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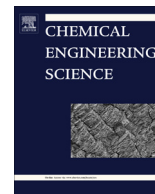
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A model for diffusion of water into a swelling particle with a free boundary: Application to a super absorbent polymer particle



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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:

$$\theta_b = \theta_{max} - (\theta_{max} - \theta_0)e^{-kt}. \quad (6)$$

Eq. (6) is valid provided that the initial and boundary conditions are compatible such that $\theta_b = \theta_0$ at $\partial\Omega$ for $t = 0$.

2.3. Swelling of a spherical particle

Eqs. (1) and (4) can be simplified to describe the swelling of a sphere with initial radius $R_0 > 0$. Let $R = R(t)$ being the radius at time $t > 0$. Assuming radial symmetry, Eq. (1a) is rewritten in terms of radial coordinates:

$$\frac{\partial\theta(r,t)}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial\theta(r,t)}{\partial r} \right) \quad \text{for } 0 < r < R(t) \text{ and } t > 0 \quad (7)$$

Eq. (4) can be rewritten for radial coordinates by realizing that $(\bar{v} \cdot \bar{n}) = \frac{dR}{dt}$ and $\nabla\theta|_{\partial\Omega(t)} \cdot \bar{n} = \frac{\partial\theta}{\partial r}|_R$, so that we obtain:

$$D \frac{\partial\theta}{\partial r} \Big|_R = (1 - \theta_b) \frac{dR}{dt} \quad (8)$$

Eq. (8) complies with a volume balance of a swelling spherical particle, on which we elaborate in Appendix A. We introduce a diffusive reference time $t_r = \frac{R_0^2}{D}$. Then, Eqs. (6)–(8) are made dimensionless using the following parameters:

$$T = \frac{t}{t_r} \quad (9a)$$

$$r^* = \frac{r}{R_0} \quad (9b)$$

$$R^*(T) = \frac{R(t)}{R_0} \quad (9c)$$

This leads to the set of equations:

$$\frac{\partial\theta}{\partial T} = \frac{1}{r^{*2}} \frac{\partial}{\partial r^*} \left(r^{*2} \frac{\partial\theta}{\partial r^*} \right) \quad \text{for } 0 < r^* < R^*(T) \text{ and } T > 0 \quad (10a)$$

$$\frac{\partial\theta}{\partial r^*} \Big|_{R^*} = (1 - \theta(R^*, T)) \frac{dR^*}{dT} \quad \text{for } T > 0 \quad (10b)$$

$$\theta|_{r^*=R^*(T)} = \theta_{max} - (\theta_{max} - \theta_0)e^{-KT} \quad (10d)$$

where:

$$K = \frac{R_0^2 k}{D} \quad (10e)$$

Note that K is the only dimensionless group in this problem. It represents the ratio of characteristic time scales of diffusion $\left(\frac{R_0^2}{D}\right)$ over that of water uptake $\left(\frac{1}{k}\right)$.

2.4. Spatial transformation

Eqs. (10) form a moving boundary problem as R^* changes with time. To simplify the numerical implementation of Eqs. (10), we transform them to an equivalent problem on a fixed domain, by defining a new spatial variable (Caldwell and Kwan, 2004; Kutluay et al., 1997)

$$X = \frac{r^*}{R^*(T)} = \frac{r}{R(t)} \quad \text{where } 0 \leq X \leq 1. \quad (11)$$

By writing $\varphi(X, T) = \varphi\left(\frac{r^*}{R^*(T)}, T\right) \equiv \theta(r^*, T)$, we can use the chain rule of differentiation to obtain the following relationships:

$$\frac{\partial\theta}{\partial r^*} = \frac{\partial\varphi}{\partial X} = \frac{1}{R^*(T)} \frac{\partial\varphi}{\partial X} \quad (12)$$

$$\frac{\partial\theta}{\partial T} = \frac{\partial\varphi}{\partial T} + \frac{\partial\varphi}{\partial X} \frac{\partial X}{\partial T} = \frac{\partial\varphi}{\partial T} - \frac{r^*}{[R^*(T)]^2} \frac{dR^*(T)}{dT} \frac{\partial\varphi}{\partial X}. \quad (13)$$

