Consolidation and column performance of several packing materials for liquid chromatography in a dynamic axial compression column

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Abstract

The mechanical properties of four different packing materials for preparative liquid chromatography were investigated. Their compression kinetics and consolidation behavior were measured under dynamic compression stress in a 5-cm I.D. axial compression column. The internal and external porosities, the packing density, the permeability, and the efficiency of these columns were also measured. The materials studied included two spherical silica-based materials for preparative chromatography, NovaPak C_{81} (6 μm) and Hyperprep HS BDS C_{18} (12 μm), another octadecyl bonded silica material made of irregular shaped particles, Baker 1-130 C_{18} (130 μm), and an unmodified alumina (50 μm). The first two packing materials showed much higher mechanical stability than the third one which experienced extensive particle breakage under high compression stress. The material with the smallest spherical particles (average size, 6 μm) gave a stable, rigid column, but, either because it contains fine particles or because of a small degree of particle breakage, it caused problems. Maintenance after unpacking a column and cleaning the piston frit was difficult. This could lead to a significant decrease of the productivity. The behavior of the fourth column material, unmodified alumina, is very different from the ones of all silica-based materials so far studied; it is not superior to that of the three silica-based materials presented here. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

The importance for chromatographic performance of the consolidation behavior of beds of packing materials under stress has been demonstrated in previous publications [1–6]. These results were recently placed into perspective in the wider framework of the column packing process [7]. The previous systematic work, however, has been carried out with a small number of silica-based packing materials, IMPAQ and Zorbax from BTR Separations (Wilmington, DE, USA) [1–4], Kromasili from Eka Nobel (Bohus, Sweden) [3,4], and Hyperprep from Shandon HPLC (Cheshire, UK) [5]. In this report,

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we extend the study to other materials, including some with much bigger particles and an alumina material. As in previous reports, we investigated the consolidation behavior of these materials in a dynamic axial compression (DAC) column and the properties and performance of the DAC columns prepared with them. It has been confirmed recently that the dynamically compressed columns and the slurry-packed columns are heterogeneous both radially and axially [8–14].

The main goal of our continued exploration in this area is to learn the nature and origin of the column heterogeneity and its influence on the efficiency of columns in analytical and in preparative chromatography. It is not to prepare and operate preparative columns. This is why the compression of certain materials was pushed beyond what would be reasonable in production runs, until the eventual destruction of a large fraction of the particles.

2. Experimental

2.1. Equipments

An LC-50 dynamic axial compression column system (Prochrom, Champigneulles, France) was used [1,3]. The packing material is compressed by a piston moving inside a cylinder and actuated by a hydraulic jack. The column body is a stainless steel cylinder 5 cm I.D., with a maximum allowable compression pressure of approximately 100 kg/cm^2. Solvent was delivered by a dual piston pump, Dynamax SD-1 (Rainin, Woburn, MA, USA), with a maximum flow-rate of 800 ml/min and a maximum pressure of 1500 p.s.i. (1 p.s.i.=6894.76 Pa). The detector was a SpectraFocus from Thermoseparation Products (Riviera Beach, FL, USA). The UV absorbance was recorded at 254 nm. A preparative flow cell (0 to 3 mm path length) was used for most of the work. An analytical flow cell (6 mm path length) was used in some cases. The preparative cell allows a maximum flow-rate of 6000 ml/min. Samples were injected with a 6-port switching valve from Valco (Houston, TX, USA), actuated by a manual electrical switch.

The column back pressure was measured with an Omega (Stamford, CT, USA) pressure transducer (model PX603-2KG5V) and changes of the column length smaller than 1 cm with a displacement sensor (model PAA1 555 from Reagan Controls, Charlotte, NC, USA). The accuracy of this latter sensor is 0.01 mm. Larger changes were derived from the displacement of an index on the piston, measured with a ruler at an accuracy of 1 mm. The electrical signals of the displacement sensor, the pressure transducer, and the UV detector were collected with a data acquisition module from Waters (Milford, MA, USA) and recorded in a microcomputer for data analysis.

2.2. Packing materials

Four different packing materials for chromatography were used: NovaPak C$_{18}$ from Waters, Hyperprep HS-BDS C$_{18}$ from Shandon HPLC, Baker I-130 from J.T. Baker (Phillipsburg, NJ, USA), also a chemical bonded octadecyl silica, and an unmodified alumina obtained from Cohesive Biotechnologies (Franklin, MA, USA). The physical properties of these materials are listed in Table 1.

