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# Consolidation of the packing material in chromatographic columns under dynamic axial compression. I. Fundamental study

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**Abstract**

Packing materials do consolidate progressively inside chromatographic columns. The process is slow. The literature on the phenomenon of soil consolidation is critically reviewed and the concepts relevant to the behavior of sands are applied to conventional packing materials. Preliminary experimental results obtained with irregular-shaped particles are presented to illustrate the concepts introduced by and the conclusions of the literature survey. These results show that the consolidation of packing material in chromatographic columns is a slow process which may sometimes appear to take place as a series of "catastrophic" events. It involves changes in the apparent packing density of the bed which are large enough to account for the formation of large voids at the column inlet, as has been frequently reported by operators of analytical as well as large-size preparative columns.

## 1. Introduction

There is serious experimental evidence that the packing of chromatographic columns is not homogeneous. Knox and Parcher [1], Knox et al. [2], and Horne et al. [3] showed conclusively that there is a wall region in packed columns which is severely perturbed. This region extends to ca. 30 particle diameters from the wall. The column core, on the other hand, appears to be much more homogeneous. So, these authors suggested that if the sample is injected at the center of a wide enough column, the analyte bands would never have time to reach the wall region and the column performance would be as good as if the column were entirely homogeneous. If the column is narrow, however, a significant fraction of its molecules enters the wall region and propagates inside it. As a consequence of the heterogeneity of the packing in the wall region, the apparent efficiency of the column drops markedly when the band has access to it. Knox's data [1–3] were confirmed by Eon [4] who demonstrated that the local value of the axial plate height (characterizing band spreading in the direction of the flow velocity) increases as the location gets closer to the wall, that the apparent height equivalent of a theoretical plate (HETP) is not constant along the wall, around the column, and that radial compression [5] may im-

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prove markedly column performance, presumably because it reduces the density difference between the wall and the core regions.

Unfortunately, the concept of the infinite-diameter column would not be practical in preparative chromatography. A large fraction of the packing material contained in the column and of the solvent used would not be involved in the retention and the separation process. Their loss would represent a high cost to pay for a gain in column efficiency which is rarely perceived to be worth so much. For analytical applications, the equipment would be markedly more complex as local injection and detection would be required [1–7]. The HPLC equipment has evolved in a direction opposite to the requirements of operation under the infinite-diameter column concept. Although the decision of the community, instrument designers and analysts alike, to reject the concept of infinite-diameter column operation does not seem unreasonable, it does not justify our complete amnesia regarding the lack of radial homogeneity of packed columns which has been demonstrated twenty years ago.

The early experimental results of Knox [1–3] and Eon [4] were confirmed later by Baur et al. [6] and, more recently, by Farkas et al. [7]. These authors have shown that the distribution of the residence times of the molecules of a nonretained tracer in the exit cross-sectional area of a chromatographic column depends on the distance to the column center. Thus, the retention time of a nonretained band and the axial plate height vary across the column section. Baur et al. [6] found that the retention time of a nonretained tracer and the HETP along the axial direction vary with the radial position, are minimum at the column center, and maximum at the wall. Farkas et al. [7] found also that the retention time is maximum at the wall but observed a minimum at approximately two thirds of the radius from the center. The retention time remains nearly constant in the core region. The retention time is typically 6 to 10% higher at the wall and 3 to 4% lower at the ridge than in the core region [7]. The column HETP remains constant in the same core region, exhibits a weak minimum at about two thirds of a radius from the center and raises very rapidly close to the wall where it may be between three [7] and five [6] times larger than in the core region. It was also shown that these experimental results cannot be explained by a nonplanar injection [7]. The difference between the results of Baur et al. [6] and those of Farkas et al. [7] are explained by a difference in the packing technology used. It is important to note at this stage that the velocity distribution observed is opposite in the earlier work [1–4] (velocity minimum at the column center) and in the more recent one [6,7] (velocity minimum at the wall).

Early studies in gas chromatography reported an effect similar to the one observed by Knox [1–3] and Eon [4]. Giddings and Fuller [8] showed that particles segregate spontaneously during packing, the large particles accumulating along the column wall and the small ones at the center, an effect due to dry packing. A cone is formed at the column center and the large particles roll more easily to the wall. As a result of this discrimination, the packing permeability is 25 to 45% larger at the column wall than in the center [8]. This simple phenomenon could explain completely the velocity variation measured by Huyten et al. [9] across a wide column. In a study done on packed beds used as heat exchangers, Schwartz and Smith [10] had shown a velocity 30 to 100% larger at the wall than in the center, with a velocity peak at about one pellet diameter from the column wall. These results suggest that the layer of packing close to the wall has a lower density than the core. However, these experimental results were achieved with values of the column-to-particle diameter ratio of the order of 30, much smaller than in any conventional LC columns. The recent results reported [6,7], showing that the packing density is higher along the column wall, have been obtained with column-to-particle diameter ratios in the range from 100 to 1500.

Comparing the data reported in Refs. [1–4] and [8–10] on the one hand, with those of Refs. [6,7] on the other hand suggests that the difference originates in the use of dry-packing techniques in the former series of experiments, slurry packing in the latter. With slurry packing, the

velocity of the packing solvent, hence the viscous drag on the particles, are larger in the regions where the bed density is lower, thus providing for a drive toward column homogeneity. Furthermore, the mechanism leading to radial discrimination of the particles on the basis of their size, which is so effective in dry packing, is not operative in slurry packing. Thus, the systematic variations across the column of the mobile-phase velocity and the axial dispersion coefficient reported by Baur et al. [6] and Farkas et al. [7] cannot be accounted for by a systematic variation of the average particle size along the diameter. They suggest rather a nonhomogeneous density of the column packing.

Other phenomena reported in the literature could be explained by column-to-column variations of the packing density. For example, it is well known that excellent columns can be packed by mere sedimentation of a slurry but these columns are unstable, i.e., their packing collapses after a certain time, resulting into a nonhomogeneous bed, an important void at the column inlet, and possible cracks. It is often observed in analytical laboratories that well-packed columns lose their efficiency after a while. In most cases, opening the column inlet shows the beginning of the column to be empty. This phenomenon is clearly illustrated by recent results obtained in NMR imaging using a column packed by sedimentation [11]. Filling this void usually restores the column performance to its original level. This effect can be explained simply by a progressive consolidation of the column bed, resulting in a slow increase of its packing density.

The column-to-column reproducibility of retention data has always been a serious concern among chromatographers. The same is true for the reproducibility of equilibrium isotherms. It has been reported in the literature that isotherms measured under identical conditions on two columns prepared successively with the same material, using the same packing method are significantly different [12]. Recently, a systematic study has shown important differences in the packing density of series of columns, explaining the differences between the isotherms measured on these columns [13]. Other studies have shown that the packing density of columns prepared with a given packing material is different depending on the type of column used: analytical column, dynamic axial compression column, dynamic radial compression column [14,15]. The important conclusion is that various independent observations suggest that the density of a packing material is not a physical property characterizing it in the same way as its density can characterize a solvent.

A chromatographic bed is submitted to compression stress of various origins. In addition to axial [15] or radial [14] compression which are now widely used in preparative chromatography or to annular compression which has also been suggested, a bed is always subject to several types of stress. First, the inlet pressure also causes a compression of the entire bed due to the pressure gradient which acts on each particle of the packing, while the inlet pressure acts on the entire bed: withdrawing the exit frit and applying a high inlet pressure results usually in the expulsion of the entire packing material from the column. The friction of the bed against the column wall opposes the sliding movement of the bed. Second, the viscous flow of the mobile phase results in an intense friction which tends to move particles along the column in the direction of the flow. Finally, the presence of the mobile phase may change the interaction energy between particles, e.g., if of electrostatic origin. These stresses are continuously applied during column operation and may cause more or less extensive reorganization of the packing whenever one particle moves or breaks.

The application of stress to any material causes strains. Solid mechanics is the science studying the relationships between applied stress, resulting strains and the ensuing deformation of the material [16]. In the particular case of column packing, we deal with an unusual solid, which has no proper shape, like a liquid, and can deform almost as freely. The structure of the packing is a skeleton of solid grains enclosing voids filled with the mobile phase. There are weak interactions between the particles of packing material. The intensity of these interactions

depend on the nature of the surface of the particles and on their size. Spheres with a glassy surface will interact the least. Spheres with rugous surface will interact somewhat more. Irregular-shaped particles will interact the most. Small particles will interact more strongly than large particles of the same nature. These interactions will have an important role when the bed consolidates or reacts physically under compression [16].

