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Consolidation of the packing material in chromatographic columns under dynamic axial compression IV. Mechanical properties of some packing materials

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Abstract

Dynamic axial compression columns were packed with three C_{18} silica materials used as stationary phases in preparative chromatography, one made of irregular and two of spherical particles. Measurements of column length vs. time and axial compression pressure, obtained for several columns, have been previously reported. These results are discussed here in terms of packing density, internal porosity, and external porosity, as allowed by the use of independent measurements of the density of the silica skeleton and the pore volume. The compressibilities and Young moduli of the columns are calculated and compared to results obtained in soils mechanics for various soil types. The results indicate that the preparative columns packed with silica particles exhibit a behavior intermediate between that of uniform fine and medium-sized sands. The angular silica material exhibits higher compressibility than both spherical silica materials on first compression. Upon recompression, one of the spherical silicas studied exhibits high compressibility and thus elasticity, suggesting a looser packing structure than the other spherical material; this is supported by calculation of the external porosities of the two materials. Results with respect to the kinetic theory of consolidation in soils mechanics are also presented.

Keywords: Stationary phases, LC; Packing consolidation; Consolidation; Dynamic axial compression; Packing materials, mechanical properties; Axial compression columns

1. Introduction

Results have recently been reported which describe the consolidation of axial compression columns which have been filled with several brands of commercial C_{18} silica packing materials used as stationary phases for reversed-phase HPLC [1–3]. These experiments yielded the column length contraction which occurs when the applied axial compression pressure (ACP) is increased in stepwise increments, in the presence of a packing or slurry solvent but without any flow of this mobile phase [1,2]. They have also yielded the kinetic response to incremental steps, or pressure-jumps of the ACP. These experiments indicate that an underlying smooth consolidation of the packing materials occurs under applied pressure, but are invariably accented

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by abrupt jumps or contractions which appear to be random in nature, except for a material whose particles are very regular, smooth spheres. The final packing density and performance of these columns depends somewhat on the nature of the slurry solvent used to suspend the packing [3]. It is not necessarily true, however, that the packing density is reflected by the column performance or efficiency in any manner. These observations illustrate a fundamental void in our understanding of the consolidation process and its importance in column packing.

A homogeneous consolidation of the stationary phase material during the packing process is an important requirement for the attainment of a highly efficient column. Otherwise packing voids or regions of low density, hence high external porosity and permeability, will be formed, imparting a nonhomogeneous flow profile of the mobile phase and resulting in a dispersed and perhaps asymmetrical band profile. When a void is formed at the column inlet, multimodal bands may even result. Therefore, the determination of the packing conditions under which bed homogeneity can be achieved are of utmost interest. To attain this knowledge, a correlation between the packing density, the external and internal porosities of the packing, and the column permeability is needed to begin to assess the geometry of the consolidated bed. Comparison with theoretical results of the consolidation process is then needed to further our current understanding of the packing process so that it may be appropriately optimized, and in turn the column efficiency and resolution achieved in preparative chromatography can be maximized.

This work details the results of several consolidation experiments which have been previously reported, with respect to soils mechanics theory and an independent assessment of the internal and external porosities of the beds. Results are contrasted to those attained on analytical-sized and semi-preparative columns for one of the packing materials studied. Such comparisons illustrate the fundamental differences in packing geometry that are achieved for the two types of chromatography, analytical and preparative, and the two types of packing procedures used, consolidation under friction stress caused by a high flow-rate of percolating solvent and the application of a high external mechanical stress (axial and radial compression technologies [5,6]).

2. Theoretical

This section recalls a number of definitions classical in the study of the properties of beds of particulate materials, be it land masses in geology or soil mechanics, catalyst beds, adsorbent columns, heat exchangers in chemical engineering, or chromatographic columns. The fundamental relationships between the parameters so defined and various characteristics of the materials used are then discussed, as they relate to the present study.

