**

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**Abstract** Capillarity traps fluids in porous media during immiscible fluid displacement. Most field situations involve relatively long time scales, such as hydrocarbon migration into reservoirs, resource recovery, nonaqueous phase liquid remediation, geological CO<sub>2</sub> storage, and sediment-atmosphere interactions. Yet laboratory studies and numerical simulations of capillary phenomena rarely consider the impact of time on these processes. We use time-lapse microphotography to record the evolution of saturation in air- or hydrocarbon-filled capillary tubes submerged in water to investigate long-term pore filling phenomena beyond imbibition. Microphotographic sequences capture a lively pore filling history where various concurrent physical phenomena coexist. Dissolution and diffusion play a central role. Observations indicate preferential transport of the wetting liquid along corners, vapor condensation, capillary flow induced by asymmetrical interfaces, and interface pinning that defines the diffusion length. Other processes include internal snap-offs, fluid redistribution, and changes in wettability as fluids dissolve into each other. Overall, the rate of pore filling is diffusion-controlled for a given interfacial configuration; diffusive transport takes place at a constant rate for pinned interfaces and is proportional to the square root of time for free interfaces where the diffusion length increases with time.

# 1. Introduction

Capillarity traps fluids in porous media and affects hydrocarbon migration (Dembicki & Anderson, 1989; Dickey, 1975), hydrocarbon extraction (Babadagli, 2007; Chatzis et al., 1983; Muggeridge et al., 2014; Oren et al., 1992), groundwater contamination by nonaqueous phase liquids and subsequent remediation efforts (Essaid et al., 2015; Rao et al., 1997; Soga et al., 2004), geological CO<sub>2</sub> storage (Andrew et al., 2014; Espinoza & Santamarina, 2010), and sediment-atmosphere interactions (Gens, 2010; Shin & Santamarina, 2011).

Laboratory studies often focus on short-term fluid trapping during either wetting or nonwetting fluid invasion (e.g., classical work by Dullien, 1992, and Lenormand et al., 1983). Displacement patterns and trapped fluid distribution in short-term invasion reflect the competition between capillary, viscous, and gravitational forces within the given porous network topology. Related processes include a wide range of pore-scale instabilities such as Haines jumps and snap-offs (Berg et al., 2013; Jang et al., 2016; Rossen, 2003) and viscous or capillary fingering at the macroscale (Lenormand et al., 1988; Zhang et al., 2011). Several studies have investigated trapped fluid morphology and mass transfer during flushing (Conrad et al., 1992; Corapcioglu et al., 2009; Miller et al., 1998; Schnaar & Brusseau, 2006; Singh et al., 2016).

However, long-term recovery, remediation, and storage involve additional processes that are inconsequential in short-term invasion. The few studies that explored the evolution of trapped fluid volume and morphology over time under quiescent conditions report interface relaxation and fluid reconfiguration (X-ray tomography; Schlüter et al., 2017), diffusion and vanishing of entrapped gas (Adam et al., 1969), contaminant release (Seyedabbasi et al., 2012), and matrix-fracture mass exchange (Parker et al., 1994; Polak et al., 2003). In this context, we highlight that nonaqueous phase liquids (NAPLs), CO<sub>2</sub>, and air have low—yet not insignificant —solubility in water, even though they are often treated as immiscible (Mercer & Cohen, 1990; Spycher et al., 2003).

This experimental pore-scale study explores the fate of trapped fluids after invasion and displacement (i.e., after the flow by advection) and examines the roles of diffusion, capillarity, wettability, and pore geometry on changes in saturation and fluid distribution over time.

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**Figure 1.** Experimental setup. A capillary tube filled with a preselected fluid is immersed into the water-filled flat beaker. The water level in the beaker is maintained constant by the autofilling bottle.

# 2. Experimental Study

We use time-lapse microscopy to record the evolution of trapped fluids in capillary tubes under quasi-static conditions. The experimental setup (Figure 1) consists of a stereo microscope (Leica DMS300) and a flat glass beaker; the autofilling bottle maintains a constant water depth in the glass beaker (h = 12 mm). The capillary tube is fixed to the base of the beaker; we fill it with the preselected fluid and flood the beaker with water. There is no pressure gradient acting on the capillary; both ends are submerged and not connected to the atmosphere (unlike the boundary conditions in Gruener et al., 2012). The evolution of pore filling is recorded using time-lapse photography; the time interval between photographs varies from 1 to 10 min/frame to avoid aliasing internal processes. Experiments last from 2 days to over 6 months.