A bed of packing material has little elasticity (although it is not entirely negligible, as we will see later). If a certain amount of packing material is compressed, as it is during the procedure of packing the column or afterward during its operation, the particles and the packing skeleton are placed under stress and at least one will deform. Depending on the rigidity of the particles, widely different results may be observed. If the packing is made of plastic materials, such as gels of crosslinked polyacrylamide particles, the particles deform easily, filling the void between them. The external porosity of the bed decreases rapidly and consequently the permeability decreases dramatically. As polymers tend to flow unless they are strongly crosslinked, their deformation is permanent. The particles do not recover their initial shape when the stress is released and the column permeability does not return to its initial value. This sets a rather low limit to the maximum pressure at which the column can be operated. For this reason, gels and many polymer-based packing materials are not mechanically suitable for high-performance chromatography in spite of otherwise attractive performance. An abundant literature originating from a single well [17] has tried to make virtue from this drawback. This should not delude the separation chemist [18]. Although there are cases in which a most favorable equilibrium thermodynamics can offset the consequences of the inability of the particles of a packing material to withstand a relatively high pressure drop, this drawback constitutes a more and more definitive roadblock.

If the packing material is made of hard, strong (under compression), brittle material, such as silica, alumina, zeolites, or other inorganic substances, the particles deform very little until the break point is reached. The nearly entire stress is conveyed to the skeleton which has to deal with it [16]. Some grains will slide or roll over their neighbors while other ones may break apart. The volume occupied by the packing material decreases accordingly. When the stress is released, however, there is no mechanism and little driving force for the particles which have moved to return to their initial position in the bed. The volume rebound is not so great as the compression. It is limited to the elastic compression of the particles and of the skeleton, both rather small [16]. In the same way as soil on an oft travelled footpath, at the bottom of a rut, or on a dirt road hardens progressively and remains permanently hardened (rain or shine), the packing in a chromatographic column becomes more compact as a response to the stress applied to the packing. This phenomenon is accompanied by a decrease of the external porosity and the column permeability. Although this is not intuitive, the apparent density of the packing is not a constant. It depends on the size of the column (diameter and length), on the packing method used, and on the previous consolidation history of the column.

At this stage we must introduce a distinction between the two different consolidation processes which are used in the packing of chromatographic columns. Analytical columns are consolidated under the influence of the viscous stress applied to the particles by the solvent stream percolating through them. Fluid mechanics shows that this stress is equivalent to the stress afforded by an intense gravity field acting parallel to the column axis. This equivalence will be discussed in a later report [19]. Dynamic compression columns are consolidated under the influence of mechanical compression of the bed by a compression stress applied through a piston (axial compression [15]), or the column wall (radial compression [14]). In this latter case, the stress is not distributed through the entire packing, as in the former case, but conveys from a surface toward the inside of the packing. Because of friction between particles and between the packing bed and the wall, the distribution of stress inside the column bed is not

homogeneous [20]. Because the stress applied to a liquid conveys instantaneously and homogeneously, two different situations are possible depending on whether the container of packing material is open or closed. If it is closed, the liquid is under compression and, because liquid compressibility is small, the packing material is under weak stress. This situation will not be considered further in this work. If the container is open, as a chromatographic column, the liquid is under no stress, unless there is a flow. The packing material is under the mechanical compression stress, distributed heterogeneously through the bed. In the case of a dynamically compressed chromatographic column, the viscous stress due to the local flow velocity (or rather to the pressure gradient) which is described above adds to the mechanical stress.

The main difference between soils such as sand and chromatographic beds is that the latter are entirely confined in a closed vessel, so the packing cannot shear. There is still a stability problem in our case, and the particles can break. Another significant difference is in the particle size distribution, somewhat wider in soils [16] than in packing materials. Other major differences are in the orders of magnitude. In most current problems of soil mechanics the volume involved are millions or billions times larger than in chromatography, the time scale is similarly much longer (typically years), while the pressure gradients and the flow velocities are much lower. Nevertheless, the phenomena observed are similar in nature. If a given mass of packing is compressed, its volume decreases. This results from a combination of (i) the compression of the individual, solid particles, (ii) the compression of the particle skeleton, (iii) the compression of the mobile phase surrounding the particles (which is negligible), and (iv) the escape of the mobile phase from the interstitial voids, between the particles. As far as the classical, silica-based phases are concerned, the contribution of the first phenomenon is negligible and it is accurate enough to consider only the fourth one. For polymeric phases, the first and last phenomena are significant. The process by which the bed responds to the external compression and settles, is called consolidation [16]. The extent of consolidation depends on the compression pressure applied. The phenomenon is not instantaneous. Results of soil mechanics suggest that the kinetics is different for a dry bed and for a wet one [16].

Finally, we must recognize that the interactions between the packing material and the mobile phase are important in any study of packed bed stability. If a glass column packed with silica, and fed by gravity, is left to dry, its bed cracks in a random fashion and voids extending across the entire column can be seen. Admittedly, HPLC columns made of stainless steel or titanium tubings are more consolidated than conventional columns made of glass tubes which cannot stand any significant pressure[1]. Nevertheless, this suggests that the packing density (expressed in weight of silica per unit volume of column) depends on the presence of a liquid phase and probably on its nature. This is confirmed by another phenomenon, which is ignored in soil mechanics, but may have to be taken into account in chromatography, although it has not been documented yet.

The apparent density of a sedimented bed depends on the surface tension of the solid particles and the liquid in contact [22]. When the mobile-phase composition changes, so does its surface tension. This may cause a change of the apparent density of the packing material, provided it can accommodate it. This phenomenon has been applied by Barford [22] to the measurement of the surface tension of packing materials. It may not play an important role with chemically bonded $C_{18}$ silica because these materials are not wetted by water-rich solvents, anyway. However, it is probably significant in hydrophobic interaction chromatography. If the packing is strongly consolidated, there will be no change in its density, unless the stress becomes strong enough to break some particles. If the packing is only weakly consolidated, a concentration gra-

[1] Unfortunately, we cannot see the packing material inside our metal columns. This may provide another illustration to the profound comment of Eyring, "What the eye does not see, does not bother the mind" [21].

dient, caused either by a change in the mobile phase composition or by the injection of a large sample, may lead to an increase in the packing density. Like other causes of increased consolidation, this effect should be transient and after a certain time, the bed should remain stable under the experimental conditions used. There is no mechanism for the extent of consolidation to decrease when the stress which caused it is removed. The particles cannot bounce back to their original position.

The goal of this work is to present new data on the extent of the consolidation of the packing material in chromatographic columns, on the difference between consolidation and elasticity of the bed, and on the time scale of this phenomenon. Further publications will apply these new concepts to the study of various packing materials used in preparative chromatography [23].

## 2. Theoretical

Sands are the types of soil closest in properties to packing materials for chromatography. The main difference between sands and packing materials is in the particle size distribution. Sands are very heterogeneous, with a range of particle sizes extending over several orders of magnitude, from a few mm to less than 1000 Å. As a consequence, their porosity in compacted beds can be as low as 27%. They are also nonporous and stronger than the porous silica particles used in HPLC.

### 2.1. Kinetics of consolidation

The time lag during compression of sands [16], hence most probably of all packing materials, is mostly of a frictional nature. After a compression increment is applied, there is no uniform and smooth reordering of the particles, but an irregular, chaotic succession of local build-up of stress between groups of particles, leading to a rupture of the equilibrium, grains rolling over each other or being separated abruptly by the local avalanche of grains resulting from the break-up of a bridge at some distance. As a consequence, consolidation tends toward a limit following a quasi-exponential decay with a pseudo time constant which may be of the order of hours for a small preparative column and increases with increasing bed volume.

The simplest case of consolidation considered in soil mechanics is the one which results from linear compression (i.e., compression in one direction). This case applies exactly to the situation encountered in dynamic axial compression and in chromatographic columns which are not dynamically compressed but where the bed is stressed by the pressure applied to the top of the bed (the inlet pressure) and the shear force generated by the friction of the mobile phase percolating through the bed. Typically, plots of the void volume versus the compression pressure can be represented by the following equation:

$$e = \frac{\epsilon_e}{1 - \epsilon_e} = e_0 - C_c \log \frac{P}{p_0} \quad (1)$$

where $e$ is the void ratio or ratio of the volume fraction of the column available to the mobile phase percolating around the particles to the volume occupied by the particles assumed to be nonporous, $\epsilon_e$ is the external, interparticle, or interstitial porosity, $e_0$ is the void volume at the reference pressure $p_0$, usually the atmospheric pressure, $P$ is the compression pressure, and $C_c$ is a numerical coefficient. The compression diagram is a plot of the void ratio, $e$, versus the logarithm of the compression pressure, $P$. As an example, Fig. 1 shows a typical compression diagram recorded for a sample of a well-known packing material having irregular-shape particles (see Section 3 for relevant details). This diagram will be discussed later together with the reasons for the broken plot (dotted lines). Suffice it to say at this stage that Eq. 1 is approximately valid for the consolidation of the dry-packing material (solid line) and is valid in a certain pressure range for the consolidation of the wet material (dotted lines). Note that, because the particles are porous, the total porosity which is derived directly from the value of the hold-up volume should be corrected for the contribution of the internal porosity. The latter cannot be measured simply but is estimated by assuming that the