2.1. Packing density and porosity.

The column packing density is calculated from a measurement of the exact amount, M_s, of packing material (previously dried under specific conditions) placed in the column, and of the known geometrical volume of the column. A knowledge of the density of the packing material used, ρ_s, allows the derivation of the volume occupied by the actual skeleton

$$V_s = \frac{M_s}{\rho_s} \tag{1}$$

This volume includes the volume of the inaccessible or closed pores which is different for each packing material, as it depends on the specifics of the process used. Accordingly, the density of each packing material is different, all the more since this includes the volumes occupied by both the silica skeleton and the bonded alkyl groups, for which a correction can be derived [7]. The density is derived from a pycnometric measurement (see Section 3). The fraction of the column occupied by the stationary phase skeleton is then

$$\epsilon_s = \frac{V_s}{V_c} \tag{2}$$

where V_c is the total or geometrical volume of the column. In dynamic axial compression, this volume decreases as the bed consolidates under the compression stress during the experiment.

The void volume fraction of the column is expressed as the total porosity:

$$\epsilon_T = 1 - \epsilon_s \tag{3}$$

This void volume fraction consists of the interstitial, or external porosity and the internal pore volume, or internal porosity:

$$\epsilon_T = \epsilon_e + \epsilon_i \quad (4)$$

The internal porosity is determined from a measurement of the total pore volume:

$$\epsilon_i = \frac{V_i}{V_c} \quad (5)$$

where V_i is calculated from the specific pore volume, V_p, obtained from nitrogen sorption measurements:

$$V_i = V_p M_s \quad (6)$$

The external porosity is determined by the difference of the total and internal porosities. Note that

$$\epsilon_s + \epsilon_e + \epsilon_i = \epsilon_s + \epsilon_T = 1 \quad (7)$$

2.2. Void fraction, compressibility, and modulus

The void fraction is defined as the ratio of the external porosity to the fraction occupied by the packing material (including the pore and the skeleton volumes):

$$e = \frac{\epsilon_e}{1 - \epsilon_e} \quad (8)$$

Clearly, the void fraction is the fraction of the column volume available to the stream of mobile phase. It will characterize the hydrodynamic properties of the column which do not depend on the importance of the internal porosity.

The compressibility of the column bed can then be expressed as the slope of a plot of the void fraction versus the axial compression pressure:

$$a_v = -\frac{de}{dP} \quad (9)$$

where P is the axial compression stress (usually reported as a pressure[2]) and a_v is the compressibility coefficient.

In the theory of stress-strain relationships, one may express the modulus of a material as the stress applied over the strain produced [4]. For the case of dynamic axial compression columns in preparative chromatography, we assume that the stainless steel tube does not flex nor shear under normal operating conditions and that only the case of uniaxial loading or confined compression is operative. The elasticity constant in this case is Young's modulus, or equivalently the constrained modulus:

$$E = \frac{PV}{\Delta V} \quad (10)$$

where V and ΔV are the initial column volume and the change of column volume, respectively, under an axial compression stress P, which is the ACP. Eq. (10) is related to Eq. (9) by

$$a_v = \frac{1 + e_0}{E} \quad (11)$$

where e_0 is the initial void ratio. The modulus or compressibility coefficient can be calculated for initial and repeated loadings of the stress. For pulverulent materials, it usually depends on the previous history of the sample. Different packing materials, can be compared with each other on the basis of their modulus and the values of these moduli can be compared with the results of documented experiments on soils samples in the literature to obtain insight on the geometry and stability of column beds.

2.3. Permeability and consolidation kinetics

The column permeability, k, is introduced as a proportionality coefficient in Darcy law:

$$u = \frac{k \Delta P}{\eta L} \quad (12)$$

where u is the average linear flow velocity of mobile phase through the stationary phase, ΔP is the column inlet pressure, η is the mobile phase viscosity, and L is the column length. A plot of u vs. $\Delta P/\eta L$ yields the column permeability at the particular ACP applied.