2.3. Samples

Uracil (C$_4$H$_4$N$_2$O$_2$, M_r=112, from Aldrich, Milwaukee, WI, USA), at concentrations between 0.1 and 0.8 g/l, was used to measure column efficiency because it is not retained with the mobile phase selected (methanol–water, 40:60, v/v). Thus, column efficiency includes the effects of all the contributions to band spreading which originate in the mobile phase but only a small contribution due to the resistance to mass transfer in the stationary phase (the contribution of diffusion through the internal pore volume, only).

Polystyrene standards, with molecular masses ranging from 456 to 20 600 000, were used for inverse size-exclusion chromatography (ISEC) of all the materials studied. These samples were obtained from Supelco (Bellefonte, PA, USA) and Tosoh (Tokyo, Japan). The mobile phase was methylene chloride (CH$_2$CI$_2$), and the peaks were detected by a UV spectrophotometer detector.

2.4. Procedures

The DAC column was packed successively with

Table 1
Physical properties of packing materials

	NovaPak C$_{18}$	Hyperprep HS BDS C$_{18}$	Baker I-130 C$_{18}$	Unmodified alumina
Manufacturer	Waters	Shandon HPLC	J.T. Baker	Cohesive
Average particle diameter (μm)	6	12	130	50
Particle shape	Spherical	Spherical	Irregular	Spherical
Specific surface area (m^2/g)	120	282	312	5.04
Average pore size (Å)	60	92	130	546
Apparent density (g/ml)	0.91	0.60	0.375–0.575	na
Specific pore volume (ml/g)	0.3	0.64	1.1	0.0689

each material and tested, following the procedure briefly described below. Comprehensive descriptions of the packing and test methods for the axial compression column have been published previously [1]. For each column packing, the dry mass of each material was measured. Masses round 240 g were used in all cases, resulting in columns of markedly different lengths (Table 3, later) because of the large differences in either the internal porosity (silica samples) or the skeleton density (silica versus alumina particles). The particles were mixed with 800 ml of isopropanol and turned into a thick slurry. After the slurry had been left settling for a few hours, the top portion or supernatant was removed to eliminate the fine particles and the dust. The slurry volume made was approximately 800 ml after this last procedure was finished. The slurry was then poured into the empty, precleaned column. Column compression began immediately, and the compression pressure increased step by step to obtain the compressibility curve.

During each compression step, the column length was recorded. The back pressure was measured at several solvent velocities, within the limits of pressure (1500 p.s.i.) and maximum flow-rate allowed by the pump (800 ml/min). The samples used for the measurements of the column efficiency and for the ISEC experiments were all injected twice and the results were averaged. The injection volume was 0.5 ml, unless specified otherwise.

Column unpacking is usually a simple and straightforward operation. By opening the top flange and raising moderately the compression pressure, the piston pushes the packed column material which comes out as a single body cylinder [8], in most cases. The material of this body is brittle but holds sufficiently strongly to be taken in the hand without breaking. However, unpacking columns packed with the big particles of Baker I-130 was more delicate and required great care in order not to alter the smooth finish of the metal surface of the column. The Baker I-130 column did not come out easily even when a high piston pressure, close to 90 kg/cm^2, was applied. The packing body was stuck in the column, demonstrating a high friction coefficient of the material against the wall. It is not surprising that the friction of a bed of coarse, irregular particles be higher than that of a more conventional material. To remove the bed, the top part of the body had to be crumbled into individual particles, which was relatively easy, and taken away by hand. The top part of the bed was mostly brittle and the particles were only loosely bound together. Eventually, the column material was removed by breaking up the cylindrical body into small pieces. The bottom part of the bed (against the piston) was much harder. The packing density increased markedly from the top of the bed to its bottom. This phenomenon took place only with the longest column packed and seems to be related to the particles being large and irregular. This type of packed column is far from homogeneous, as shown in another recent paper [14].

Samples of the packing material located either close to the edge of the piston and the cylinder wall or close to the top of the bed were collected during the unpacking of each column. Samples of the virgin packing materials were also taken. All these samples were analyzed for their particle size distribution

using a Coulter LS1 30 (Coulter Scientific Instrument, Miami, FL, USA).