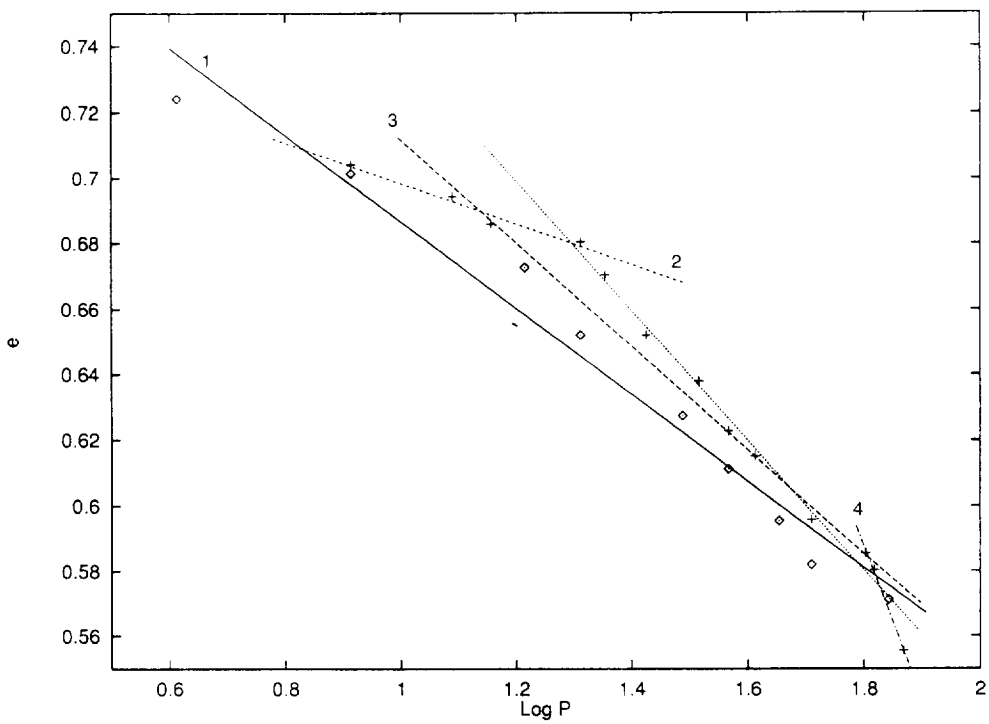


Fig. 1. Compression diagram. Plot of the void ratio versus the compression pressure for the dry (◇) and wet (+) packing material: 1 = compression of the dry packing; 2 = compression of the wet packing, least-squares fit of the first five data points on a straight line; 3 = compression of the wet packing, least-squares fit of data points 4 to 12 on a straight line; 4 = compression of the wet packing, least-squares fit of the last three data points on a straight line.

internal porosity is constant and independent of the stress applied to the particles and that the external porosity of the material sedimenting freely is 41%. Fig. 2 illustrates the kinetics of the bed consolidation. These results are discussed later for their significance in chromatography.

Two phenomena explain the finite rate at which a bed of sand or the packing of a chromatographic column consolidates. The first is the frictional nature of the compression process, just explained. Thus, consolidation is expected to be slower with irregular and rugous particles than with spherical or smooth particles, *not that this may necessarily affect the chromatographic performances themselves*. The second is the finite time it takes to eliminate the mobile phase inside the skeleton of particles when compression takes place. This hydrodynamic lag is due to the finite permeability of the bed which controls the escape of the mobile phase. Its importance increases with decreasing particle size and increasing column length. The particle size distribution of the silica materials for chromatography is narrower than that of sand and their average diameter is much larger than the finest sand grains found in nature, so their consolidation appears to be faster.

The theory of the kinetics of consolidation of Terzaghi [24] neglects the frictional lag and takes into account only the hydrodynamic lag. This theory assumes that the void ratio, $e$, decreases linearly with increasing pressure, which is only approximate since we have said above that the experimental data are better fitted by a logarithmic dependence (Eq. 1). When the pressure applied to the sample is increased from $P_1$ to $P_2$, there cannot be a change in strain of the packing unless part of the mobile phase flows out. If the column is closed and the compression pressure applied to the bed is raised while the liquid is

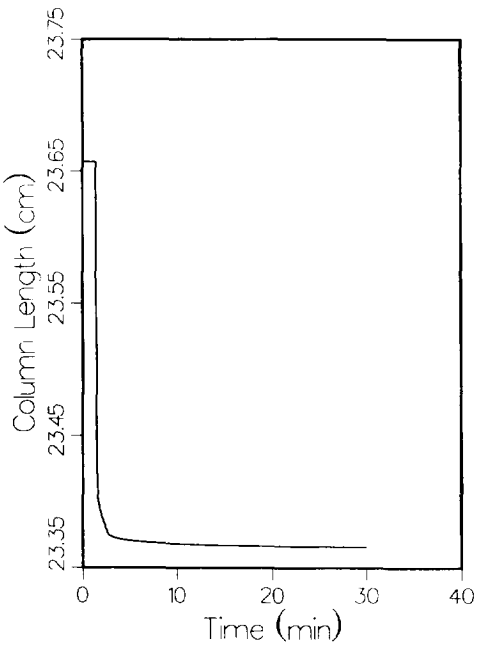


Fig. 2. Kinetics of the consolidation of the dry-packing material. Plot of the column length versus time at constant compression pressure after a pressure jump from 4.2 to 8.4 bar.

unable to leak out, the only change which occurs is due to the compression of the liquid and the silica itself, a very small change. Fig. 3 illustrates the phenomenon.

Consider a differential element of the packing material, in the middle of a column filled with mobile phase, but with no flow-rate; hence the static pressure of the mobile phase is atmospheric. A constant compression pressure, $P_1$ is applied to the packing. Initially, the state of this packing is represented by the point A, with void ratio $e_1$ and pressure $P_1$. At time $t = 0$, the compression pressure is raised to $P_2$, but the void ratio remains the same and the pressure $\Delta P = P_2 - P_1$ is applied to the liquid, forcing it out of the bed through both ends of the column. The liquid cannot exit instantaneously. At time $t = \infty$, the compression pressure applied to the bed has become $P_2$ and the void ratio $e_2$; the state of the packing is represented by point C. At an intermediate time, $t$, the bed is compressed with the pressure $P$ and the void ratio is $e$, the state being represented by point B. The liquid inside the element of the bed is under the pressure $\delta P = P_2 - p$. Thus, $\delta P$ decreases from $\Delta P$ to 0, while the pressure supported by the bed increases from $P_1$ to $P_2$ and the bed consolidates, its void ratio decreasing from $e_1$ to $e_2$. The consolidation ratio, $U$ is given by:

$$U = \frac{e_1 - e}{e_2 - e_1} \tag{2a}$$

$$= \frac{p - P_1}{P_2 - P_1} = 1 - \frac{\delta P}{\Delta P} \tag{2b}$$

The first equation above is the definition of the consolidation ratio; the second results from the assumption that the void ratio decreases linearly with increasing compression pressure. This assumption is expressed by considering the coefficient:

$$a_v = \frac{e_1 - e_2}{P_2 - P_1} = -\frac{\mathrm{d}e}{\mathrm{d}P} \tag{3}$$

as a constant. This coefficient is called the coefficient of compressibility of the packing. The consolidation ratio, $U$, increases from 0 to 1 during the process, while the hydrostatic pressure inside the bed dissipates from $\Delta P$ to 0 (we assume here that there is no flow; this restrictive assumption will be waived later).

The Terzaghi theory [16,24] 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 negli-

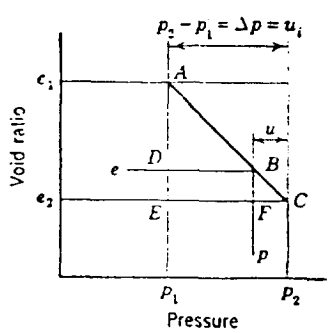


Fig. 3. Relationship between the pressure and the void volume for a small pressure increment.

gible; (4) the compression and the flow are unidimensional and parallel; (5) Darcy's law [25] is valid; (6) the parameters considered are independent of the pressure.

In fact, all these assumptions are valid in the case of the packing of chromatographic columns. They are indeed better fulfilled than in the case of most sand deposits. Darcy's law gives the rate of change of volume of liquid under a pressure gradient as:

$$\frac{\partial V}{\partial t} = -\frac{kS}{\eta}\frac{\partial p}{\partial z} \tag{4}$$

where $V$ is the volume of fluid, $z$ the position, $k$ the column permeability, $p$ the local pressure, $S$ the cross-sectional area of the column, and $\eta$ the mobile-phase viscosity. It has been shown that Darcy's law is valid in a porous medium as long as the Reynolds number is lower than 1 [26]. Typical values of Reynolds numbers in liquid chromatography are lower than 0.01 [27].