The column permeability is related to the external and total porosities of the column through the Blake–Kozeny relation:

$$k = \frac{d_p \epsilon_e^3}{h_0 \epsilon_T (1 - \epsilon_e)^2} \quad (13)$$

[2] Note that, while pressure in a liquid is isotropic and conveys very fast, at the speed of sound, stress in a solid does neither. Because of friction between the particles and between the bed and the column wall, stress varies axially and radially, and adjusts slowly when the stress is changed. However, the units are the same and the ACP is the stress applied to the piston reported to its cross-sectional area.

where d_p is the particle diameter and h_0 is a geometrical factor somehow related to the particle shape. If k is determined from Darcy law, Eq. (13) can be solved for h_0, which is assumed to be constant for a particular packing material.

The coefficient of consolidation is defined as

$$C_v = \frac{k(1+e)}{a_v \eta} \tag{14}$$

It is used to scale a dimensionless time variable, useful to describe the kinetics of consolidation [1,4,8]. The dimensionless time is

$$\tau = \frac{4C_v}{L^2} t \tag{15}$$

The consolidation ratio is expressed experimentally as

$$U = \frac{e_1 - e}{e_2 - e_1} \tag{16}$$

where e_1 and e_2 are the initial and final void ratios. The theory of consolidation of Terzaghi [1,4,8] indicates that the consolidation ratio is related to time through

$$U = 1 - \sum_{m=0}^{\infty} \frac{2}{M^2} e^{-M^2 \tau} \tag{17}$$

where $M = (2m+1)\pi/2$. The Terzaghi theory assumes that consolidation is kinetically limited by the rate of expulsion of the liquid from the external void space of the bed. It is of interest to see if this is the case in preparative chromatographic columns.

3. Experimental

The details of the packing procedure and the consolidation experiments have been reported elsewhere [2,3,9]. Three different packing materials have been studied. The main characteristics of these materials are given in Table 1.

The average particle sizes were derived from measurements made with a Coulter counter. The other measurements reported in Table 1 were obtained by Micromeritics (Norcross, GA, USA), the density by pycnometry (i.e., by measuring the volume inaccessible to helium in a known weight of material), the specific surface area and the average pore size from nitrogen adsorption isotherm determinations, using the BET method [7,10]. The volume average particle size were derived from previous experiments [2].

The packing materials are compared with respect to their individual porosities (Eqs. 3–5,7), compressibilities (Eq. 9), and moduli (Eq. 10). The consolidation experiments made are comprised of a first and second compression series. In the first series, the column is consolidated under ACP, starting with a sedimented bed under zero stress (gravity compression only). After the last ACP step is applied, the compression stress is released and a second compression series is carried out.

Both long and short 5 cm I.D. columns were studied. The long columns were packed with 238 g of packing material in the Impaq and Zorbax studies, corresponding to column lengths of between 17 and 27 cm, depending on the ACP applied. The Kromasil column had 180 g of material, with a column length of between 15.5 and 22 cm. The short columns had ca. 30 g of silica, yielding lengths between 2 and 3 cm.

The kinetic experiments were performed simultaneously with the static length vs. ACP experiments above, the time profile of contraction being recorded after the pressure increments had been applied. A

Table 1
Physical characteristics of the packing materials used in this study

Packing material	Particle diameter (μm)	Specific surface area (m^2/g)	Average pore size (Å)	Density (g/ml)	Specific pore volume (ml/g)
Impaq	20	164.7	113.1	1.4871	0.4656
Kromasil	13	151.7	95.7	1.5674	0.3646
Zorbax	10	92.3	126.6	1.8039	0.2931

number of these profiles have been reported [1,2]. After the bed was stabilized, the final recording was used for the L vs. ACP plots.

The details of the packing procedure developed and the performance observed for the analytical and semi-preparative size columns prepared and discussed here are given separately, in [11]. These experiments were performed with the Zorbax material. Analysis of the consolidation kinetics theory is also performed on the Zorbax material for the axial compression columns, using Eqs. (13–17).