Using expressions 12 and 13 in Eq. (10a) gives:

$$\frac{\partial\varphi}{\partial T} - \frac{r^*}{[R^*(T)]^2} \frac{dR^*(T)}{dT} \frac{\partial\varphi}{\partial X} = \frac{1}{X^2 [R^*(T)]^2} \frac{1}{R^*(T)} \frac{\partial\varphi}{\partial X} \times \frac{\partial}{\partial X} \left(X^2 [R^*(T)]^2 \frac{1}{R^*(T)} \frac{\partial\varphi}{\partial X} \right). \quad (14)$$

Multiplying this equation by $[R^*(T)]^2$ and using Eq. (11) results in

$$[R^*(T)]^2 \frac{\partial\varphi}{\partial T} = \frac{1}{X^2} \frac{\partial}{\partial X} \left(X^2 \frac{\partial\varphi}{\partial X} \right) + X R^*(T) \frac{dR^*(T)}{dT} \frac{\partial\varphi}{\partial X}. \quad (15)$$

Finally, we introduce variable $Z(T) = \frac{1}{2}[R^*(T)]^2$ in Eqs. (15) and (10b). This results in the following transformed set of equations:

$$2Z(T) \frac{\partial\varphi}{\partial T} = \frac{1}{X^2} \frac{\partial}{\partial X} \left(X^2 \frac{\partial\varphi}{\partial X} \right) + X \frac{dZ(T)}{dT} \frac{\partial\varphi}{\partial X} \quad \text{for } 0 < X < 1 \text{ and } T > 0 \quad (16a)$$

$$\frac{dZ(T)}{dT} = \frac{1}{1 - \varphi|_{X=1}} \frac{\partial\varphi}{\partial X} \Big|_{X=1} \quad \text{for } T > 0 \quad (16b)$$

$$\varphi|_{X=1} = \theta_{max} - (\theta_{max} - \theta_0)e^{-KT} \quad (16c)$$

$$\varphi(X, 0) = \theta_0 \text{ for } 0 < X < 1. \quad (16d)$$

Because of the coordinate transformation in Eqs. (12) and (13), the conservative form of Eqs. (10) transformed into a non-conservative form in Eqs. 16. To maintain mass conservation, Van De Fliert and Van Der Hout (2000) as well as Van Noorden and Pop (2007) employed a mass-based transformation that resulted in a conservative but complex formulation. The coordinate transformation in Eqs. (12) and (13) could in principle lead to a loss of mass in the computations. However, keeping the discretization sufficiently small, the effect is limited.

2.5. Discretization

To solve Eqs. (16), we use the forward Euler scheme, following the work on one-dimensional Stefan's type problems by Kutluay et al. (1997) and the work on swelling particles by Bouklas and Huang (2012). We discretise the spatial domain of $X = [0, 1]$ into N segments of size ΔX and we introduce time step ΔT . Let φ_i^k denote the approximation of $\varphi(i\Delta X, k\Delta T)$ where $i = 0, 1, 2, \dots, N$ and $k = 0, 1, 2, \dots$. Note that $i = 0$ represents the centre of a sphere and $i = N$ represents the boundary of a sphere. Eq. (16a) is solved using a forward Euler scheme, where the diffusion is evaluated by a mid-point scheme:

$$2(Z^k) \frac{\varphi_i^{k+1} - \varphi_i^k}{\Delta T} = \frac{1}{(X_i^k)^2 \Delta X} [J_{i+\frac{1}{2}}^k - J_{i-\frac{1}{2}}^k] + X_i \frac{dZ}{dT} \Big|_i^k \frac{\partial\varphi}{\partial X} \Big|_i^k \quad (17)$$