As long as the bed is in the process of consolidation, the permeability is not constant along the column. We assume, however, that the bed remains radially homogeneous. We consider a slice of column of thickness d$z$. The flow-rates of the mobile phase entering and leaving the slice are, respectively:

$$F_{v,i} = \frac{k}{\eta}\left(-\frac{\partial p}{\partial z} + \frac{\partial^2 p}{\partial z^2}\frac{dz}{2}\right)S \tag{5a}$$

$$F_{v,o} = \frac{k}{\eta}\left(-\frac{\partial p}{\partial z} - \frac{\partial^2 p}{\partial z^2}\frac{dz}{2}\right)S \tag{5b}$$

where $k$ is the column permeability, as derived from Darcy's law at low flow-rates, $S$ is the cross-sectional area of the column, and $\eta$ is the mobile-phase viscosity. The difference is the volume which has left the slice during the consolidation process. It is also equal to the rate of change of this volume, thus:

$$-\frac{kS}{\eta}\frac{\partial^2 p}{\partial z^2} = \frac{\partial}{\partial t}\left(\frac{e}{1+e}S\,dz\right) \tag{6}$$

Because of the definition of $e$, the volume occupied by the particles in the slice is $Sdz/(1+e)$, and this volume remains constant. Hence, combination with Eq. 3 gives:

$$\frac{k}{\eta}\frac{\partial^2 p}{\partial z^2} = \frac{a_v}{1+e}\frac{\partial p}{\partial t} \tag{7a}$$

$$C_v\frac{\partial^2 p}{\partial z^2} = \frac{\partial p}{\partial t} \tag{7b}$$

with $C_v = k(1+e)/(a_v\eta)$. Eq. 7b describes the kinetics of bed consolidation in the presence of a liquid. This equation can be solved in closed form [16]. The solution depends on the value of the dimensionless time:

$$T = \frac{4C_v}{L^2}t \tag{8}$$

where $t$ is the time and $L$ is the length of the column, which is assumed to be drained at both ends, as is the case in liquid chromatography with an axial compression column if the entrance is left open (see Section 4). The variation of the column permeability during the consolidation is not taken into account, although it may not be negligible.

When the experiment is carried out under static conditions, with a constant initial pressure, $P_0$, and with no flow, an analytical solution of Eq. 7 is given by [16]:

$$p = \sum_{m=0}^{m=\infty}\frac{2P_0}{M}\left(\sin\frac{2Mz}{L}\right)e^{-M^2T} \tag{9}$$

where $P_0$ is the initial pressure of the liquid in the column, before the compression experiment begins, $m$ is an integer, and $M = (2m+1)\pi/2$. Then, under these same static conditions, the local consolidation ratio, $U_z$, is given by the equation:

$$U_z = 1 - \sum_{m=0}^{m=\infty}\frac{2}{M}\left(\sin\frac{2Mz}{L}\right)e^{-M^2T} \tag{10}$$

The average consolidation ratio for the entire column is given by:

$$\overline{U} = 1 - \sum_{m=0}^{m=\infty}\frac{2}{M^2}e^{-M^2T} \tag{11}$$

However, it is possible to show [16,24] that this equation applies also in the case of a linear

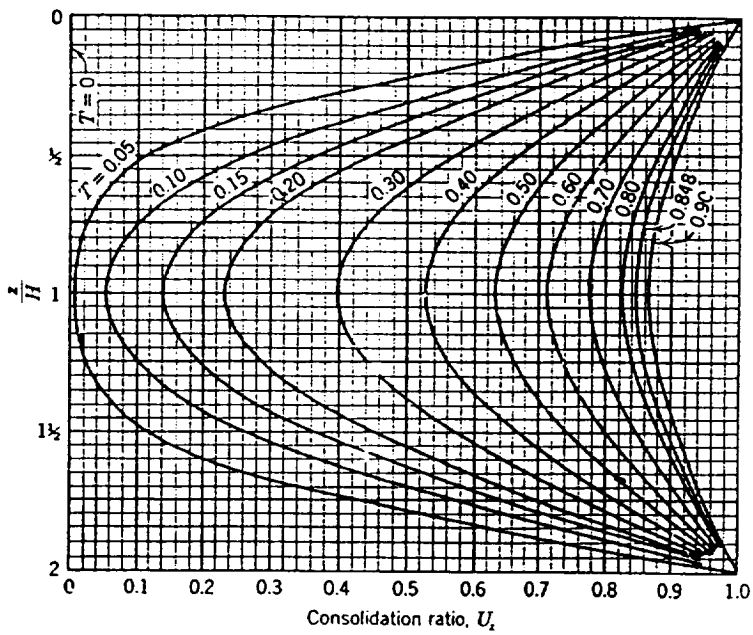


Fig. 4. Dependence of the local consolidation factor on time and on the position in the column. Reduced coordinates, see Eq. 7.

pressure gradient along the column, that is under the conventional conditions under which chromatographic columns are operated.

Fig. 4 illustrates the dependence of the local consolidation ratio as a function of time and position in the column, in the case of a constant pressure of the liquid in the column (i.e., under static compression of the bed). The column has a height equal to $2H$, is open for drainage at both ends and is supposed to have a diameter large compared to its length, so that friction of the packing against the wall has a negligible effect. Fig. 5 shows the variation of the average consolidation ratio as a function of time. This ratio increases rapidly with the dimensionless time, $T$. In the case of consolidation without flow (curve

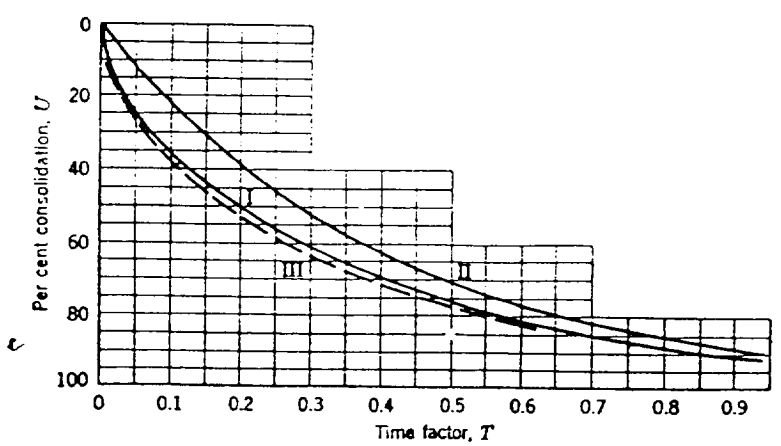


Fig. 5. Consolidation curve. Increase in the average consolidation factor of the column as a function of time. $T$ is given by Eq. 8.

I) is 50% after 0.2 $T$, 80% after 0.57 $T$, and 90% after 0.87 $T$. So, the value of $T$ is an important characteristic of packing materials for preparative chromatography. The other two curves in Fig. 5 correspond to consolidation in the presence of two different types of lateral stream of water percolating through the soil, a case of importance in soil mechanics but irrelevant in chromatography.

### 2.2. The time constant of consolidation

The value of the time constant of consolidation is given by Eq. 8. We need to translate the parameters involved in this equation into parameters which are more conventional in chromatography. The column permeability is given by the Blake–Kozeny eqation [26]

$$k = \frac{d_p^2 \epsilon_e^3}{h_0(\epsilon_i + \epsilon_e)(1 - \epsilon_e)^2} \tag{12}$$

where $d_p$ is the average particle diameter, $\epsilon_i$ is the internal porosity of the packing (or volume fraction of the column occupied by the stagnant mobile phase, inside the particles), and $h_0$ is a geometrical constant, usually of the order of 180, but which can vary from one packing material to the next and is probably somewhat smaller for spherical particles than for irregular ones. The void ratio, $e$, is the ratio of the volume available to the flowing mobile phase and the volume occupied by the particles, so:

$$e = \frac{\epsilon_e}{1 - \epsilon_e} \tag{13}$$

The compressibility coefficient, $a_v$, is also related to the external porosity:

$$a_v = -\frac{de}{dP} = \frac{-1}{(1 - \epsilon_e)^2} \frac{d\epsilon_e}{dP} \tag{14}$$

Accordingly, $T$ becomes:

$$T = \frac{4}{h_0} \frac{\epsilon_e^3}{(\epsilon_i + \epsilon_e)(1 - \epsilon_e)} \frac{-1}{d\epsilon_e/dP} \frac{d_p^2}{L^2} t \tag{15}$$

The parameter $h_0$ cannot be changed. There is little which can be done about the mobile-phase viscosity, as the solvent is selected for chromatographic reasons, to maximize the separation factor and to obtain a reasonable value of the retention. The values of the porosities in most packing materials are close and there is little we can do about them. The second factor of the RHS of Eq. 15 does not vary by a factor 2 in the entire range of packing materials available and of experimental conditions used, if we do not take into account the influence of the consolidation itself. There are few data available at present, if any, regarding the packing compressibility, $d\epsilon_e/dP$. So, the time scale in column compressibility is essentially controlled by the ratio $(L/d_p)^2 = N^2\ h^2$, that is by the column efficiency required ($N$) and by the column quality ($h$). The last term in Eq. 15 may vary by orders of magnitude from one column to another. The most efficient columns will tend to consolidate much more slowly than the least efficient ones.