4. Results and discussion

4.1. Axial compression columns

The total, internal, and external porosities of the various columns studied as a function of the ACP for the first compressions are reported in Fig. 1, Fig. 2 and Fig. 3 . The total and external porosities decrease with increasing ACP. The internal porosity increases with ACP because the total column volume decreases. If the internal porosities are reported to the actual volume of the particles (i.e., if they are divided by $1-\epsilon_e$ to calculate the particle porosity), as it is conventional in engineering, they become constant. The decrease of the void ratio of each column during their first compression are compared in Fig. 4. The variations of the void ratio of these

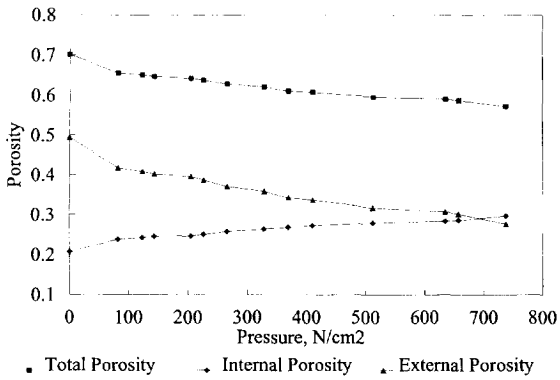

Fig. 1. Porosities of a dynamic axial compression column filled with Impaq C_{18} silica as a function of the axial compression pressure (first compression).

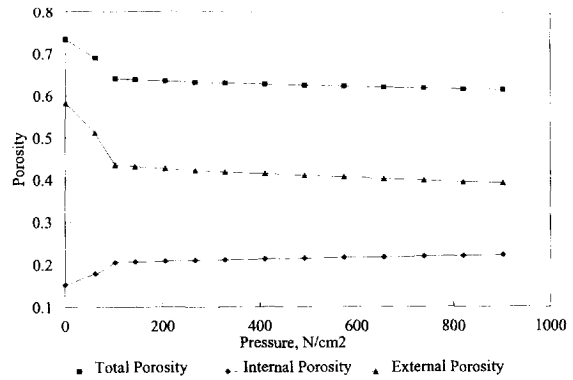

Fig. 2. Porosities of a dynamic axial compression column filled with Kromasil C_{18} silica as a function of the axial compression pressure (first compression).

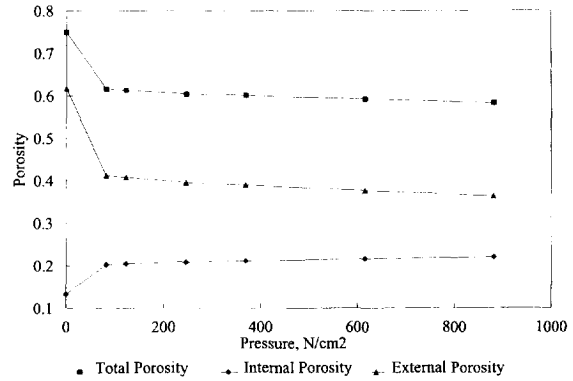

Fig. 3. Porosities of a dynamic axial compression column filled with Zorbax C_{18} silica as a function of the axial compression pressure (first compression).

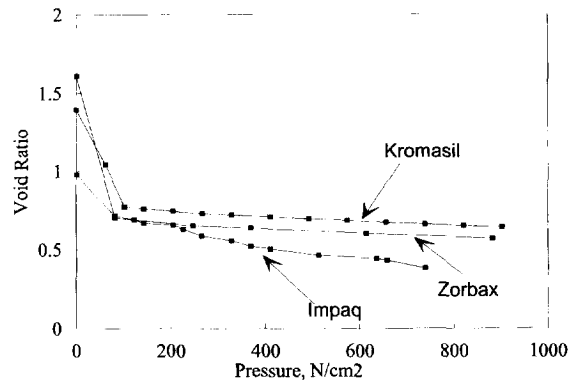

Fig. 4. Void ratios of the long axial compression columns as a function of the axial compression pressure (first compression).

