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A stochastic view on column efficiency

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ABSTRACT

A stochastic model of transcolumn eddy dispersion along packed beds was derived. It was based on the calculation of the mean travel time of a single analyte molecule from one radial position to another. The exchange mechanism between two radial positions was governed by the transverse dispersion of the analyte across the column. The radial velocity distribution was obtained by flow simulations in a focused-ion-beam scanning electron microscopy (FIB-SEM) based 3D reconstruction from a 2.1 mm × 50 mm column packed with 2 μm BEH-C_{18} particles. Accordingly, the packed bed was divided into three coaxial and uniform zones: (1) a 1.4 particle diameter wide, ordered, and loose packing at the column wall (velocity u_w), (2) an intermediate 130 μm wide, random, and dense packing (velocity u_i), and (3) the bulk packing in the center of the column (velocity u_c).

First, the validity of this proposed stochastic model was tested by adjusting the predicted to the observed reduced van Deemter plots of a 2.1 mm × 50 mm column packed with 2 μm BEH-C_{18} fully porous particles (FPPs). An excellent agreement was found for $u_i = 0.93u_c$, a result fully consistent with the FIB-SEM observation ($u_i = 0.95u_c$). Next, the model was used to measure $u_i = 0.94u_c$ for 2.1 mm × 100 mm column packed with 1.6 μm Cortecs-C_{18} superficially porous particles (SPPs). The relative velocity bias across columns packed with SPPs is then barely smaller than that observed in columns packed with FPPs (+6% *versus* + 7%). $u_w = 1.8u_i$ is measured for a 75 μm × 1 m capillary column packed with 2 μm BEH-C_{18} particles. Despite this large wall-to-center velocity bias (+80%), the presence of the thin and ordered wall packing layer has no negative impact on the kinetic performance of capillary columns. Finally, the stochastic model of long-range eddy dispersion explains why analytical (2.1–4.6 mm i.d.) and capillary (<400 μm i.d.) columns can all be packed efficiently ($1 < h_{min} < 2$) with particles of size larger than 2 μm. In contrast, the model predicts that 0.4–1.2 mm i.d. columns and 2.1 mm i.d. columns cannot be packed well ($h_{min} > 3$) with sub-2 μm particles and with 1 μm particles, respectively.

1. Introduction

From a sole theoretical viewpoint, it is expected that the minimum reduced plate heights (RPHs), h_{min}, of infinite diameter columns (characterized by the absence of wall and border effects on analyte dispersion) should be around 0.5, 0.7, and 0.9 when packed with non-porous particles (NPPs), SPPs, and FPPs, respectively [1–8]. From an experimental viewpoint, it is noteworthy that h_{min} around 1.0 has actually been observed but under specific conditions: (1) by gently (no pressure applied) dry-packing 200–220 μm NPPs in a 2.4 cm inner diameter (i.d.) ×16.6 cm column [9]; (2) by slurry-packing capillary columns for a column-to-particle diameter ratio (or bed aspect ratio), (d_c/d_p), smaller than 7 such as a 12 μm i.d. capillary column packed with 5.0 μm FPPs [10], a 21 μm i.d. capillary column packed with 5.0 μm FPPs [11], or a 3 mm i.d. column packed with 480 μm glass beads [12,13]; (3) by slurry-packing sub-3 μm SPPs in a very large number of 4.6 mm i.d. ×10 cm columns and by picking up a column at 3σ standard deviation above the mean efficiency [14–18]; or (4) by slurry-packing a 75 μm i.d. ×1 m capillary column with 2 μm FPPs at very high pressures (30 000 psi), using highly concentrated slurry suspension (200 g/L), and by applying sonication (80 kHz) [19].