### 2.3. Limitation of the consolidation theory

The theoretical discussion presented in the previous two sections assumes that the time required for the consolidation to take place is essentially controlled by the flow of the liquid expelled from the packed bed. Any other contribution is neglected. In this work, we assume that the particles are elastic but rather rigid. Thus, each particle adjusts rapidly to the stress received from its neighbors. It may deform locally (elastically or not) or it can break, but it does it quickly; there is no plastic flow of the particles. This could be different for rigid resin-based particles which may flow somewhat before they eventually break. Soft gels would flow quickly and obstruct the interparticulate channels, which makes them unsuitable for preparative HPLC. Any delay in the consolidation must result from the time required for the particles to move around each other and, in so doing, to decrease the phase ratio. This time is called the plastic time lag.

In soil mechanics, two steps are recognized during the compression of a material. The primary compression is fast and controlled by the

permeability of the bed. The hydrostatic pressure falls to 0 at the end of the primary compression stage. During the secondary compression, the rate of compression is so slow that the escape of water takes place freely and the kinetics is controlled by plastic resistance. The plastic time lag is more important for clays than for sands but it could still be significant for packed beds, although actual binding can take place between packing particles. There is no information available at this time on this property. The plastic lag time depends on the energy of the particle–particle interactions. Thus, differences between the consolidation kinetics of irregular and spherical particles, if any were to be found, could be explained by a higher plastic time lag for the former, due to stronger interactions between its particles. Such differences could be explained also by the narrow size distribution of the particles used in chromatography. This distribution results in a much larger value of the interparticle porosity and a much larger average volume of the cavities between neighbor particles in columns than in sand beds.

Since there is no clay nor any colloidal material in packing materials for chromatography, it is easy to handle the same materials either dry or wet and to do so without affecting their integrity, something which is difficult for soils and present little interest in the applications of soil mechanics. Although the structure of a wet and a dry column are different, the study of the consolidation of dry-packing materials may provide some clues regarding the importance of this effect.

## 3. Experimental

### 3.1. Principle

Tests carried out in soil mechanics are done with samples between 2.5 and 5 cm thick and 10 cm wide, using successive pressure increments increasing by a factor 2 and starting from a rather low value of 1/8 kg/cm$^2$. We have modified these experimental conditions although the literature shows that they are required for reproducibility. As a matter of fact, what is required is the standardization of the determinations to permit valuable comparisons. We have carried out the experiments reported here with 15–25 cm long beds in a 5-cm diameter column. Thus, the results are not directly comparable to those obtained on sands. The main difference is in the much different aspect ratio ($L/d_c$), 3 to 3.5 in our experiments versus 0.5 in soil mechanics, a large difference because the distribution of stress inside the bed is different and depends on $L/d_c$. Also, we have used a larger initial pressure of 4 kg/cm$^2$ and larger pressure increments.

These changes present the advantage of giving a test which is more closely relevant to our purpose, the study of chromatographic beds under experimental conditions close to those used in the practical applications. Differences between experimental results obtained on large-size columns and those extrapolated from our data could be significant for columns having an aspect ratio lower than 2, but no information on this question is available yet. Further studies will involve measurements made with beds of different lengths [23].

### 3.2. Equipment

We used a dynamic axial compression column, 5.0 cm I.D. and 59 cm long (maximum), LC.50.VE.500.100 (Prochrom, Champigneulles, France). The piston is actuated by a hydraulic jack driven by an air compression pump from Haskel (Burbank, CA, USA). A pressure up to 100 bar may be applied to the packing material.

### 3.3. Packing material

Because the results presented here are preliminary, have been obtained with a single packing material, and are not clearly related to the chromatographic performance of the material under the conventional conditions used in preparative chromatography, it seems unfair at this stage to give the origin of the material used for the experiments. This information will be given later, with data regarding a number of other similar products of various origins [23]. The material used is a $C_{18}$ bonded silicagel, made of

irregular-shaped particles, with an average size between 15 and 20 $\mu$m and an average pore size of 100 Å. It was dried in a beaker for 12 h at 120° prior to use.

### 3.4. Procedures

During the following operations, the column length was monitored using a position sensor previously described [14]. The range of the sensor is approximately 0.8 cm, while the changes measured in the column length totaled approximately 6 cm. This required adjustments of the sensor position during the experiments.

*Dry compression*

An amount of 238 g of packing material was weighed and dried, then poured into the empty column with a funnel. Before closing the column top, the piston was brought slowly upward until the silica level reached the column rim. The burst of a few air bubbles on the top of the packing was observed during this process, illustrating clearly that pouring a powder in a vessel results in a low-density packing. After the piston had been stopped, the upper side of the column was tapped 20 to 30 times with the handle of a small hammer, which brought the level of the packing material slightly down. The piston was raised again and the operation repeated three times. Afterward, the top flange was closed, with its frit resting directly in contact with the top of the bed. The column was compressed at 4.1 bar, and then by increasing progressively the compression pressure to 69.7 bar. The initial column length was 24.38 cm, the final length 22.22 cm. At each new set pressure, the column length was monitored continuously until apparent stabilization, which usually took about 30 min, although may be quite insufficient some times (see later). Then, the new pressure was set.

*Decompression*

The design of the equipment does not permit to perform gradual decreases of the compression pressure. The leak of the hydraulic system is too small. The compression mechanism is switched to neutral, the new desired compression pressure is set, and the equipment is switched back on compression, at the new set value.

*Wetting a dry packing*

After completion of the compression and decompression experiments on the dry-packed bed, the mobile phase (methanol–water, 40:60, w/w) was introduced into the column at an axial compression of 73 bar. After about an hour and a half, the column length had decreased and stabilized again and the solution was replaced by pure methanol. Then, it was observed that, after a few minutes, air bubbles began to leave the column. Methanol–water mixtures below 50:50 do not wet chemically bonded silica, which explains the tardy gas expulsion. After a few hours, the column length had stabilized at 18.9 cm. Then, a series of determinations of the column efficiency were made, using nonretained acetone as the probe.

*Slurry compression*

An amount of 238 g of packing material was weighed and dried, then slurried in 900 ml of isopropanol. The slurry was poured into the column and left to sediment. The supernatant was collected periodically with a large syringe and the piston brought up slowly until the slurry level reached the top of the column. After 4 h, when a total of 300 ml of isopropanol had been collected, the top flange was closed, a graduated cylinder was connected to the column exit to collect the expelled solvent, and the axial compression was applied at 1 bar. The length of the column was measured manually and the displacement sensor set to follow the changes in the column length. The first compression step was to 4.1 bar. The pressure was then raised by a series of steps to a maximum of 73.8 bar, at which pressure crushing noises began to be heard. A total volume of liquid of 153.2 ml was collected. The initial column length was 27.3 cm, the final one 19.1 cm, corresponding to a volume reduction of 161.0 ml. The difference can be explained by evaporation loss during 4 h, error in the determination of the initial column length, and losses during the closing of the top flange.

The maximum pressure during recompression

was 77.9 bar. After the end of the experiments, the column was washed with fresh methanol and equilibrated for a few hours in closed circuit. Its efficiency was then measured using acetone, with a compression pressure of 57.4 bar, at a length of 18.9 cm.

## 4. Results and discussion

### *4.1. Consolidation of a dry bed of packing material*

Fig. 2 shows a typical example of the consolidation kinetics obtained with the dry-packing material. The column had been previously stabilized at 8.2 bar for 30 min. After 2 min in the experiment, the pressure was raised to 16.4 bar. The column length decreased initially very rapidly, then much more slowly. In this case, it was completely stabilized after 30 min. Similar results were obtained at all compression pressures.

Fig. 6 shows the plot of the column length after stabilization versus the compression pressure (circles). Consolidation progresses with increasing compression pressure and appears to tend toward a limit which is nearly reached at 70 bar, when the column length has decreased by approximately 10% from its initial value. These experiments are long when high compression pressures are applied and it is difficult to make sure that equilibrium is reached. An experiment to measure the extent of rebound at decompression was started after the reading at a compression pressure of 69.7 bar (highest stress in Fig. 6). This was done by releasing the gas pressure in the Haskel pump (see Section 3). However, the leakage of the hydraulic system was so low that the pressure had not decreased significantly after 6 h. The column length had decreased from 22.22 to 22.19 cm. However, the following morning, after 16 h, the pressure had decreased to 57.4 bar and the column length to 21.9 cm. Then, the decompression procedure described in Section 3 was used. This explains the jump between the last compression point (Fig. 6, circle) and the first decompression data point (Fig. 6, dot). The variation of the column length with the compression pressure upon column decompression is also shown in Fig. 6. It is practically insignificant. The rebound is from 21.9 to 22.03 cm, i.e., less than ca. 0.6%.