3. Results and discussion

3.1. Compression and compressibility

The four different packing materials were compressed step by step from an initial compression stress of approximately 20 kg/cm^2 to a maximum compression stress of approximately 90 kg/cm^2. The step increment of compression stress was 10 to 20 kg/cm^2. After reaching the maximum stress, the column was decompressed to zero stress and then recompressed (second compression). Some columns were decompressed a second time, after being kept compressed for several days, to be compressed one more time (third compression). Changes in the column length were monitored by the displacement sensor for considerable periods after each step increase of the compression stress. The compression or consolidation [2,4] curves recorded during the successive stress steps applied on the same bed for each material are shown in Figs. 1–4. The NovaPak

Fig. 1. Consolidation of NovaPak C_{18} after application of a step increase in the compression stress. The curve shown is typical of the behavior of this product.

column is very stable under compression stress. Its length drops immediately after the application of the increased stress and it remains almost constant afterwards, as seen in Fig. 1. Only one typical compression curve is shown in Fig. 1 because all the other consolidation curves, including those acquired during the second compression, are very similar, regardless of the rate of application of the compression stress. The only change from curve to curve is in the magnitude of the length jump (see later). This behavior is typical of spherical particles [4]. The Hyperprep column is also quite stable after the initial jump which follows the application of an increased compression stress. However, a later drop of the column length is occasionally observed during the first compression, when the column is maintained a long time under constant compression stress, as seen in Fig. 2a. This late drop in the column length is indicative of a metastable state of consolidation. It was not seen during the recompression processes, as shown in Fig. 2b and c. This behavior has been reported previously for materials made of nearly but not quite perfectly spherical particles [4].