Tests involve borosilicate glass capillaries to represent water-wet pores and perfloroalkoxy alkane capillaries for oil-wet pores. Figure 2 describes the geometry and size of all capillaries used in this study. The tubes have

a (1) circular cross section, (2) circular section with a thin internal rod of borosilicate glass sitting inside the tube, and (3) a square cross section. The two noncircular cross sections allow capillary water invasion along corners, in analogy to preferential invasion along the irregular geometry of natural pores. Capillaries are not pretreated and only used once. The tested fluid pairs represent various gas-liquid and liquid-liquid interactions: air-water, benzene-water, hexane-water, and toluene-water (DI water: milli-Q water; benzene, hexane, and toluene: from Sigma-Aldrich). Figure 3 lists their mutual solubilities, diffusion coefficients, and interfacial tensions.

# 3. Results

The experimental study allows comparisons between gas-water and liquid-water interactions, water-wet and oil-wet systems, and different pore sizes and geometries. Salient observations based on water-air systems follow. Then, we present complementary results obtained with other fluid pairs in subsequent sections.

## 3.1. Short Term: Initial Corner Flow and Water Vapor Condensation

Figure 4 shows snapshots of the evolution of water saturation within an initially air-filled capillary tube during the first 800 min of water submersion. Two cases are shown: (a) a capillary tube with a circular cross section and (b) the same cylindrical tube with a thin rod sitting at the bottom (see Figure 2 for geometric details).

Cross-section	Length [mm]	Diameter/ Width [mm]	Volume [mm³]	
d	8	0.94	5.55	
d d d d rod	8	0.94 (0.17 for d <sub>rod</sub> )	5.55	
w v r	3-4	0.1	0.04	

Figure 2. Capillary tubes: sizes and cross sections.

Fluids		Molecular structure <sup>♥</sup>	Density [Kg/m³]	Solubility in water [g/L]	Diffusion coefficient [cm²/s]	Water solubility [g/L]	Diffusion coefficient [cm²/s]	Interfacial tension with water [mN/m]
Air	O2 21%; N2 78%	<b>•••</b>	1.2	0.0089 (O <sub>2</sub> ) 0.0138 (N <sub>2</sub> ) (1atm) [25 °C]	2×10 <sup>-5</sup> (O <sub>2</sub> ); 2×10 <sup>-5</sup> (N <sub>2</sub> ) [25 °C]•	0.017	0.242•	72
Hexane	C <sub>6</sub> H <sub>14</sub>	ိန္နဲ့ လွန္	660.3*	0.014*	0.85×10⁻⁵ [25 ° C] <b>*</b>	0.009*	Not found	51*
Benzene	C <sub>6</sub> H <sub>6</sub>	ိစ္စရီ ၁၈၇၆ <sub>၁</sub>	876.5*	1.733*	1.02×10 <sup>-5</sup> •	0.582*	Not found	35 *
Toluene	C <sub>7</sub> H <sub>8</sub>		866.9 <b>*</b>	0.542 [25 °C] <b>*</b>	0.85×10 <sup>-5</sup> ◆	0.464 [25 °C] <b>*</b>	6.19×10⁵ [25 °C]∙	36 [25 °C] <b>*</b>

Demond and Lindner (1993)

Haynes (2014)

Montaomery (2007)

Figure 3. Fluid properties. Data gathered at 20 °C unless otherwise noted.

Water evaporates into the air-filled capillary and starts condensing on the capillary wall adjacent to the waterair interface (Figure 4a). Water droplets first appear close to the water-air interface and then develop into the center of the capillary. Droplets closer to the water-air interface also have a larger volume. The condensation pattern reflects the gradual diffusive transport of the water vapor from the water-air interface to the space inside the capillary.