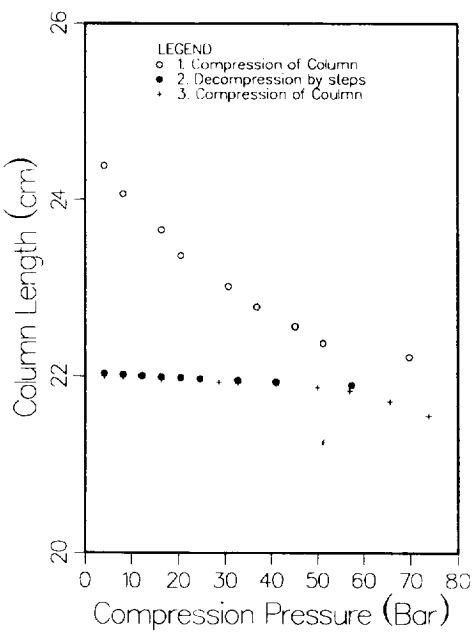


Fig. 6. Compression (○), decompression (●), and recompression ( + ) curves of the dry-packing material.

The recompression of the packing after decompression does not result in a significant decrease in the column volume up to 60 bar. At higher pressures, however, the column length decreases again and is reduced to 21.55 cm after recompression up to 73.8 bar. The fact that recompression from 0 to 60 bar shows no change in the column length demonstrates that the bed was completely consolidated at a pressure of 60 bar when it was decompressed. However, consolidation would certainly progress further at higher pressures, as the following results will show. Experiments cannot be carried out at pressures above 75 bar without crushing the particles.

Fig. 1 includes the compression diagram of the dry-packing material (solid line). This diagram has been derived from the data in Fig. 6, assuming an external porosity equal to 0.42 for the bed at the beginning of the compression.

This value is somewhat arbitrary, although consistent with results obtained with other dry-particle beds [9,10,26]; however, we have checked that changes in this initial value of the porosity between 0.40 and 0.43 have negligible effects on our conclusions (with only minor changes in the values of the empirical parameters derived from the data). We also assume that the volume of the particles remains unchanged, hence the volume of solid and the pore volumes remain constant. In other words, we assume that the consolidation reduces only the external porosity. The compression diagram of the dry packing shown in Fig. 1 (solid line) shows that, except for the first one, slightly low, the data points exhibit a linear relationship, in agreement with Eq. 1. The coefficient $a_v$ calculated from the slope of the least-squares straight line is equal to 0.13.

Fig. 7 shows a plot of the external porosity, calculated using the same data, versus the pressure. A satisfactory linear relationship is found, except for the first data point, which deviates slightly, and the last one, which is markedly off. The slope of the least-squares straight line for the central 7 data points gives a value of $d\epsilon_e/dP$ equal to $-1.0 \cdot 10^{-3}$ bar$^{-1}$. Introduction of this value in Eq. 15, with an average external porosity of 0.39, an internal porosity of 0.355, $h_0 = 180$, gives for a 25-cm long column packed with 15-$\mu$m particles, a reduced time, $T$, equal to 0.0104 $t$ (s). In this case, the consolidation of the packing should be rapid, taking less than 100 s. With a 50-cm long column, packed with 5-$\mu$m particles, the time constant becomes almost 1 h (3500 s), still not unreasonably long. Note, however, that the consolidation of the packing of a chromatographic column is not instantaneous, even under dynamic compression.

### 4.2. Wetting a bed of dry packing

Introduction of a stream of a methanol–water solution (40:60, w/w) results in an immediate contraction of the packing, by about 1.4% (from

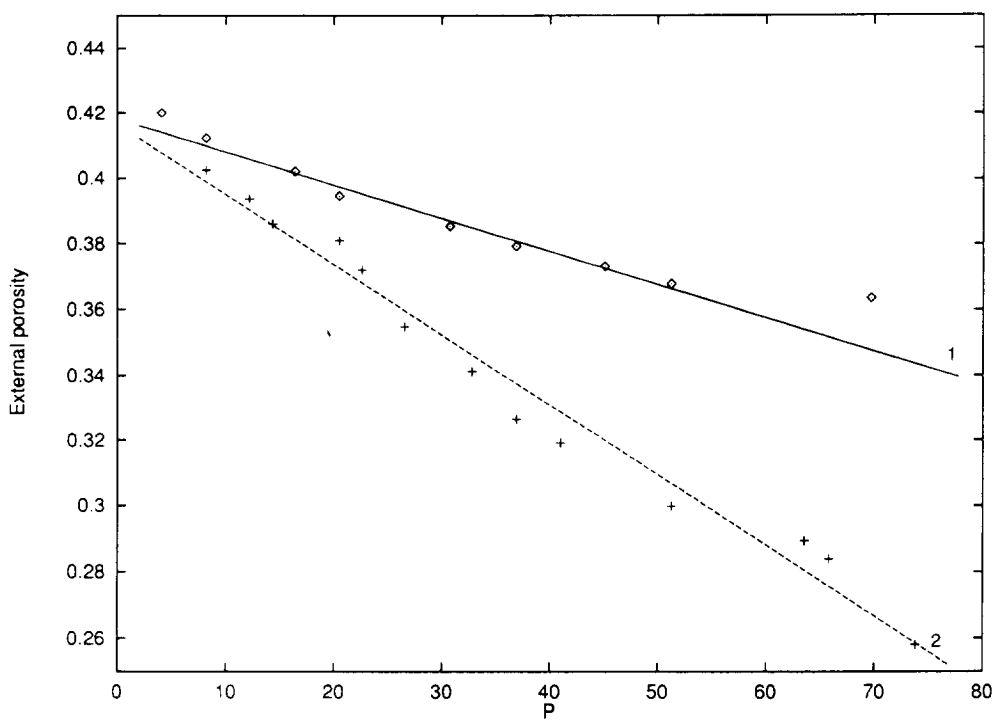


Fig. 7. Plot of the external porosity of the column bed versus the compression pressure: 1 = compression of the dry packing (◇); 2 = compression of the wet packing (+).

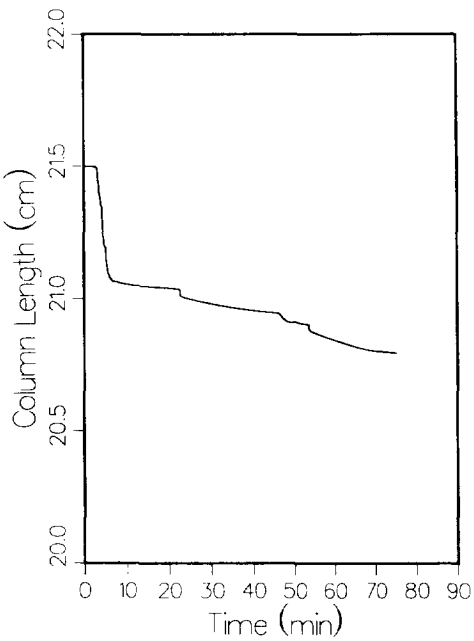


Fig. 8. Shrinking of a bed of dry packing material when wetted by a 40:60 (w/w) methanol–water solution.

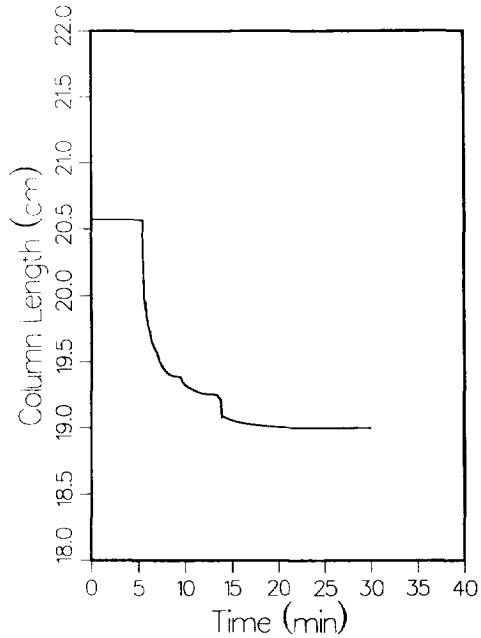


Fig. 9. Shrinking of a bed of packing material wetted by a 40:60 methanol–water solution when this solution is replaced by pure methanol.

21.50 to 21.19 cm), followed by a further, slow decrease in the column length. The data obtained are shown in Fig. 8. The recording was stopped after 82 min, the sensor being at the end of its range and having to be adjusted. After this adjustment, the column length shrank by an additional 1% after another hour (not shown).