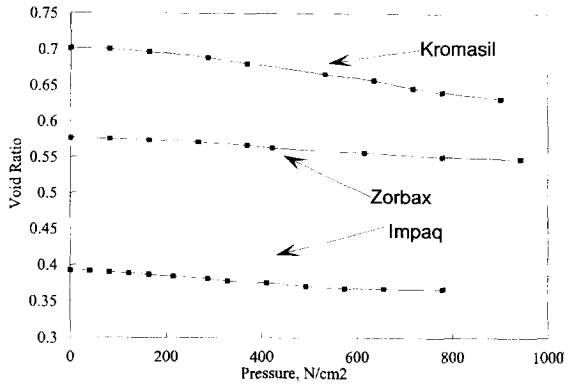

Fig. 5. Void ratios of the long axial compression columns as a function of the axial compression pressure (second compression).

columns during their second compression are given in Fig. 5. The behaviors of the two columns packed with spherical silica particles (Kromasil and Zorbax) are similar. The total and external porosities are always lower at a given applied ACP for the Zorbax material. This latter result is independent of the lower specific pore volume of this material, a parameter which is unrelated to the external porosity. The behavior of the irregular Impaq material is different, with consolidation occurring to a greater extent in this material. The slopes of the linear portions of the curves shown in the figures yield the compressibility coefficients. These coefficients are given in Table 2. The angular Impaq material has the highest compressibility during the first compression while spherical Kromasil and Zorbax compress identically. The second compression reveals, however, that Kromasil has the highest elasticity. This can also be seen by noting that the Kromasil bed expands the most between the end of the first compression and the beginning of the second compression.

These results may be influenced somewhat by particle breakage and aggregation. The Impaq material has been seen by electron microscopy [2] to fracture or at least to chip the most, followed by Zorbax. The Kromasil material retains its integrity to the largest extent [2]. If the material fractures or aggregates, it cannot rebound according to its original geometry. Note that consolidation has not taken place under a compression stress reported high enough for the particles to break extensively [1]. For all columns during their first compression, the quasi-linear range of compressibility was established very early, after the first ACP step from an initial stage in which no ACP was applied and only the sedimentation of the bed was observed. For a few experiments two steps were needed to reach the quasi-linear range. This range persisted to the final ACP for all but a few experiments in which the void ratio decreased more dramatically at the highest compression stresses, signifying possibly the onset of extensive particle breakage [1].

The Young modulus can be calculated similarly, and the respective values for the three materials under initial and repeated compression are also given in Table 2. The values reported here for the first compressions are indicative of fine or medium-sized sands [4]. Angular materials generally yield moduli which are of lower magnitude than spherical or rounded materials. This is observed in the first compression but not necessarily in the second compression. The modulus should increase significantly upon repeated loadings [4]. The dramatic increase in modulus for the Impaq material, however (almost an order of magnitude), suggests that the particles are breaking under the applied ACP, as has been noted above, and that a dense packing has resulted. This is confirmed by a faster decline in the external porosity (compare Fig. 1 and Figs. 2 and 3). This is also in agreement with the recommendation of the manufacturer of axial compression columns to apply a lower ACP to irregular particles than to spherical ones. The

Table 2
Compressibilities of various packing materials under dynamic axial compression

Material	a_v (cm^2/N) 1st compression	E (MN/m^2) 1st compression	a_v (cm^2/N) 2nd compression	E (MN/m^2) 2nd compression
Impaq	$5.0 \cdot 10^{-4}$	39.8	$4.3 \cdot 10^{-5}$	327
Kromasil	$1.6 \cdot 10^{-4}$	151	$8.4 \cdot 10^{-5}$	203
Zorbax	$1.6 \cdot 10^{-4}$	155	$3.4 \cdot 10^{-5}$	465

Zorbax material undergoes a significant increase in modulus from the first to the second compression (nearly three-fold), whereas the Kromasil material displays only a marginal increase by comparison. This behavior is indicative of a looser packing for the Kromasil column, as looser packings yield lower moduli under repeated loadings [4]. This conclusion is supported by the higher void ratio of the Kromasil column.