We introduce the following approximations:

$$J_{i+\frac{1}{2}}^k = (X_{i+\frac{1}{2}}^k)^2 \left(\frac{\varphi_{i+1}^k - \varphi_i^k}{\Delta X} \right) \quad (18a)$$

$$J_{i-\frac{1}{2}}^k = (X_{i-\frac{1}{2}}^k)^2 \left(\frac{\varphi_i^k - \varphi_{i-1}^k}{\Delta X} \right) \quad (18b)$$

$$\frac{\partial\varphi}{\partial X} \Big|_i^k = \frac{\varphi_{i+1}^k - \varphi_{i-1}^k}{2\Delta X} \quad (18c)$$

$$\left. \frac{dZ}{dT} \right|^k = \frac{1}{1 - \varphi_{i=n}^T} \frac{\varphi_{i=n}^k - \varphi_{i=n-1}^k}{\Delta X} \quad (18c)$$

$$Z^{k+1} = Z^k + \left. \frac{dZ}{dT} \right|^k \Delta T \quad (18d)$$

$$\varphi_{i=n}^{k+1} = \theta_{max} - (\theta_{max} - \theta_0) e^{-K(T^k + \Delta T)} \quad (18e)$$

Following the forward Euler scheme, φ_i^{k+1} can be solved explicitly by:

$$\varphi_i^{k+1} = \varphi_i^k + \left(\frac{\Delta T}{2Z^k X_i^2 \Delta X} \right) [J_{i+\frac{1}{2}}^k - J_{i-\frac{1}{2}}^k] + \left(\frac{\Delta T X_i}{2Z^k} \right) \left. \frac{dZ}{dT} \right|^k \frac{\partial \varphi}{\partial X} \Big|_i \quad (19)$$

A zero-flux boundary condition at the centre of the sphere is imposed by considering Eq. (18a) at $i = 1$ differently, namely: $J_{i-\frac{1}{2}}^k = 0$, and $\left. \frac{\partial \varphi}{\partial X} \right|_i = \frac{\varphi_{i+1}^k - \varphi_i^k}{\Delta X}$.

The minimum time step for this set of equations is given by the minimum time step for a forward Euler scheme for linear diffusion, which must satisfy $\Delta T < \frac{1}{2}(\Delta X)^2$ (note that ΔT and ΔX are dimensionless). Although, the main process is that of linear diffusion, the expansion of the particle resulted in an additional convective term (see Eq. (16a)). This may cause the time-step to be smaller than that of linear diffusion. We applied a safety factor of 0.01 on the minimum time step to ensure that the computed water distribution had non-oscillatory behaviour. After a mesh-independency check, we set N at 300. The mass convergence of the numerical simulation was determined by computing the solid volume after swelling (i.e. after large times), for which we know the exact solution in dimensionless term, namely: $\frac{4}{3}\pi$. The mass loss was always less than 0.005 times the initial mass.

We simulate experiments by Esteves (2011), who has studied the swelling of spherical SAP particles. In that study, θ_0 was zero and the maximum value of $\frac{R}{R_0}$ at equilibrium was 2.79, which yields $\theta_{max} = 0.95$. These values were used for numerical computation.

3. Results

In this work, two distinctive kinetic processes are identified, namely: diffusion of water into a spherical particle and the water uptake at the particle surface (i.e. boundary of the modelling domain) of that particle. Those two processes yield three types of swelling kinetics, with the value of K as indicator. The first type is where water uptake at the particle surface is instantaneous

($K \rightarrow \infty$) and thus diffusion controls the swelling kinetics. The second type is where diffusion of water is faster than the uptake of water at the particle surface (i.e. $K \ll 1$). Finally, the third type is where the value $K = O(1)$. Then, both diffusion and water uptake balance and both affect the swelling kinetics. In what follows, we will evaluate all three regimes, compare our results to experiments and discuss the usefulness of parameter K in practical applications.

3.1. Instantaneous water uptake at the surface

In this section, we assume that the SAP material at the surface instantaneously absorbs water to the maximum capacity θ_{max} such that diffusion controls the swelling kinetics. Thus, in the numerical scheme, Eq. (18e) reduces to $\varphi_{i=n}^{k+1} = \theta_{max}$. Fig. 1a shows the distributions of φ within the particle at different times. These are indeed diffusive profiles of water migrating into a sphere. Fig. 1b shows the same diffusive profiles, but now in terms of dimensionless radius r^* , which shows the increase in particle radii and the subsequent shift in diffusive profiles.