Finally, pure methanol was introduced (Fig. 9). The column shrank again rapidly, by more than 5% in the first 7 min. Gas bubbles were observed in the exit stream. After 30 min the column length has decreased by a total of 1.57 cm since liquid began to be introduced into it. The initial column length (24.6 cm) has been reduced to 19.0 cm at the end of the series of experiments. This loss of nearly a quarter has been achieved at constant mass of packing and, practically, at constant total volume of the particles. The loss is due to a decrease of the sole external porosity. The granulometric analysis done on samples of packing material taken from the region close to the wall and the piston, where the stress is highest in an axial compression column, shows that breakage has taken place but to a limited extent [23].

### 4.3. Column efficiency, dry-packed column

The column efficiency was measured, as a function of the mobile-phase velocity, after the series of experiments described above was completed. The results are shown in Fig. 10. The efficiency is very poor, reminiscent of what was obtained in preparative gas chromatography columns which had to be dry-packed [28]. The simple pouring technique used here resulted in reduced efficiencies of the order of 50 or larger [8,9,28]. It is important to report that the values found initially were still worse and that, after a few hours, the efficiency improved, particularly at high flow-rates, the slope of the slanted asymptote decreased, as if some local reorganization, with minimum change in volume, had taken place under the influence of the continu-

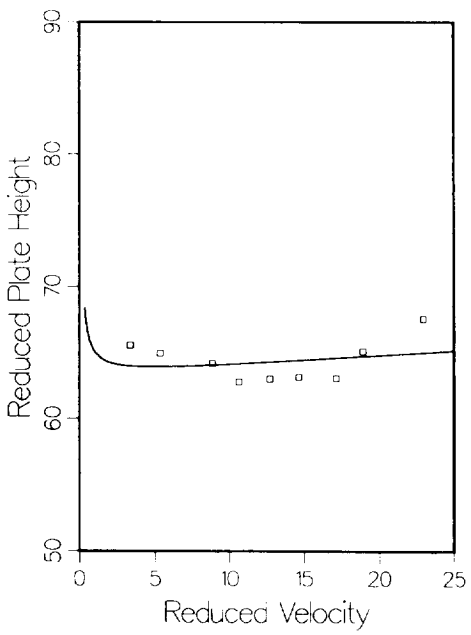


Fig. 10. Efficiency of the consolidated dry column after wetting by pure methanol. Solute: acetone (nonretained).

ous stream of eluent. No change in the column length was observed, however.

We explain the poor column efficiency under these experimental conditions (the reduced plate height is around 65) by particle size discrimination across the column, a well-known effect which accompanies dry packing in nearly all cases [8,9,28]. This effect has often been reported and is strongly documented [8,9]. The abundant literature [28] on the packing technology of gas chromatographic columns provides further justifications. For this reason and because of the profound difference in the behavior of wet and dry packing under compression, work was not pursued on this issue and efforts were shifted to the study of the consolidation of beds obtained by the more conventional slurry method. However, because some, who ignore the troubles encountered by a past generation, may be attracted by the idea of resuscitating the old dry-packing technique, we felt it appropriate to report the results obtained and to point out the poor efficiency achieved.

### *4.4. Consolidation of a bed of wet-packing material*

While the data recorded for the consolidation kinetics of a wet packing at low or moderate compression pressure tend to be like that shown in Fig. 2 for a dry bed, a different behavior is observed at high pressures, when the bed has already lost a significant fraction of its interparticle void volume. Fig. 11 shows a typical consolidation curve obtained at high pressures. While the plots of the extent of consolidation versus time are different for the dry (Fig. 2) and the wet (Fig. 11) packing, the latter are quite similar to the plots illustrating the consolidation kinetics during the wetting of the column packing (Figs. 8 and 9). The presence of a liquid seems necessary for the abrupt collapses observed (Figs. 8, 9 and 11) to take place. Like for some other features of the consolidation curves, it is difficult at this stage to determine which ones are general and to be found in the consolidation of all packing materials and which ones are specific of the

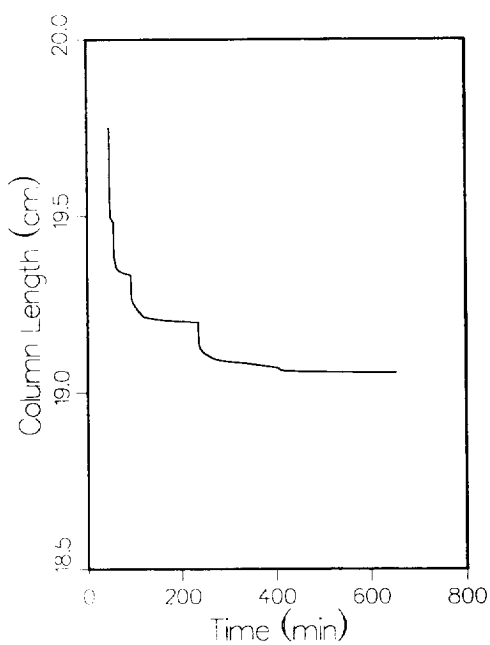


Fig. 11. Consolidation kinetics under isobar conditions of the wet-packing material after compression from 65 to 74 bar.

material used here. At any compression pressure, the degree of consolidation achieved in wet compression is higher than in dry compression. This may be due to a reduction in the interparticle interaction energy caused by the presence of the solvent. We have seen in the study of dry packing that the dielectric constant or the dipole moment of the solvent is less critical to explain consolidation than the wettability, since methanol induces a stronger increase in packing density than water–methanol mixtures. This conclusion, however, does not necessarily extend to the consolidation of beds of silica particles.

The unexpected result is certainly the random character of the process. Catastrophic events, in the probable form of avalanches inside the packed bed, take place for no apparent reasons. They occur after long periods, up to several hours. This phenomenon may explain the formation of holes at the beginning of columns after a certain time during which satisfactory performance is recorded. At the end of the experiment illustrated in Fig. 11, the column was whipped 20 times with a rubber vacuum hose to no effect[1]. It seems that total consolidation had been achieved at the operating pressure. Nevertheless, this phenomenon slows down considerably the kinetics of consolidation of the packing compared to what is predicted by the Terzaghi theory [16,24]. For irregular-shaped particles at least, the frictional lag to consolidation causes a much more serious problem than the hydrodynamic lag.

Fig. 12 shows the plot of the column length as a function of the compression pressure. The curve obtained is qualitatively similar to the one recorded during dry packing. However, the quantitative differences are important. The same amount of packing was used in both experiments (238 g). Within 0.1 cm, the same final length was obtained at nearly the same compression pressure. However, dry packing itself could not

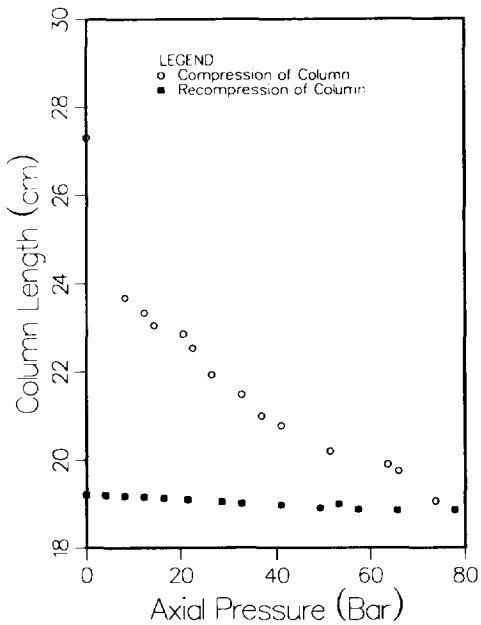


Fig. 12. Compression (○) and decompression (■) curves of the wet-packing material.

reduce the column length by more than ca. 10% and the final consolidation is achieved by percolating methanol through the bed. By contrast, wet packing reduces the column length directly to 19.06 cm, corresponding to a final density of 0.636 g/ml. The same density cannot be achieved with dry packing unless the bed is wet with methanol afterward, in which case the same packing density is achieved. The decompression curves are nearly identical for dry and wet packing. With the wet-packed bed, recompression up to 80 bar gives a curve which overlays the decompression curve, showing that the phenomenon involved is limited to elastic deformation of the particles and of the bed structure. The bed has been completely consolidated at 80 bar.

