



A model for diffusion of water into a swelling particle with a free boundary: Application to a super absorbent polymer particle



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HIGHLIGHTS

- A model is developed for water diffusion in a swelling particle with a free boundary.
- A kinetic law is introduced to describe water uptake along the particle surface.
- The model is simplified for swelling of spherical particles.
- Diffusivity and water uptake at the particle surface govern the swelling kinetics.
- The model agrees well with experimental data from literature.

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ABSTRACT

In this work, a model is developed for describing the swelling of an individual particle, made of Super Absorbent Polymers (SAP). Governing equations for the water uptake at the particle surface, diffusion of water into the particle and the subsequent swelling of the particle are developed for an irregularly shaped particle. The modelling domain is assumed to have a free and moving boundary, thus a moving particle surface, to account for the increase in particle size. In addition, the entrance of water through the particle surface is modelled as a first-order kinetic process. The proposed model is then simplified for a spherical particle, made dimensionless, projected onto a fixed grid, and solved using an explicit numerical scheme. A dimensionless number is defined as the ratio of kinetics of water uptake at the particle surface to the water diffusivity. Using this dimensionless number, three regimes of swelling kinetics can be identified: (i) diffusion is limiting, (ii) water uptake is limiting, or (iii) both processes are limiting. Numerical results indicate that experimental data from literature can be reproduced when assuming water uptake kinetics at the particle surface to be very fast; i.e. instantaneous, thus diffusion being the controlling mechanism. Of course, for SAP particles having a different composition, the particle surface may slow down the swelling kinetics. Our model is compared to three other models found in the literature. They all give a similar result but with different diffusive coefficients.

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1. Introduction

Super Absorbent Polymers (SAPs) are used in a variety of applications, for example: (i) to absorb fluids in hygienic products (Buchholz and Graham, 1998); (ii) to control shrinkage in cement pastes (e.g. Snoeck et al., 2015); (iii) to regulate moisture content in soils (e.g. Woodhouse and Johnson, 1991); (iii) to remove water from a pathogen suspension in order to increase the pathogen concentration to a detection limit (Xie et al., 2016). SAPs are hydrophilic polymers that are lightly cross-linked and some SAPs have been

reported to absorb demineralized water up to 1000 times their initial weight and saline water up to 30 times (Zohuriaan-Mehr and Kabiri, 2008). When SAP particles form a bed, not only the particle properties but also the properties of the bed become important for the performance of the SAP particles and their corresponding swelling behaviour.

To investigate the behaviour of a bed of swelling SAP particles, a macro-scale model can be employed; see for example Diersch et al. (2010). Macro-scale models require relations to describe the dynamics of swelling. They are typically parameterized using experiments and thus are not always physically based. Another method is to employ a grain-scale model, such as the Discrete Element Method, DEM (Sweijen et al., 2017). DEM is a particle model

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that can describe the movement of individual particles inside a packing of spheres during deformation and/or swelling. For DEM simulations of swelling SAP particles, an expression is needed to describe the swelling rate of individual particles as a function of the particle size, which evolves with time. There exist empirically-based expressions that are obtained from fitting experimental data of swelling particles (see e.g. Omidian et al., 1998; Esteves, 2011; Kabiri et al., 2003). For DEM simulations, a simple expression is preferable as it reduces the numerical computations. But, one would be interested to know whether such an expression can be linked to a physically-based relation for the degree of swelling evolving over time. For this purpose, a rigorous fully-coupled model of fluid diffusion into a swelling particle (including its deformation) is needed (see e.g. Huyghe and Janssen, 1997).

Water transport in a swelling grain has previously been studied by Radu et al. (2002), who studied drug release from a one-dimensional swelling polymer. They modelled non-linear diffusion (Fujita-type diffusion) inside a particle having a free boundary at the surface of the particle as well as an internal boundary inside the polymer, which mimics the transition from dry polymer to hydrated polymer. The problem of transport in a domain that has a free boundary is a well-studied problem, where the free boundary is often referred to as a Stefan type boundary condition. Examples are the work by Van Noorden and Pop (2007), who have developed a model of cations and ions diffusion in a domain that has a free boundary, to study dissolution and precipitation of crystal. Van De Fliert and Van Der Hout (2000) developed a mathematical model for drying of paints, where pigments and resins are conserved but solvents can evaporate over a moving boundary, thus making it a diffusive and evaporation problem. Weiqing (1990) studied solidification due to superheating (or cooling) in which thermal diffusivity is coupled to a free boundary.