Remarkably, for most usual combinations of column i.d. and particle size, the observed h_{min} of random sphere packings confined into straight cylindrical column tubes are typically around 1.5 and 2.0 for SPPs [20–23] and FPPs [24–26], respectively. It has been recognized for a long time that the origin for the gap between the observed and the maximum theoretical column performance was due to the flow unevenness of the mobile phase across the column i.d. [10,27–41]. Radial flow heterogeneity is directly related to the variation of the local bed density (or bed void fraction) across the column i.d. which results from the radial distribution of the pressure stress applied to the particles during slurry packing and

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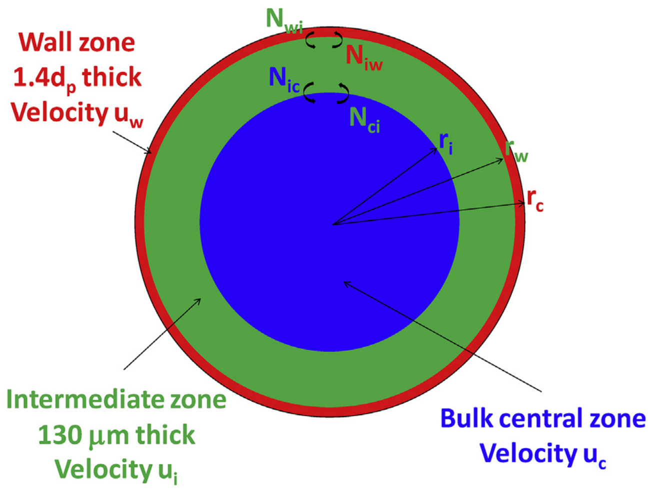

Fig. 1. Delimitation between the distinguishable wall (red color), intermediate (green color), and bulk (blue color) regions present in slurry-packed columns. In the wall region, the particles are ordered and loosely packed relative to the bulk region. In the intermediate region, the particles are randomly and densely packed relative to the bulk region. The dimensions are not on scale. The symbols N_{wi}, N_{ic}, N_{iw}, and N_{ci} represent the number of molecular transfers from the wall to the intermediate region, from the intermediate to the bulk region, from the intermediate to the wall region, and from the bulk to the intermediate region, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

bed consolidation [42–45]. The stress experienced by the particles in the wall region is found higher than that in the bulk region of the column because of the presence of the fixed column wall [43]. Reising et al. have recently imaged the actual spatial distribution of 2 μm BEH-C_{18} particles in a consolidated bed, which was carefully extruded from a commercial 2.1 mm i.d. ×50 mm stainless steel column [38]. This study revealed the existence of three distinguishable coaxial zones based on the intensity of the average flow velocity in these three zones (see Figs. 1 and 2): (1) a thin (1.4 particle diameter wide), loose, and orderly packed region at the very wall of the column (the velocity is 1.5 times the bulk velocity); (2) a thick (130 μm wide), dense, and randomly packed intermediate region (the velocity is 0.95 times the bulk velocity); and (3) the bulk randomly packed region (the bulk velocity is the reference velocity). The velocity discrepancies between these three zones explain why the experimental h_{min} value is as large as 1.7 for this commercial column [46] instead of 0.9 when considering the sole dispersion through the bulk region of this column [3–6].

Despite the on-going efforts towards the development of systematic and optimized slurry-packing procedures [19,47–51], which eventually depends on the column format and on the nature of the particles to be packed, h_{min} values of 1.0 have never been observed with typical 2.1–4.6 mm i.d. analytical columns. In a recent work, a general theory of analyte dispersion along a packed column was derived and used to establish a direct relationship between the structural heterogeneity of slurry-packed beds and their kinetic performance [46]. The results showed that h_{min} of 1.0 (FPPs) or 0.7 (SPPs) can eventually be observed provided that the difference between the bed density in the intermediate region and that in the bulk region is reduced. Accordingly, it was suggested packing columns at lower pressures (maximizing the risk of forming unstable beds) from concentrated suspension slurries and/or packing particles with a rougher external surface in order to level off the variations in particle density across the column diameter. These strategies were only partially successful since h_{min} of columns packed with either FPPs at low pressures and high slurry concentrations or with rough SPPs are still as large as 1.7 [50,52–55] and 1.4 [15–18,20–22], respectively. It should be noted that cohe-