The compression diagram of the wet column is shown also in Fig. 1 (dotted lines). Surprisingly, the data points are not correctly fitted by one single straight line but rather by three different ones. At low pressures, up to approximately 20 bar, the data points are on a line which is much

[1] Whipping the column was an attempt at rapidly triggering a collapse of local instabilities of the packing. It is not suggested as a reliable procedure to improve the quality of the column packing.

less steep than the one observed for dry packing, with a slope $a_v = 0.062$ (versus 0.132 for dry packing). The intermediate points are on a line with a slope $a_v = 0.20$, slightly steeper than the dry-packing points, and the last three points, above 63 bar, on a steep line of slope $a_v = 0.47$. The first stage involves mere slippage of the particles over each other, leading to a closer packing [20]. Rapidly, the particles become too close to each other to move easily, which limits the process. It gives place to the second stage of consolidation, the formation of temporary vaults protecting small voids. These vaults are compressed, deformed and give way by abrupt slippage or breakage of the keystone. The second break of the plot (at ca. 63 bar) corresponds to the onset of the third mechanism of consolidation, particle breakage. This explanation is in agreement with the independent observation that crushing noises are heard around 65 bar with this material. A similar broken-line plot has been reported in the compression of particles into pellets (e.g., drug tablets) [20]. It has been given the same explanation. The two break points observed in the compaction of magnesium carbonate (particle size, 200–240 mesh, B.S.) took place at 13 and 70 bar, respectively [20]. These values are very close to those found in this work. All the data points have been determined after waiting for hours, which largely exceed the time constant of the compression (see below). We have yet no satisfactory explanation for the different behavior of beds obtained by dry- and wet-packing techniques under compression. The phenomenon is under investigation.

It remains possible, however, that we are attempting to overinterpret the results. The plot of the external porosity versus the pressure in Fig. 7 shows a straight line with a slope of $-2.1 \cdot 10^{-3}$ bar$^{-1}$. The scatter of the data points is expected, given the small variations of the porosity measured. However, the trend is clear. The value of $d\epsilon_e/dP$ being twice as large as for the dry compression, the time constant of compression would be double. This time remains negligible in practice, except for columns having an unusually high efficiency. The need to wait an indeterminate period of time for the relaxation of the bed instabilities (see Fig. 10) remains the controlling factor in the consolidation of column beds.

The packing density can easily be derived from our results. A plot of the packing density versus the compression pressure (not shown) is very well approximated by a straight line of equation $Pd = 0.500 + 0.00184P$, where $Pd$ is the packing density. This relationship permits a rapid calculation of the apparent pressure of consolidation of a column bed when knowing its packing density. This parameter is an indication of the bed stability.

### 4.5. Column efficiency, wet-packed column

The results obtained are shown in Fig. 13. They are much better than with the dry-packed column since the minimum reduced HETP is 6. Much better results ($h_{min}$ around 3) are obtained routinely with a more conventional slurry-packing technique than the one used here [14]. This is probably in connection with the observation that fast compression of the slurry tends to give

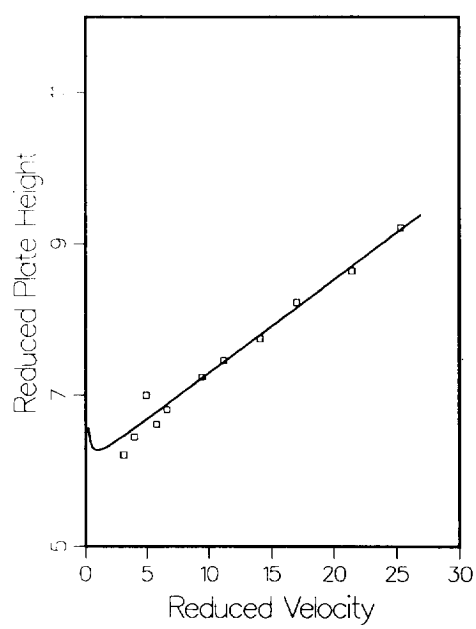


Fig. 13. Efficiency of the consolidated column after wet compression of the packing. Solute: acetone (nonretained).

better efficiencies than slow compression. There are, however, many reports in the literature that sedimentation gives highly efficient but unstable columns (e.g., Ref. [11]). The sedimentation step in our slurry-packing procedure does not let the slurry undisturbed for the whole operation, which may explain the fair efficiency of the column.

## 5. Conclusion

The results obtained are in excellent agreement with the predictions derived from soil mechanics and demonstrate the considerable uncertainty surrounding the concept of packing density. The dry-packed column contains 238 g of silica material. If we assume an approximate density of silica of 2.21, this weight corresponds to a total volume of solid of 107.7 ml. Initially, the dry bed has a length of 24.9 cm, hence a volume of 488.9 ml, a packing density of 0.487, and a total porosity of 0.778, taken at 0.78 in the following, approximate calculations. Estimating the external porosity at 42% gives an internal porosity of 0.36 and a total pore volume of 176 ml. The final column length is 19.1 cm, hence the packing volume is 375.0 ml, the packing density is now 0.635. Assuming that the volume occupied by the pores and by the solid have remained constant (i.e., assuming that the particles are not compressible to any significant extent), the volume left for the external porosity is 87.4 ml, giving an external porosity of 0.24, an extremely low value, which is comparable to that of compressed sands. This value is slightly lower than the one obtained by wet packing at the same compression pressure.

A packing density of 0.547 g/cm$^3$ was found for an analytical column packed with the same material as the one used here. Using the relationship given previously between the packing density and the compression pressure, we find that this analytical column was consolidated at 25.5 bar only. Both the value of the consolidation pressure and that of the packing density are rather low. It would not be surprising in such a case that some additional consolidation takes place slowly, during operation of the column. An increase of the packing density by up to 10% could easily occur, with a correlative decrease of 10% in the column length. The formation of a void of such a magnitude at the column inlet would cause a dramatic loss of efficiency. The phenomenon could come at any time, or could possibly be triggered by a minor shock to the column.

Further work is in progress to unravel the intricacies of the relationships between the structure of the column bed and the performance of the column. The behavior of different packing materials used in preparative chromatography will be investigated and the results obtained with materials with different shapes (spherical vs. irregular), average size, and average pore size diameter (which may affect breakage resistance) [23]. So will be the homogeneity of the column packing in the radial and the axial directions. The distribution of stress in a compressed bed of particles is certainly not homogeneous as is the distribution of the hydrostatic pressure. This is demonstrated by the obvious differences in packing densities between the two ends of a column. Accordingly, it is highly probable that the column packing density is not homogeneous either, whether in the axial or the radial direction. The uneven consolidation of the packing in a column provides a source of explanation for the chromatographic phenomena observed by others [1–4,6,7].

It may seem surprising that a research field as extensively investigated in the past as the behavior of packing materials for liquid chromatography still contains nearly unexplored areas. This might be interpreted as meaning that the knowledge accumulated so far on this issue is sufficient for our needs. A proof that this conclusion is not correct has been recently given by the investigation of the behavior of chromatographic bands by NMR Imaging [11]. While the minimum reduced HETP of the column measured with a conventional UV detector was between 2.1 (first measurements) and 5 (after several experiments had degraded its performance), the same HETP measured from the local thickness of the band seen inside the column by the NMR

imager was 1.0, although injection had to be done with a 150-cm long, 0.8 mm I.D. connecting tube to place the column far enough from the instrument magnet. We should never forget that there is no theoretical lower limit to the column reduced HETP, although the opposite is widely believed. Long ago, Giddings [29] has reported a reduced HETP well below 1 in gas chromatography, for a column packed with glass beads covered with a thin layer of liquid as the stationary phase. It should be possible to achieve routinely an efficiency in that range. However, we are of the opinion that we can never approach that goal without a much more profound knowledge of the properties of consolidated beds of packing materials.

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**List of symbols**

| | |
|---|---|
| $\Delta P = P_2 - P_1$ | Compressibility coefficient. |
| $C_c$ | Numerical coefficient. |
| $C_v$ | Coefficient of consolidation. |
| $d_c$ | Column diameter. |
| $d_p$ | Average particle diameter. |
| $e$ | Void volume fraction (volume available to the mobile phase around the particles). |
| $e_0$ | Void volume at the reference pressure ($p_0$). |
| $e_1$ | Initial void ratio |
| $e_2$ | Final void ratio. |
| $h_0$ | Constant in the Blake–Kozeny equation. |
| $k$ | Permeability of the packing. |
| $L$ | Column length. |
| $P$ | Compression pressure. |
| $P_1$ | Initial value of the compression pressure. |
| $P_2$ | Final value of the compression pressure. |
| $p$ | Pressure. |
| $p_0$ | Reference pressure (usually the atmospheric pressure). |
| $S$ | Cross-sectional area of the column. |
| $T$ | Dimensionless time, $T = 4C_v t/L^2$, Eq. 8. |
| $t$ | Time. |
| $U$ | Consolidation ratio. |
| $V$ | Volume of fluid. |
| $z$ | Position along the column. |
| $\Delta P = P_2 - P_1$ | Excess pressure applied to the liquid. |
| $\epsilon_e$ | External, interparticular, or interstitial porosity. |
| $\epsilon_i$ | Internal porosity or porosity of the particles. |
| $\eta$ | Mobile phase viscosity. |

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