The behavior of the Baker I-130 column is quite different from that of the previous two columns, especially during its second and third compressions. During the first compression (consolidation curve in Fig. 3a), the same phenomenon takes place at each step of increasing compression stress. First, the column length drops rapidly, then it remains metastable for a certain time and it decreases again, through delayed collapses, while the column is kept under constant stress. As previously reported for irregular-shaped particles [2], the delay of these collapses is random and of the order of 0.5 to 2 h. The total decrease in column length following steps of comparable amplitude is much larger than with the other two packing materials (the scale units of the y-axis in Figs. 1, 2a and 3a, are 0.2, 1.0, and 5.0 mm, respectively). During the second compression (Fig. 3b), which took place immediately after the first one, the column length is stable and exhibits only the expected degree of elastic behavior under moderate stress, up to 66 kg/cm^2 [6]. However, under high compression stress, close to the maximum (85 kg/cm^2), collapses take place again. Usually, a second or any further compression causes only a moderate, reversible decrease in the column
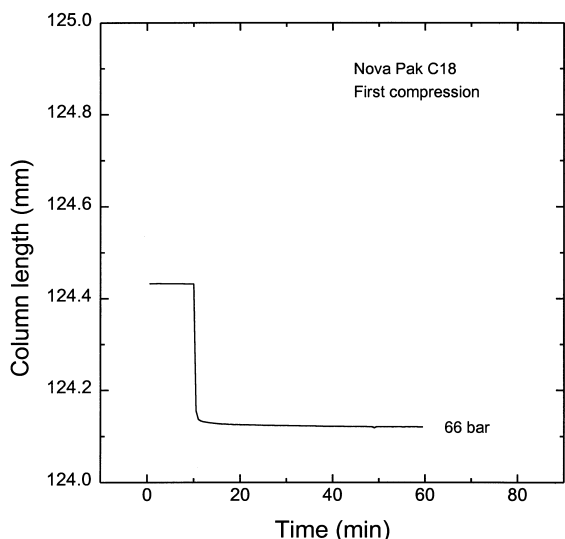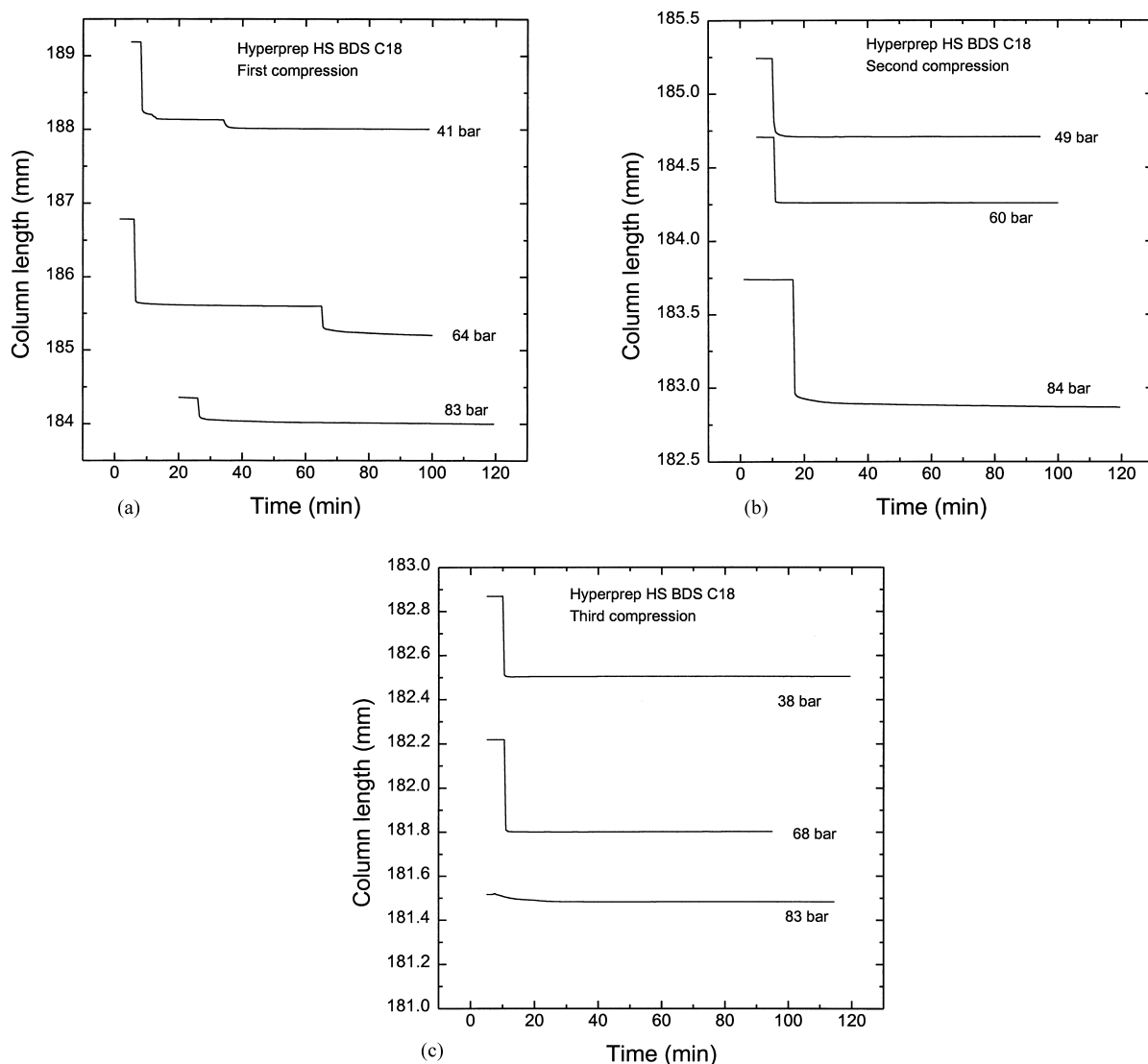
Fig. 2. Consolidation of Hyperprep HS-BDS C_{18} after application of a step increase in the compression stress: (a) First compression of the column; (b) second compression of the column; (c) third compression of the column.

length, proportional to the pressure applied, the consolidated packed bed reacting as another piece of elastic material. Such an elastic behavior was observed with Baker I-130 up to a stress of only 66 kg/cm². Under higher values of the stress, the column collapses and its length reduces through successive jumps, which are indicative of particle breakage (see later). This confirms that packing materials made of irregular particles should not be compressed beyond ca. 40 kg/cm², as suggested by the manufacturer of the column skid.