3.1.1. Comparison with other models

In Fig. 2, the swelling of a spherical particle is plotted as the radius versus time, using three models found in the literature and our model for instantaneous water uptake at the particle surface. Expressions for radius and absorption ratios as function of time are given in Table 1. Obviously, the results are strongly affected by the value of diffusion coefficient. If we use the same diffusivity, the model by Sweijen et al. (2017) gives a similar initial swelling rate as the model presented here (see Fig. 2a). But, the swelling rates starts to deviate when $\frac{R}{R_0}$ is larger than two, after which the model presented in this paper yields a larger swelling rate. The initial swelling rates of the models by Buchholz (1998) and Omidian et al. (1998) are significantly lower than in our case. Alternatively, we used different values for the diffusion coefficient in different models to have them approach our result as closely as possible. This required reducing the value of diffusion coefficient by multiplying it with a factor D_{scale} . Results are shown in Fig. 2b and values of D_{scale} are given in Table 1.

3.2. Kinetic water uptake at the surface

When the diffusion of water is assumed to be much faster than the uptake of water at the particle surface (i.e. $K \ll 1$), θ will be almost constant over r^* . Thus, $\theta(r^*, T)$ will approach $\theta(T)$ when K approaches zero, where the value of $\theta(T)$ is given by expression

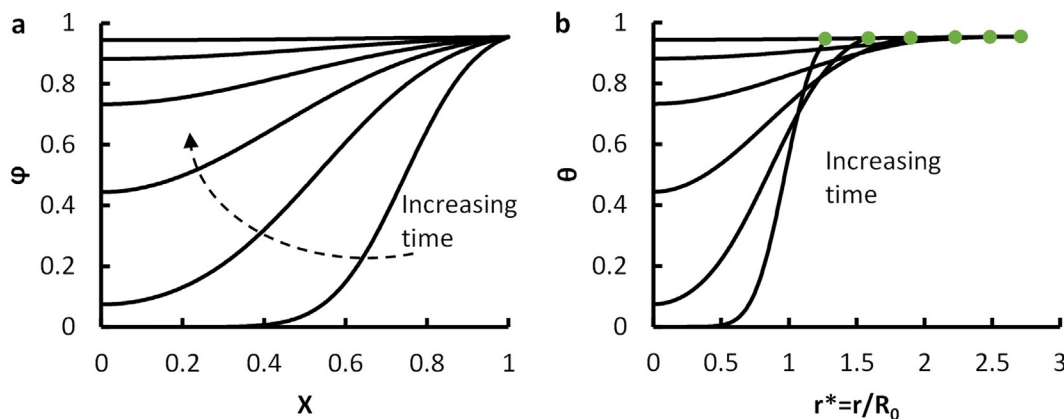


Fig. 1. Profiles of volume fraction of water for instantaneous water uptake at the particle surface, using $\varphi|_{X=1} = \theta_{max}$, for (a) $\varphi(X, T)$ and (b) $\theta(r^*, T)$ with the green symbols representing the boundary of the sphere. Note that the maximum values of both φ and θ is $\theta_{max} < 1$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