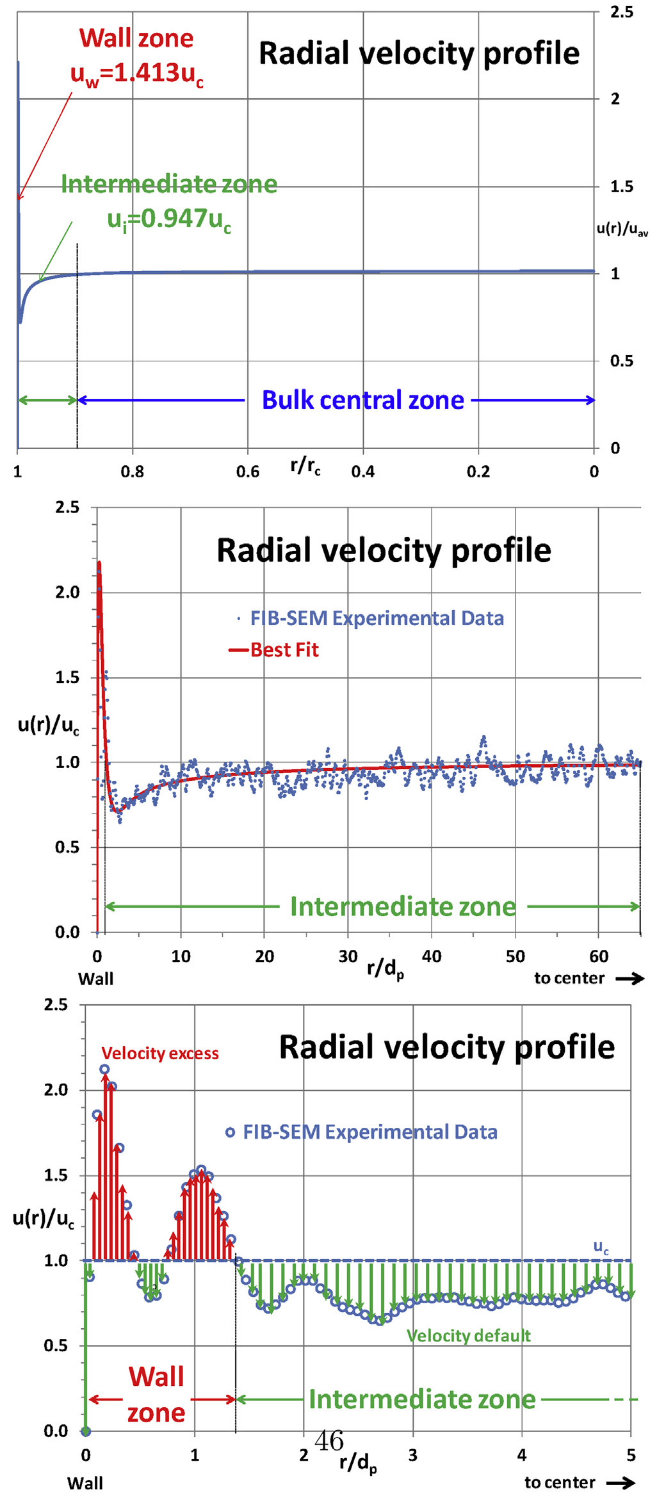

Fig. 2. Radial distribution of the interstitial linear velocity $u(r)$ observed across a 2.1 mm i.d. × 50 mm column packed with 2 μm BEH-C_{18} particles [38] revealing the delimitation between the three column zones (wall, intermediate, and bulk zones) schematically represented in Fig. 1. (Top graph) On the y-axis, the local velocity is normalized to the average velocity u. The x-axis represents the radial position normalized to the column inner radius and varies from 0 to 1. (Middle graph) On the y-axis, the local velocity is normalized to the bulk velocity u_c. The x-axis represents the radial position or the distance from the column wall expressed as the number of particle diameters which varies from 0 to 65. (Bottom graph) Same as in the middle graph, except the zoom on the radial distance from 0 to only 5 particle diameters from the column wall.