Although the moduli of the spherical materials considered here (Kromasil and Zorbax) are in between the values documented for fine and medium-sized sands, the particle sizes of these materials are more in between those of fine sands and silts. It seems that the chromatographic materials have a lower compressibility than expected, based on their particle size alone. The reason for this behavior is not known at present, but it may be due to wall effects[3] or friction between particles which may suppress or reduce the vertical movement of the bed, and/or the narrow particle size distribution exhibited by chromatographic packings relative to soil samples. In the latter case, the bed cannot consolidate to the same extent since there are not as many small particles which can squeeze in between larger particles.

The general behavior of the short columns is similar, but the relative differences between columns is different, as shown in Fig. 6. The short Kromasil column was observed to consolidate to an even lesser extent than was observed for the long column. This result is not intuitive and is currently under further investigation. A possible explanation is that the void volume became trapped in the short column. Radial and longitudinal redistribution of the particles is not as easily accomplished within the shorter length, although great attention is paid to achieve a good radial distribution of the initial slurry. By contrast, the compression of the Impaq and Zorbax materials in a short column was greater than that observed for long columns, for the Zorbax significantly so. This result is expected if the extent of consolidation is limited by friction of the bed against the wall.

[3] To eliminate the influence of friction between the bed and the wall of the compression chamber, determination of soil compressibility and elastic modulus are performed with short columns in soil mechanics.

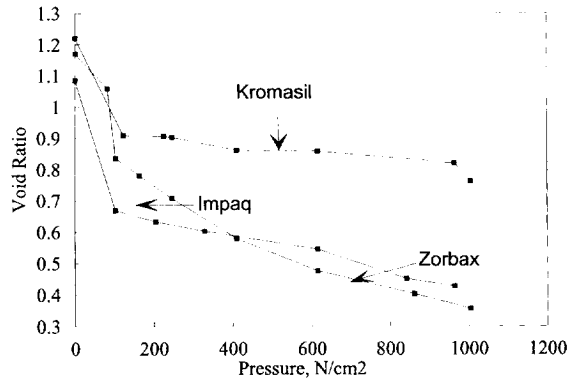

Fig. 6. Void ratios of the short axial compression columns as a function of the axial compression pressure (first compression).

4.2. Comparison between slurry packing and axial compression stress

It is interesting to compare the packing densities and porosities of the axial compression columns to the same parameters achieved with columns prepared using the conventional slurry packing method, in which the slurry is pushed into the column by a high flow-rate stream of a suitable solvent, under high inlet pressure [11]. This procedure has been adopted long ago for semi-preparative or analytical chromatographic columns. The results for such a comparison on the Zorbax material are given in Table 3.

Only the value at the highest ACP applied during the first compression series is reported in Table 3 for the axial compression column. For repeated compressions this density is attained at lower and lower ACPs, so for practical purposes in preparative chromatography this density will probably be achieved after only a few runs. The data suggests that axial compression is a more effective way to pack a dense column than using solvent flow under high inlet pressure. This may result in a bed that is more homogeneous in its geometry, which is required to minimize void volume and this certainly explains the high degree of bed stability achieved with dynamic compression columns. However, particle breakage may be more of a problem in axial compression than with the slurry packing technique. The differences between the two packing methods may have serious consequences on the scalability of results between the preparative and analytical regimes if retention

Table 3
Comparison of packing densities as a function of column dimension and packing technique

Column dimensions	Packing density (g/ml)	Total porosity	External porosity
25.0×0.46 cm	0.7198	0.6010	0.3900
9.8×1.0 cm	0.7244	0.5985	0.3862
16 ×5.0 cm[a]	0.7509	0.5837	0.3636

[a] Evaluated at the highest ACP during the first compression series: 881.5 N/cm^2.

times and band profiles are affected by the packing density and geometry in chromatographic columns. Initial results have indicated that this might indeed be the case [12,13].