In the tube shown in Figure 4b, the high initial curvature next to the internal rod at the base  $(1/r_{arc} > 2/r_{main})$ promotes capillary-driven water flow along corners (Bico & Quéré, 2002; Dong & Chatzis, 1995; Weislogel, 1996). Rapid corner flow expels air out of long capillaries within seconds after the tube is submerged in water









**Figure 5.** Long-term pore filling processes in the air-water system: (a) a cylindrical capillary and (b) a cylindrical capillary with a thin internal rod to create a noncircular cross section. Time starts when the air-filled capillary is submerged in water. Capillary: borosilicate glass, d = 0.94 mm. Capillaries are fixed to the beaker's base with epoxy resin. The gradual yellowing observed in images show the epoxy response to long time light and water exposure.

(countercurrent imbibition; see Unsal et al., 2007). The condensation of water on the wall is more uniform in this case in comparison to Figure 4a because the fast initial invasion along the corners places water throughout the full length of the tube.

#### 3.2. Long-Term Pore Filling Processes

Figure 5 presents the evolution of pore filling in the water-air system during the first 120 days. There are two concurrent transport sequences: (1) water evaporation, transport, and condensation into the air-filled space and (2) air dissolution and diffusion out of the capillary tube. Water drops condense on the pore walls, gradually enlarge, and may form a water collar inside the capillary. Eventually, collars become unstable and suddenly close-in to form water blocks across the pore. These newly formed water blocks split the air bubble into segments. The interfacial energy decreases as small droplets coalesce into water blocks.

Water blocks develop close to the open ends of cylindrical tubes and anywhere inside the noncylindrical capillaries where corner flow facilitates water transport into the capillary (Figure 4, day 20). These blocks continue to grow by water vapor diffusion and condensation and by merging water droplets that have condensed on the nearby pore wall. Eventually, water blocks connect with the water in the container.

## 4. Analyses

# 4.1. Diffusive Transport

Trapped air diffuses into the water and gradually leaves the capillary. The underlying processes combine pressure dissolution and diffusion. First, the air pressure in the capillary is higher than outside the capillary (Young-Laplace equation, assuming perfect wetting. See radii of curvature in Hsu et al., 2012):

$$p_{\rm air} - p_{\rm water} = \frac{2\gamma}{r} \tag{1}$$

where  $\gamma$  is the surface tension and *r* is the radius of the capillary tube. Second, gas solubility in water  $c_p$  is pressure-dependent (Henry's law):

$$c_p = H^{cp}p \tag{2}$$

where Henry's constant is  $H^{cp} = 7.1 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1} \cdot \text{atm}^{-1}$  for nitrogen and  $H^{cp} = 14 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1} \cdot \text{atm}^{-1}$  for oxygen at 20 °C. Therefore, the solubility of air in water inside the capillary is higher than in the surrounding bulk water and the concentration gradient sustains air transport.

#### 4.2. Rate of Capillary Filling

Figure 6 shows pore filling data for different fluid-pairs. The volume of trapped gas or hydrocarbon decreases over time in all tests.

The displaced defending fluid may form an external droplet at the end of the capillary and gradually dissolve into the surrounding bulk water. Figure 6a displays the dissolution rate of a spherical benzene droplet in water. The analytical solution accurately predicts the changing droplet radius a(t) as a function of the initial radius  $a_0$  (m), the diffusion coefficient D (m<sup>2</sup>/s), the saturated concentration  $c_{sat}$  (kg/m<sup>3</sup>), the concentration in the far field  $c_0$  (kg/m<sup>3</sup>), and the fluid density  $\rho$  (kg/m<sup>3</sup>; see derivation in the Appendix A; Crank, 1979; Epstein & Plesset, 1950):

$$a(t)^{2} - a_{0}^{2} = -\frac{D(c_{\text{sat}} - c_{0})}{\rho}t \quad \text{spherical diffusion}$$
(3)

Experimental results show that the interface can either remain pinned to the end of the capillary pore or move-in symmetrically from both open ends (Figure 7). For example, the air-water interfaces in Figure 3a are either pinned or stay at the edge of the capillary before day 40 and move into the capillary on day 50. Consequently, the pore filling rate also changes as shown in Figure 6b. When pinned interfaces control transport, the dissolution rate is constant, and the length filled with water x is linear with time t in a capillary of radius r (see derivations in the Appendix A):

$$x = \frac{2D(c_{sat} - c_0)}{\rho r} t \quad \text{pinned interface}$$
(4)

However, when the interfaces move into the capillary as the defending fluid dissolves into the water, the filled length x increases with  $t^{1/2}$  (see Appendix A):

$$x = 2\sqrt{\frac{2D(c_{\text{sat}} - c_0)}{\rho}t} \quad \text{free interface}$$
(5)

Thus, the pore filling rate becomes slower as the diffusion length increases in the free interface model. Model predictions agree with experimental measurements and associated microphotography sequences that identify either pinned or free interfaces. Figure 6 shows data and fitted models for pore filling processes in benzene-water, toluene-water, and air-water. The pinned and free interface models are two extreme conditions. The true evolution of saturation shown in Figures 4 and 5 demonstrates complex behavior with additional phenomena described below.