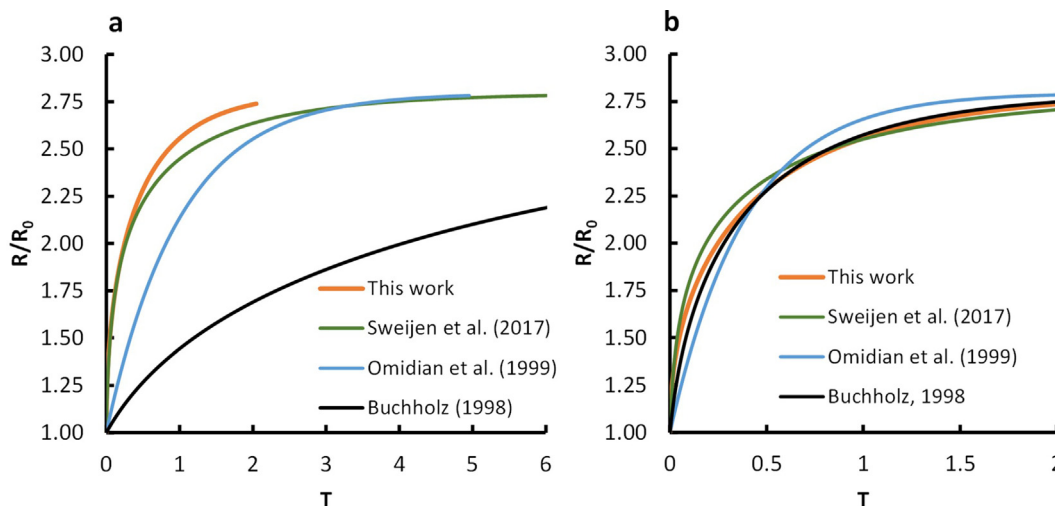


Fig. 2. Particle radius as function of normalized time T for four different models: (a) assuming a constant value of D for all equations and (b) all equations were fitted to the curve obtained in this work by multiplying the diffusion coefficient with D_{scale} reported in Table 1.

Table 1
Equations found in the literature describing the swelling of one SAP particle.

Equation	D_{scale}	Reference
$\frac{R}{R_0} = \left(\frac{R_m}{R_0} - 1\right)(1 - e^{-kt}) + 1$	0.39	Omidian et al. (1998)
$\frac{dQ}{dt} = \frac{\pi^2 D}{R_0^2} (Q^{max} - Q)$	0.069	Buchholz (1998)
$\frac{dQ}{dt} = \frac{3Dr_s}{(r^2)^2} \left(\frac{Q^{max}-Q}{Q}\right)$	0.70	Sweijen et al. (2017)

Note that: $Q = \frac{M_w + M_s}{M_s}$ with M_w being the mass of absorbed water and M_s the mass of dry SAP. Assuming a spherical particle and incompressibility of water, equations by Buchholz (1998) and Sweijen et al. (2017) can be rewritten in terms of $\frac{dR}{dt}$ which would yield $R(t)$ by numerical integration. The equation by Omidian et al. (1998) contains a kinetic constant k that is assumed to be equal to $\frac{D}{R_0^2}$. The values of diffusion coefficients were reduced by a factor of D_{scale} to obtain plots in Fig. 2b.

10 d. Therefore, the swelling rate of a particle is then solely dependent on the water uptake rate at the surface of the particle, i.e. water that enters the particle is instantaneously redistributed by diffusion. To derive an equation for $R^*(T)$, consider the following volume balance:

$$V(T) = V_0 + V_w(T) \quad (20)$$

where $V(T)$ is the total volume of a spherical particle, V_0 is the initial volume and $V_w(T)$ is the volume of absorbed water. Hence:

$$\frac{4}{3}\pi(R^*)^3 = \frac{4}{3}\pi + \int_0^{R^*} \theta(T)4\pi r^2 dr \quad (21)$$

which yields:

$$(R^*)^3 = 1 + \theta(T) \times (R^*)^3. \quad (22)$$

Finally, we obtain:

$$R^*(T) = \sqrt[3]{\frac{1}{1 - \theta(T)}} \quad (23)$$

in which $\varphi(T)$ is given by Eq. (16c). Formula 23 is plotted in Fig. 3 for $K = 0.5$.

3.3. Intermediate regime of water uptake and diffusion

Next, we consider situations where $K = O(1)$; i.e. both diffusion and water uptake at the surface balance and both affect the swelling kinetics. We have solved the full set of equations in 16 to simulate the swelling of a sphere for K values ranging from 0.5 to 100.

Results are shown in Fig. 3. For large values of K (i.e. >10) the solution will converge to the case of instantaneous water uptake along the particle surface (see Section 3.1) and thus diffusion becomes the rate controlling process. This fact is supported by the diffusive profiles of φ in Fig. 4a, b. In contrast, for smaller values of K (i.e. $K \leq 1$), the solution will converge to that of Eq. (23), where the profiles of φ are relatively flat compared to larger K values, because diffusion is much faster than water uptake along the particle surface (see Fig. 4c, d).