4.3. Consolidation kinetics

The kinetics of consolidation of packed beds in chromatography does not have an adequate theory at the present time. In soil mechanics, the limiting rate constant for the consolidation of beds is assumed to be the expulsion of the liquid from the external void space [1,8]. This expulsion takes place through the ends of the bed, from where the liquid can be drained. Thus, fluid expulsion from the heart of the bed proceeds through the already consolidated ends of the bed, which have a reduced external porosity, hence permeability. The process can be modeled through a partial differential equation. An analytical solution of this equation is possible with a few simplifying assumptions which are valid in the case of column beds[4]. The following demonstrates the validity of these assumptions, primarily that of neglecting the frictional lag due to particles moving against one another.

The column permeability of the Zorbax packing was calculated using the Darcy law (Eq. 12) to be between $1.4 \cdot 10^{-9}$ and $2.2 \cdot 10^{-9}$ cm^2 for four trials at ACPs between 123 and 902 N/cm^2. The correlation coefficients of the u vs. ΔP measurements were excellent with the worst trial at 0.988. These permeabilities agree with that calculated for the L vs. ACP static experiments at ACPs corresponding to those used in the Darcy measurements. This check was performed by solving the Blake-Kozeny equation (Eq. 13) for the geometrical constant using the Darcy permeability and porosities, and then solving it again in the static experiments for k using the Darcy-derived h_0 and the static porosities. The largest discrepancy for the column permeability between the two experiments was 10% amongst the four trials.

The consolidation kinetics data was reported in Ref. [2] and consists of length vs. time measurements after a specified jump from low to high ACP. Using the data collected independently on the skeleton and pore volume fraction (see Section 3), the resulting data can be expressed in terms of the void fraction (Eq. 8) vs. time. The column permeability vs. time can also be calculated since Eq. (13) holds as shown above. The compressibility in the region of the pressure jump is approximated well by the value reported in Table 2, because the e vs. P curve is quite linear in this range. Thus Eq. (14) can be used to calculate the coefficient of consolidation vs. time, and Eq. (15) for the dimensionless time variable. The compressibility of the first compression is used, as this is when the kinetic experiments were performed. If the appropriate values are substituted into Eq. (14) and Eq. (15), the coefficient of consolidation is seen to be of the order of 100 cm^2/s and τ/t on the order of 1.4 s^{-1}. Using Eq. (17), the column should be 95% consolidated ($U=0.95$) at its new ACP in less than 1 s! Experimentally, 95% consolidation is achieved after approximately 25 min with the Zorbax material and 8 h with the Impaq material. However, with the Kromasil material, the required time for 95% consolidation is of a few s, i.e., in agreement with the prediction of the theory within the experimental errors (see Ref. [2], Fig. 2).

[4] The Terzaghi theory of consolidation neglects the frictional lag between particles and makes the following assumptions: (1) the bed is homogeneous; (2) the bed is completely saturated with the mobile phase (no residual gas); (3) the compressibility of the mobile phase and of the particles are negligible; (4) the compression and the flow are unidimensional and parallel; (5) Darcy law is valid; (6) the parameters considered are independent of the pressure [1,8].

Thus, the kinetic theory of consolidation in soils mechanics is inadequate for the case of axial compression columns and most packing materials used in chromatography. The reason for that failure is most probably because the theory neglects the frictional lag while the limiting kinetic term is related to the friction of the particles against each other as the column consolidates and to the possible effect of friction of the bed against the column wall. This result supports the conclusions from the static experiments above, where the observed low compressibility relative to soils samples could be due to frictional stress. Note, however, that the same type of consolidation kinetics is observed for long and short Impaq columns [2], while the friction stress has been reduced by nearly an order of magnitude in the latter case.