#### 4.3. Other Phenomena Involved in Pore Filling

In general, experimental results show that diffusion controls the long-term pore filling process. However, other concurrent phenomena identified in this study affect pore filling. These are described next.

## 4.3.1. Condensation

Surface heterogeneities and defects create favorable sites for vapor condensation as the water vapor saturates the capillary in the air-water system (Kalikmanov, 2013; Lopez et al., 1993; Zhao & Beysens, 1995). Due to a reduction in the number of suitable nucleation sites, water condensation on the nonwetting perfloroalkoxy alkane capillary tube is much slower and sparser than the condensation on the water-wet borosilicate glass. There is no observable water vapor condensation in the benzene-water and toluene-water systems. The low solubility and diffusivity of water in these liquids decrease the possibility of nucleation, and condensation can only occur in conditions of high supersaturation (Boistelle & Astier, 1988).







Time [min]

Best fit D = 0.81×10<sup>-9</sup> m<sup>2</sup>/s

Model	Sketch	Equation		
Dissolution of a sphere bubble/drop		$a(t)^{2} - a_{0}^{2} = -\frac{D(c_{sat} - c_{0})}{\rho}t$		
Pore filling with free interfaces	$\overbrace{x_1}^{} x_{x_1+x_2} \xrightarrow{x_2}^{}$	$x = 2\sqrt{\frac{2D(c_{sat} - c_0)}{\rho}t}$ (for x>r)		
Pore filling with pinned interfaces	Pinned interface	$x = \frac{2D(c_{sat} - c_0)}{\rho r}t$		
Pore filling with one pinned interface	× Pinned interface	Between free interfaces case and pinned interfaces case		







**Figure 8.** Unbalanced capillary pressure due to unequal radii of curvature  $r_1 < r_2$  cause capillary driven flow (case: Benzene-water system in 0.1-mm capillary).

#### 4.3.4. Instabilities

#### 4.3.2. Corner Flow

Corner flow rapidly transports water into the noncircular capillaries. In the absence of gravitational effects, corner flow continues until a constant radius of curvature develops along the full length of exposed corners (Figure 4b; Mason & Morrow, 1984, 1991, 1994).

# 4.3.3. Unbalanced Capillary Forces

Pore edges and surface roughness allow for various stable interface geometries, which can cause asymmetrical interfaces at both ends, unbalanced capillary forces and flow (Morrow, 1970). Fluid interfaces undergo a slow relaxation after fast fluid invasion as fluids redistribute to reduce the surface energy and finally reach hydrostatic equilibrium (Schlüter et al., 2017). Figure 8 demonstrates capillary-driven flow in a benzenewater system: the radius  $r_2$  of the meniscus on the right side is initially larger in comparison to the meniscus on the left  $r_1$ ; therefore, benzene is displaced to the right. The difference in radii becomes larger, and the length of the benzene droplet rapidly decreases in the capillary. The expelled benzene forms a spherical droplet outside the tube where diffusive transport is more effective (i.e., the model in equation (3), rather than equation (4) or (5)).

Various instabilities affect the evolution of pore filling. Water collars gradually become unstable, form water blocks, and split the fluid trapped in the capillary (Figure 9a). Converging or diverging pore geometries near pore throats (e.g., the enlargement at the end of the capillary in Figure 9b) induce snap-offs and external bubbles detach from the capillary (see related analyses in Yu & Wardlaw, 1986, and Roof, 1970). Snap-offs change the fluid distribution, leave disconnected trapped fluids, and affect the pore filling process in porous networks (Sahloul et al., 2002).