3.4. Comparison with experiments

To test our model and the importance of K , we have plotted experimental data by Esteves (2011) who measured the radius of roughly spherical SAP particles as a function of time. Hence, these experimental results should compare to our model of spherical particles. In Fig. 3, experimental data is plotted as a function of dimensionless time and fitted to our simulations for instantaneous water uptake at the particle surface ($K = \infty$). In order to convert real time of experiments to dimensionless time, a diffusion coefficient is required following Eq. (9a). This diffusion coefficient is thus a fitting parameter that has been set to $D = 6.0 \times 10^{-5} \text{ cm}^2 \text{ min}^{-1}$. Our results for finite values of K did not yield a good match to experimental data, whereas $K = \infty$ did result into a good match. This can be explained by the fact that SAP particles in the work of Esteves (2011) did not have a coating layer and therefore we do not expect kinetics of water uptake at the surface of the particle.

3.5. Implications and application of the value of K

In practice, the kinetics of water uptake at the particle surface can be beneficial for the commercial design of SAP particles or other swelling products. The kinetics can be changed by applying a coating or a membrane to the surface of the particle. Such a treatment basically affects the value of parameter K . For example, slowing-down of the initial swelling rate can be beneficial for a bed of SAP particles. If the initial swelling rate is too large, the pores between SAP particles may clog before all water has infiltrated into the particle bed, leaving parts of the particle bed dry, which of course is inefficient. Slowing-down of the initial swelling rate by applying a coating layer, may allow water to redistribute completely inside a particle bed before the swelling becomes significant.

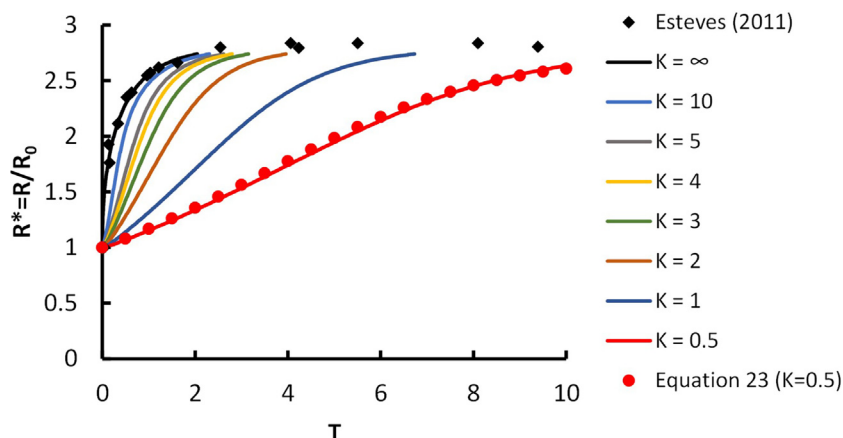


Fig. 3. Swelling of a sphere expressed as $R^*(T)$, the value of K is increased from 0.5 to infinity. symbols indicate experimental data by Esteves (2011), using $D = 6.0 \times 10^{-5} \text{ cm}^2 \text{ min}^{-1}$ and red symbols indicate the solution of Eq. (23) using $K = 0.5$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

