

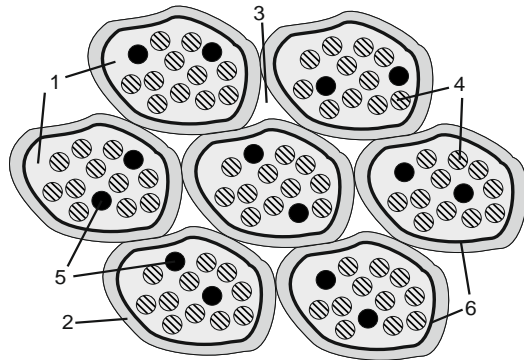
Scale analysis of the generalized supercritical fluid extraction model for diffusive mass transfer in polydisperse packs

A.A. Salamatin

Kazan Federal Univ., Dept. Aerohydromechanics, Kremlyovskaya Str. 18, 420008 Kazan, Russia; fax. +7 (843) 292-72-79, e-mail: arthouse131@rambler.ru

Elaborate supercritical fluid extraction (SFE) models conventionally distinguish between different mechanisms of the solvent mass transfer on the macro-scale level of porous packing bed in the vessel and micro-scale level of single particles. While macro-scale modelling is traditionally based on spatially averaged convective mass balance equations, generally accounting for axial dispersion effects [1-4], the principles of particle-scale models are not so well established or, even, understood. As a rule, two limiting approaches are discussed and employed in SFE data interpretation; they are the shrinking core (SC) model [1, 2] and broken and intact cells (BIC) model [3, 4]. The latter one assumes high longitudinal permeability of the internal microscopic channels (cell walls), resulting in lumped parameter system approximation with average solute concentration in the ground material. On the other hand, the SC model considers the case of high transversal permeability of the cell membranes and assigns all the mass transfer resistance to diffusion along the transport channels. Consequently, the narrow diffusive front moves inside each particle and separates the shrinking oil-filled core from the outer depleted transport zone. Obviously, there exists a wide intermediate range of the ground-plant-material properties when typical rates of solute diffusion across the cell membranes are on the same order as those through the particle, along its transport channels, and the two above (SC- and BIC-) limits fail to describe the SFE process on the micro-scale level.

A generalized SFE model for diffusive solvent-mass transfer in particles is proposed and analysed in this study on the basis of scale analysis. Each (spherical) particle is considered as



an agglomerate of cells (Fig. 1). Every cell is considered as a lumped system containing solvent (1) with dissolved-solute concentration θ_s and droplets (4) of undissolved oil with volume-averaged density x (initial value x_0). The cells are bounded by cell membranes (6) surrounded by cell walls (2) which together with intercellular voids (3) compose the so-called apoplast transport system with solute concentration θ_a and apparent diffusion coefficient D_a . For finite solute saturation

concentration θ_* , the relationship between x and θ_s is written as

$$\theta_s = \min \{ \theta_*; x / (1 - \varepsilon_0) \}, \quad (1)$$

where ε_0 is the cell volume fraction, occupied by insoluble substances (5). Eq. (1) implies that undissolved oil (if any) instantaneously dissolves in the solvent inside the cell up to saturation level θ_* .

Fig. 1. Schematic of internal structure of ground particles. 1 – solute, dissolved in the solvent, 2 – cell wall, 3 – intercellular space (voids), 4 – undissolved oil, 5 – insoluble substances (proteins, etc.), 6 – cell membrane (bold solid line).

Eventually, mass-balance master equations of solute diffusion inside a particle can be presented in terms of dimensionless time τ , radial coordinate r , and concentrations x , and θ_s , θ_a normalized by their respective scales τ_{sc} , a , x_0 , and θ_*

$$\delta_{cw} \frac{M}{1+M} \frac{\partial \theta_a}{\partial \tau} = (1-\varepsilon)M(\theta_s - \theta_a) + \frac{1}{6} \Delta \theta_a, \quad \frac{M}{1+M} \left((1-\varepsilon) \frac{\partial x_s}{\partial \tau} + \delta_{cw} \frac{\partial \theta_a}{\partial \tau} \right) = \frac{1}{6} \Delta \theta_a, \quad (2a)$$

$$\theta_s = \min \left\{ 1; \frac{x}{\Theta} \right\}, \quad M = \frac{a^2 \beta_c}{2D_a}, \quad \delta_{cw} = \frac{\varepsilon \Theta}{1-\varepsilon_0}, \quad \Theta = (1-\varepsilon_0) \frac{\theta_*}{x_0} \quad (2b)$$

$$\tau_{sc} = \frac{x_0}{\theta_*} \left(\frac{1}{3\beta_c} + \frac{a^2}{6D_a} \right).$$

Here, β_c is the reduced mass transfer coefficient across the cell membranes (units s^{-1}), ε (~ 0.01) is the apoplast volume fraction, a – particle radius, and τ_{sc} is the timescale of particle full depletion defined as the sum of two typical times of diffusion across the cell membrane and along the cell wall. Parameter δ_{cw} , as well as ε , is usually negligible if compared to 1, and only two dimensionless complexes, similarity numbers, Θ and M entirely specify the SFE regime.

For $\Theta \ll 1$, i.e. for plant material with high initial oil content such as seeds, two limiting cases of small (I) and high (II) values of M can be formally defined. Asymptotic expansion of Eqs. (2) in case I ($\Theta, M \ll 1$) shows that the principal-order approximation corresponds to BIC model. In case II ($\Theta \ll 1, M \gg 1$), the SC model is obtained with the width of moving diffusive front estimated as $aM^{0.5}$. At the same time, it must be emphasized that the above scale analysis performed for polydisperse packed beds with typical range of particle size, $a \sim 10^{-4}-10^{-3}$ m, reveals at D_a / β_c -ratios $\sim 10^{-7} m^2$ a wide spectrum of various SFE scenarios from BIC- to SC-limits simultaneously existing in different particle-size fractions with different M -values from $M \sim 0.1$ (for smaller particles) to $M \sim 10$ (for bigger particles). Consequently, only BIC- or SC-type limiting mass transfer models alone may not be applicable for kinetic data description on micro-scale level in case of polydisperse packed beds.

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