## 4.3.5. Changes in Wettability

Some systems exhibit a gradual change in the contact angle with time during pore filling. For example, this is observed in the toluene-water and benzene-water systems (Figure 9c). Time-dependent changes in wettability may be due to (1) the mutual dissolution of water and the trapped fluid (see images for liquid CO<sub>2</sub>-water system in Espinoza & Santamarina, 2010) and (2) the preferential dissolution of certain species, which results in the residual accumulation of less soluble components such as surfactants or long polar molecules. The change in wettability prompts different pore fluid configurations, for example, the benzene block breaks and forms films (Figure 9c). Changes in wettability may even initiate corner flow and facilitate diffusive transport with an increase in the interfacial area and a shorter diffusion distance (Sahloul et al., 2002).

# 5. Implications

Results presented above highlight the inherent time-dependent nature of pore filling. Implications are relevant to natural processes and industrial applications. Two salient examples follow.

## 5.1. Reservoirs

A defending wetting phase remains connected through narrow pore corners until the later stages of desaturation when the wetting fluid becomes isolated at grain contacts (pendular regime). On the other hand, the nonwetting fluid often forms isolated droplets (snap-offs at pore throats) and patches (bypassed zones) that rest trapped in the formation (see X-ray images in Singh et al., 2016). Isolated wetting and nonwetting fluids can be found in near-surface soils toward either end of wet-and-dry cycles, when buoyant oil, gas, or CO<sub>2</sub> migrate upward to fill a reservoir, during light non-aqueous phase liquid/dense nonaqueous phase liquid contamination and remediation, and throughout water flooding for enhanced oil recovery.

Our results demonstrate that the entrapped fluid volume gradually reduces and its morphology evolves over time as a result of dissolution and diffusion, even in closed-end pores with no throughflow. Our experiments do not reproduce interconnected pore networks under reservoir P-T conditions but do capture the essential phenomena involved in the long-term evolution of saturation. In fact, earlier core-scale experiments show that the volume of trapped gas in cores gradually reduces following a square root of time relation, and the



# (a) From collars to blocks



**Figure 9.** Other concurrent processes during time-dependent pore filling. (a) A block forms from a contracting water collar (case: Air-water system in 0.94-mm capillary). (b) Gas is displaced from the capillary by rapid water invasion along corners and forms a gas bubble at the end of the capillary (case: Air-water system in 0.94-mm noncircular capillary with an internal rod). (c) Changes in wettability (case: Benzene-water system in 0.1-mm capillary): The contact angle of a benzene droplet trapped between water fronts changes from nonwetting (left image) to wetting (center image); eventually, the benzene block breaks into a collar (right image).

evolving distribution of trapped gas implies pinned interfaces, in agreement with our pore-scale results (Adam et al., 1969).

Dissolution and diffusion-dominant pore filling gains relevance in long-term processes and in heterogeneous porous media. For example, measurements of noble gases and carbon isotopes show that  $CO_2$  dissolution into the formation water is the main cause of  $CO_2$  loss from natural  $CO_2$  reservoirs (Gilfillan et al., 2009). Diffusion causes long-term contaminant release from low permeability zones (Seyedabbasi et al., 2012) and contributes to matrix-fracture mass transfer (see computed tomography study in Polak et al., 2003).

### 5.2. Superhydrophobicity

Air trapping is a major contributor to the superhydrophobic response of natural and synthetic surfaces (Lv et al., 2017; Quéré, 2008). Typically, superhydrophobic surfaces consist of an array of micron to submicron size posts where air pockets remain trapped under otherwise wetting fluids, that is, Cassie state (Beysens, 2006; Cassie & Baxter, 1944; Koch & Barthlott, 2009; Mishra et al., 2016). This study shows that diffusion, heterogeneous condensation, and water flow along corners will gradually fill the pockets and reduce the apparent superhydrophobicity (Wenzel transition). Since water vapor prefers to condense on water-wet surfaces, the fabrication of superhydrophobic surfaces consisting of hydrophobic posts with hydrophilic tops would prevent vapor condensation in air-filled pockets and extend the superhydrophobicity effect (Varanasi et al., 2009). Alternatively, the hydrophilic surface should avoid sharp curvatures to hinder corner flow.

# 6. Conclusions

Capillarity traps fluids in porous media during immiscible fluid displacement. Short-term experimental and numerical studies fail to observe or reproduce the time-dependent filling of capillary pores. This study

explored long-term pore filling using time-lapse microphotography. The photographic sequences capture a lively pore filling history where various concurrent physical phenomena coexist.