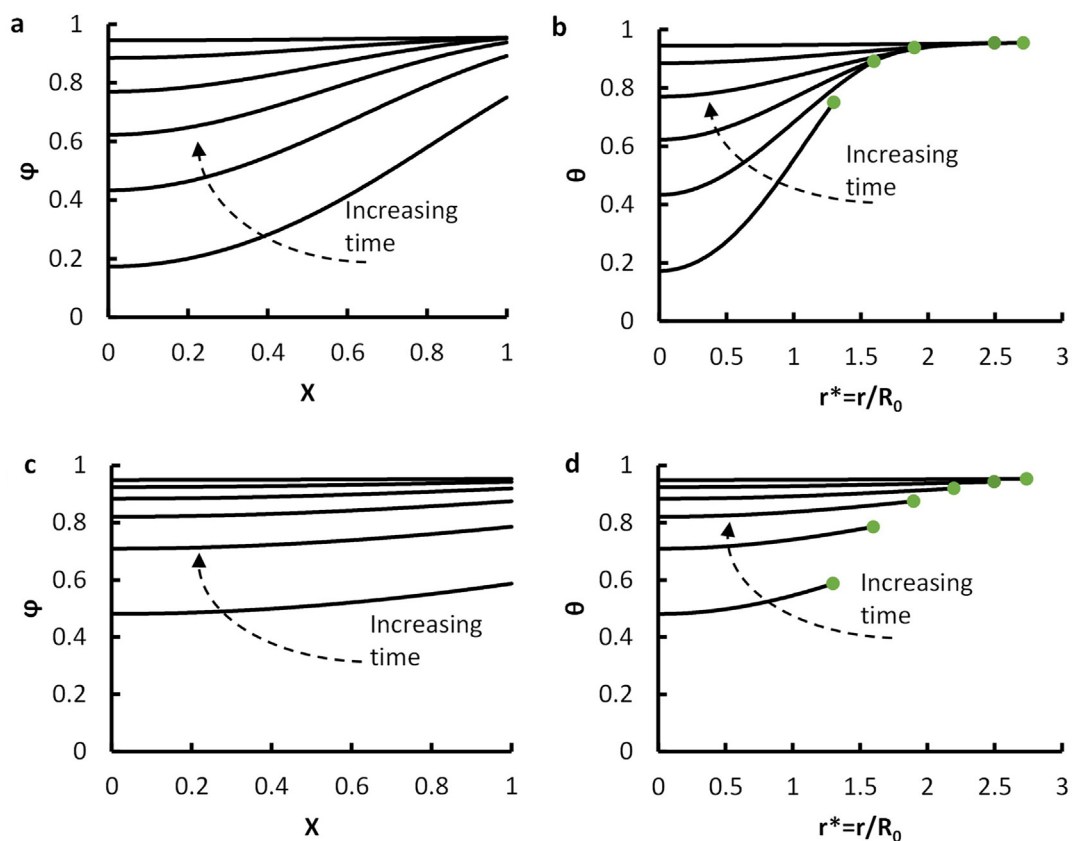


Fig. 4. Water content profiles for (a, b) $K = 10$ and (c, d) $K = 1$. Green symbols indicate the boundary of the particle. Note that the maximum values of both φ and θ is $\theta_{max} < 1$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4. Conclusion

In this research, a model is presented to describe diffusion of water into a swelling particle, where the particle surface can move freely. The model is simplified for a spherical particle and solved using an explicit forward Euler scheme. Modelling results yielded similar plots of radius over time compared to other models in the literature, albeit that they all result in distinctively different diffusion coefficients. A kinetic term was included for water uptake at the surface of a swelling particle, to study its effect on the swelling rate of that particle. Three regimes were identified based on

the controlling mechanism of swelling, namely: (1) diffusion controlled, (2) water-uptake controlled and (3) both diffusion and water-uptake controlled. By slowing down the water uptake at the surface of a particle, using for example a coating layer, the initial swelling rate can be reduced, which can be employed for engineering purposes.

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Appendix A. Free boundary condition of a swelling spherical particle

Here, a free-moving boundary condition is derived for a sphere based on the volume balance in that sphere. Let us start with a simple volumetric balance, the initial volume (V_0) and the volume of absorbed water (V_w) gives the total volume (V):

$$V = V_0 + V_w \quad (\text{A.1})$$

We may rewrite Eq. (A.1) as follows:

$$\frac{4}{3}\pi R_0^3 + \int_0^R \theta 4\pi r^2 dr = \frac{4}{3}\pi R^3 \quad (\text{A.2})$$

Next, Eq. (A.2) is differentiated over time and combined with Leibniz integral rule, which yields:

$$\int_0^R \frac{\partial \theta}{\partial t} 4\pi r^2 dr = 4\pi R^2 \frac{dR}{dt} - \theta_b 4\pi R^2 \frac{dR}{dt} \quad (\text{A.3})$$

We realize that $\frac{\partial \theta}{\partial t}$ can be replaced by $\frac{D}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial \theta}{\partial r})$ for spherical diffusion which is then integrated to yield the final boundary condition:

$$D \frac{\partial \theta}{\partial r} \Big|_R = (1 - \theta(R, t)) \frac{dR}{dt} \quad (\text{A.4})$$

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