Particle breakage is more intense with irregular-shaped particles than with spherical ones. As shown previously [4], the stress applied to the bed during its consolidation is focused onto the sharp edges of the irregular particles, which are easily broken. For
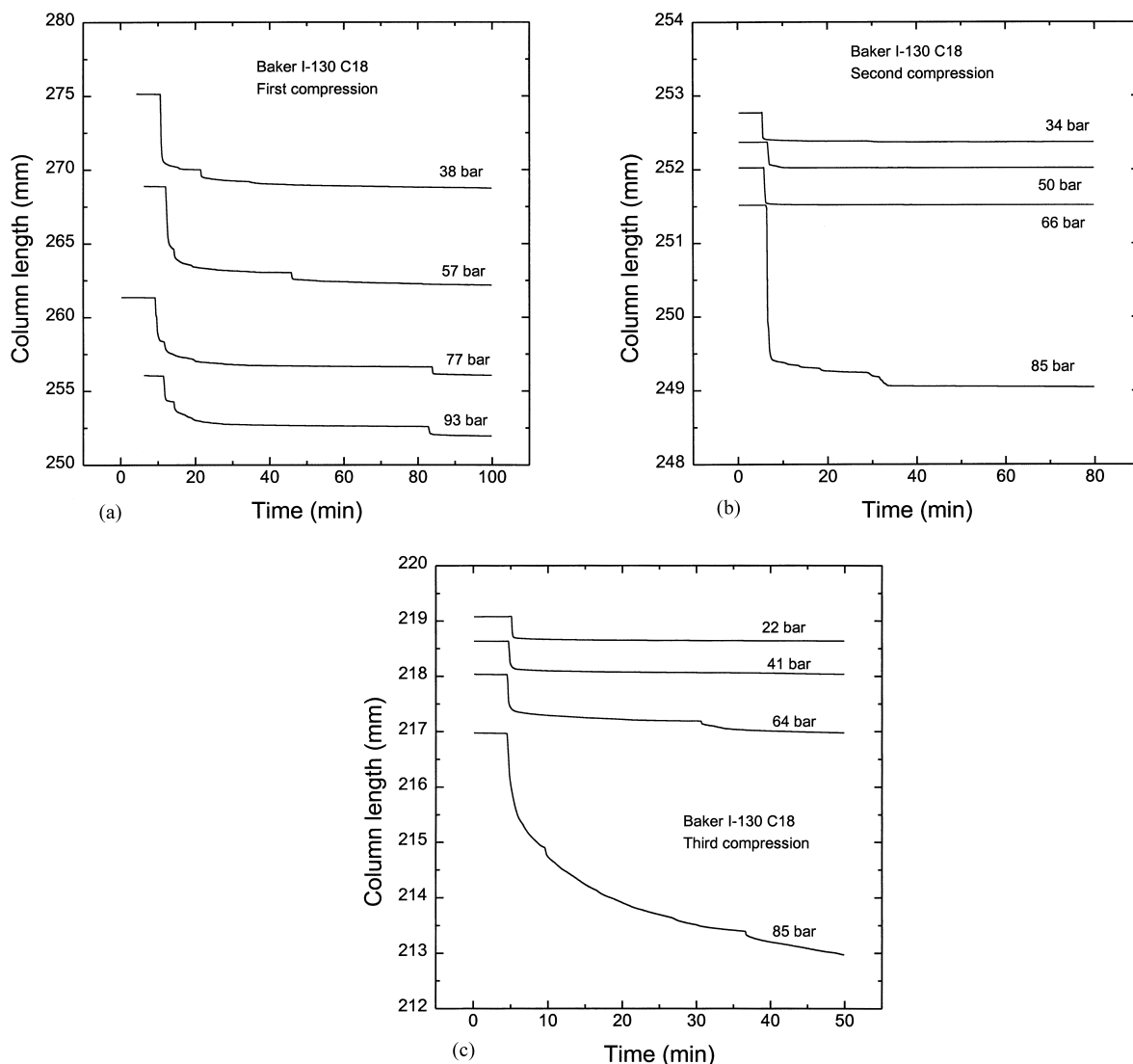
Fig. 3. Consolidation of Baker I-130 C_{18} after application of a step increase in the compression stress: (a) First compression of the column; (b) second compression of the column; (c) third compression of the column.