While a variety of complex models exist to describe the swelling of one particle, relatively simple empirical equations remain convenient for fitting experimental data. To test these empirical equations, we compare existing (semi-) empirical equations to a newly developed physically-based model, which accounts for linear diffusion of water into a swelling particle, with a free boundary. In addition, water uptake at the particle's surface is assumed to be a kinetic process in itself, which in combination with water diffusion governs the swelling rate of a particle. First, a set of equations for an arbitrary shaped particle is derived, assuming a constant polymer volume (i.e. no mixing occurs). Then, the equations are simplified for the swelling of a spherical particle and are solved numerically. Model results are compared to (semi-) empirically equations and experimental data on swelling of spherical particles from Esteves (2011). Finally, the effect of coating of particles is evaluated in terms of kinetics in water uptake along the particle's surface.

2. A numerical model of swelling of a particle

Here, a set of equations is derived to describe diffusion of water into a swelling particle that is submerged into sufficient water. We assume that the polymer and water are both incompressible. We start by describing the swelling of an arbitrary shaped particle. Then, a parameter is introduced to capture the uptake rate of water along the particle surface. Finally, equations are applied to a spherical particle.

2.1. Swelling of an irregular particle

Consider a particle that has an arbitrary initial shape filling a domain indicated by $\Omega(0)$. At time $t > 0$, the domain is given by $\Omega(t)$. At each point $\bar{x} \in \Omega(t)$, the local volume fraction of water is

denoted by $\theta(\bar{x}, t)$. A constrain is applied to $\theta(\bar{x}, t)$ using $\theta_0 \leq \theta(\bar{x}, t) \leq \theta_{max}$, where θ_{max} and θ_0 are the maximum and initial value of θ , respectively, which are both constant over time and space. Per definition, θ_{max} is smaller than unity, because unity would indicate that there is no solid present. The boundary of the domain is denoted by $\partial\Omega(t)$ at which $\theta = \theta_b$, thus θ_b is the value of θ at the boundary. The boundary has an outward normal \bar{n} and a velocity \bar{v} . Diffusion into a particle is described by the following set of equations:

$$\left. \begin{aligned} \frac{\partial\theta}{\partial t} + \text{div} \bar{q} &= 0 \\ \bar{q} &= -D\nabla\theta \end{aligned} \right\} \text{ for } \bar{x} \in \Omega \text{ and } t > 0 \quad (1a)$$

$$\theta|_{\partial\Omega(t)} = \theta_b \quad \text{for } t > 0 \quad (1b)$$

$$\theta|_{t=0} = \theta_0 \quad (1c)$$

where \bar{q} denotes the water flux and D is a diffusion coefficient which we assume to be a material constant and thus to be independent of time and location. Note that in this work, diffusion is assumed to be linear for sake of simplification (i.e. D is a constant), but water diffusion into a dry particle can be non-linear diffusion such that D would be a function of θ .

For a swelling particle, an equation for the moving boundary $\partial\Omega(t)$ is required that considers water that enters the growing particle via its boundary. Let us consider a small surface element of $\partial\Omega(t)$, with an area A , that moves in space from time t to time $t + \Delta t$. The particle grows into water, within which $\theta = 1$. This results in an excess volume of water (V_{excess}) inside the particle, near the boundary, that has to diffuse into the particle. This volume is given by

$$V_{excess} = (1 - \theta_b)(\bar{v} \cdot \bar{n})A\Delta t \quad (2)$$

This volume of water diffuses into the particle, for which we can write:

$$V_{excess} = -D\left[-\bar{n} \cdot \nabla\theta|_{\partial\Omega(t)}\right]A\Delta t = D(\nabla\theta \cdot \bar{n})A\Delta t \quad (3)$$

Combining Eqs. (2) and (3) yields the volume balance:

$$D(\nabla\theta|_{\partial\Omega(t)} \cdot \bar{n}) = (1 - \theta_b)(\bar{v} \cdot \bar{n}) \quad (4)$$

which relates the water flux at the boundary to the speed of the boundary. Eq. (4) ensures volume conservation across a moving boundary. It has been employed by Fasano and Mikelic (2002) to account for the effect of water absorption by a spherical particle on unsaturated flow of water surrounding that particle. Eqs. (1) and (4) yield a complete set of equations that can be solved for water diffusion in an arbitrary domain and its subsequent swelling. It is a classical one-phase free boundary problem for which numerous literature is available, see for example Crank (1984).

2.2. Rate of water uptake at the particle surface

The uptake of water molecules at the surface can be a kinetic process in itself. If the uptake is very fast or instantaneous, the value of θ_b is given by a constant value of θ_{max} which corresponds to the maximum absorption capacity of a hydrogel. If the uptake evolves in time, θ_b depends on time. Assuming that this behaves as first-order kinetics, one has:

$$\frac{\partial\theta_b}{\partial t} = k(\theta_{max} - \theta_b) \quad (5)$$

in which k [T^{-1}] is a kinetic constant. Similar forms of Eq. (5) have been employed to describe the swelling of hydrogels (see e.g. Buchholz, 1998), but we employ it here as a kinetic law for water uptake at the particle's surface. Integration of Eq. (5) yields:

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