In the long-term, pore filling progresses by dissolution and diffusion through two countertransport sequences: (1) water evaporation, transport, and condensation into the fluid-filled pore and (2) trapped fluid dissolution and diffusion out of the capillary tube. Water droplets coalesce to form water collars inside the capillary. Collars suddenly close-in to form water blocks across the pore and split the trapped fluid into segments.

Wetting fluids flow along corners in pores with non circular geometry. Corner flow promotes pore filling and favors uniform vapor condensation.

The pinning of one interface next to a pore-end shortens the diffusion path and maintains a high constant rate of pore filling. Unpinned interfaces move gradually away from pore ends and the diffusion length increases with time; in this case, pore filling progresses proportional to the square root of time.

The contact angle may change during pore filling because of the mutual dissolution of interacting fluids and the preferential dissolution of certain species that results in the residual accumulation of less soluble components.

Results highlight the role of time on mixed fluid conditions in porous media. Underlying long-term processes affect reservoir filling and resource recovery, contamination-and-remediation, geological CO<sub>2</sub> storage, sediment-atmosphere interaction, and the time-dependent response of super hydrophobic natural or fabricated surfaces.

# Appendix

Model A1: Dissolution of a spherical drop

Concentration *c* varies with radial distance *r* and time *t* (Fick's second law):

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r}\frac{\partial c}{\partial r}\right) \tag{A1}$$

where *D* is the diffusion coefficient. A sphere with a radius *a* immersed in a fluid with far-field concentration  $c_0$  reaches saturation concentration  $c_{sat}$  at the surface r = a. From equation (A1), the concentration gradient at the surface is (Crank, 1979; Epstein & Plesset, 1950)

$$\left. \frac{\partial c}{\partial r} \right|_{r=a} = (c_{\text{sat}} - c_0) \left( -\frac{1}{a} - \frac{1}{\sqrt{\pi Dt}} \right) \tag{A2}$$

Therefore, the mass flow from the surface is

$$\frac{dm}{dt} = 4\pi a^2 D(c_{\text{sat}} - c_0) \left( -\frac{1}{a} - \frac{1}{\sqrt{\pi Dt}} \right)$$
(A3)

On the other hand, mass conservation implies that

$$\frac{dm}{dt} = 4\pi a^2 \rho \frac{da}{dt} \tag{A4}$$

Equations (A3) and (A4) predict the rate of change in the sphere size da/dt

$$\frac{da}{dt} = \frac{D(c_{\text{sat}} - c_0)}{\rho} \left( -\frac{1}{a} - \frac{1}{\sqrt{\pi Dt}} \right) \tag{A5}$$

The approximate solution for the droplet size *a* as a function of time *t* is



$$a^2 = a_0^2 - \frac{D(c_{\text{sat}} - c_0)}{\rho}t \quad \text{for large } t \tag{A6}$$

where  $a_0$  is the initial radius of the droplet.

Model A2: Trapped fluid in a capillary: Pinned interface

The mass flow reaches steady state for a capillary with a pinned interface at the pore end:

$$\frac{dm}{dt} = 2A_1 D\left(\frac{\partial c}{\partial a}\right) = A_1 D\frac{c_{\text{sat}} - c_0}{r}$$
(A7)

where *r* is the capillary radius and  $A_1$  is the area of interface  $(\pi r^2 \le A_1 \le 4\pi r^2)$ . In this case, mass conservation implies

$$\frac{dm}{dt} = A_2 \rho \frac{dx}{dt} \tag{A8}$$

where  $A_2$  is the cross-section area. From equations (A7) and (A8), the filled length x evolves in time t as  $(A_1 = A_2)$ 

$$x = \frac{2D(c_{sat} - c_0)}{\rho r} t \tag{A9}$$

Model A3: Free interface

The mean concentration gradient is

$$\frac{\partial c}{\partial a} = \frac{2(c_{\text{sat}} - c_0)}{x}$$
(A10)

Substituting equation (A10) into equation (A7), and taking into consideration mass conservation (equation (A8)), the filled length as a function of time is  $(A_1 = A_2)$ 

$$x = 2\sqrt{\frac{2D(c_{\text{sat}} - c_0)}{\rho}t}$$
(A11)

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