4.4. External porosity of the columns

The external porosity of the compressed Zorbax column (Table 4) lies just below the experimental range observed for disordered packing structures (0.37–0.38 for stainless steel beads) [14]. Thus the slurry used to fill the column and the sedimented bed before the ACP is applied may be fairly homogeneous, which is consistent with the way they are prepared. Consolidation of this homogeneous slurry via the mere expulsion of liquid should result in a disordered bed structure. However, a structured bed (octahedric or tetrahedric) possesses lower interstitial porosity than a disordered bed and is the stable arrangement under compression stress. Movement of the particles against each other must occur, however, for the transition from disordered to ordered bed to take place. Friction prevents particles from slipping against each other.

The porosities of the other two materials studied under ACP (Kromasil and Impaq) are also given in Table 4. The Kromasil material yields an external porosity value that is just above that observed for disordered structures, larger than that of Impaq, and nearly 10% larger than that observed for Zorbax. This result is consistent with the values of the compressibility or moduli measured, which suggests that the packing structure in this case is somewhat loose. The differences between the physical properties of consolidated beds made of Kromasil and Zorbax are generally small but they are in a direction opposite to what our knowledge of the particles' properties would have lead us to expect (see SEM micrographs in [2]). Kromasil, which is made of very spherical, apparently smooth particles, consolidates quickly under stress but gives a bed which is less densely packed than Zorbax, whose particles are less spherical [2]. The reason why these two materials pack so differently needs to be explored further. Perhaps the materials shear or chip to different extents, allowing them to consolidate to varying extents. The Kromasil shears the least, therefore is not able to consolidate to the same extent as Impaq and Zorbax.

5. Conclusion

The consolidation of packing materials under dynamic axial compression depends on the nature of the packing material. The differences between the mechanical properties of the consolidated beds obtained with different materials seem to be related to the shape of the particles and to the mechanical properties of their external surface. This could explain that two spherical materials can yield different packing structures. The angular materials can break under significant compression pressures and result in denser packings than would be expected otherwise.

Table 4
Total and external porosities of packing materials under dynamic axial compression[a]

Material	Packing density (g/ml)	Total porosity	External porosity
Impaq	0.6359	0.5724	0.3818
Kromasil	0.6069	0.6128	0.3916
Zorbax	0.7509	0.5837	0.3636

[a] Measurements taken at the final ACP for the first compression series.

Significant differences are also observed between the mechanical properties of the beds obtained with axial compression as compared with those achieved with analytical-sized columns packed with the conventional slurry method. The packing is typically more dense in axial compression after any significant amount of compression has been applied. Although part of the difference may come from the much larger diameter of the axial compression column, which reduces the relative contribution of the friction of the bed against the wall to the bed stability, there are also important differences in the packing procedures. The implications of these results are that the packing methodology in column chromatography needs to be better controlled, or at least understood, in order to minimize the difference in packing geometries amongst methods and materials.

At this stage, we do not know which of the mechanical properties of the bed are important from the point of view of column performance. As a consequence, this study cannot conclude to the superiority of any one of the packing materials studied here over the others. Because the relationship between column performance and bulk properties of the packing materials used is so poorly understood, we need to carry out a number of determinations which are not obviously relevant and may prove not to be. One illustration of the difficulties encountered in trying to unravel these phenomena is the fact that the same material gives columns a markedly higher efficiency when the axial compression stress is applied very rapidly than when it is applied progressively, following a series of intermediate steps [2,9].

The assumption of a homogeneous bed cannot be ascertained by these studies. Different geometries can be homogeneous in nature, yet yield different packing densities. The measurement and consequent effects of packing inhomogeneity need to be addressed to further increase resolution and optimization routines in high-performance liquid chromatography.

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