example, an intense chipping of the particles of IMPAQ was observed [1,4]. Because of the unusual behavior of Baker I-130 during the second compression, a third compression was carried out after completion of the measurements of the column permeability and efficiency, thus long after the end of the second compression. During this third compression (Fig. 3c), the column again exhibited an elastic behavior under low stresses (i.e., below ca.·66 kg/cm^2) but serious instability was observed under high compression stress, with a significant and continuous drop of the column length. This is a clear indication of ongoing particle breakage which becomes more intense every time the column is decompressed and recompressed, probably because an increasingly large fraction of the particles are fractured during successive compressions. This behavior also explains the difficulties encountered when unpacking the column and reported earlier, in Section 2.
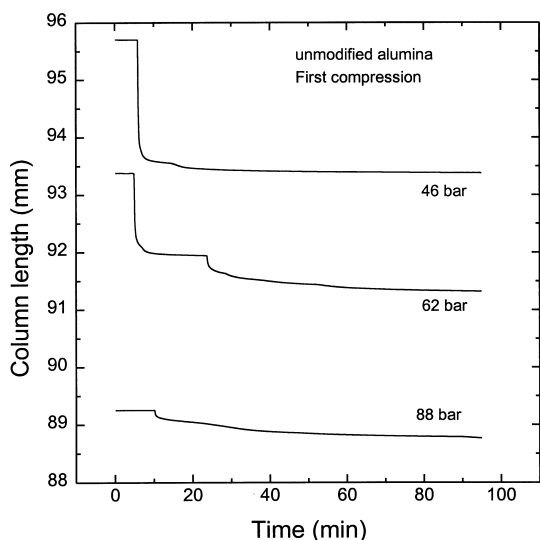
Fig. 4. Consolidation of the unmodified alumina after application of a step increase in the compression stress.

The last column was packed with bare alumina. The consolidation behavior showed no clear indication of major particle breakage (Fig. 4), although the beds obtained were slightly less stable during the first compression than those made with the two spherical packing materials (cf. Figs. 1, 2 and 4). For example, Fig. 4 shows the formation of an intermediate metastable state during compression under 62 kg/cm^2 and its progressive collapse 20 min after application of the compression step, before the eventual stabilization, which required more than an hour. This material differs from the previous one (Baker I-130) by the chemical composition of the particle skeleton (alumina versus silica) and by the average particle size, 50 versus 130 μm (Table 1). Its particles are also less irregular, although not quite as smooth as the spherical silica particles.

The shape of the particles, the smoothness of their external surface, the mechanical stability of the particles which depends on their chemical nature, on their porosity, and on the average pore size, explain the differences observed between the consolidation curves of the different materials studied. The experimental data reported in Figs. 1–4 suggest that NovaPak and Hyperprep HS-BDS are truly smooth, spherical or nearly spherical particles while the bare alumina material is not entirely so.

Fig. 5a–d show plots of the column length versus the compression stress applied during the successive compressions carried out for each material. The column length is defined as the length measured 100 min after the application of the new step of compression stress. Since the second compression experiment was performed immediately after the first one, the final lengths achieved (at a compression stress of approximately 90 kg/cm^2) during the first and the second compressions are almost the same for each column material. The third compression took place a relatively long time later (always several days, some times a couple of weeks), after all the different tests of the column (see later) had been performed. In the meantime, a compression pressure near the maximum remained applied to the column. This explains why the length of the column at the end of the study is always shorter than at the end of the first compression, even with the small-size particles (Fig. 5a and b). In other words, the length of a dynamic axial compression column does not remain constant as long as the compression stress is applied. The column length decreases continuously (but very slowly), to an extent which depends on the size and shape of the particles. In practice, however, the rate of decrease of the column length during a short period (a few hours) is not noticeable, especially for materials made of small, spherical particles.

The values of the bed compressibility ($-\mathrm{d}L/\mathrm{d}P$) and of the elasticity ($E=PV/\Delta V$, with P, applied pressure, V column volume and ΔV change of column volume upon compression to P) were derived as explained previously [6]. The values obtained from the data in Fig. 5a–d are summarized in Table 2. The compressibility of the columns was much higher during the first compression than during further ones with all the materials. This phenomenon is typical of consolidated particulate materials [6]. Particles shift in the bed under stress. There is no mechanism for the particles to rebound to their initial position when the applied stress is released. After the first compression, the bed compressibility has become very low and the bed elasticity very high (such as the top of a well-finished dirt road). Although packed with quite different materials, all the columns studied exhibit this same behavior. However, the phenomenon is more intense for the unmodified alumina than for the silica-based materials. Among the latter materials,
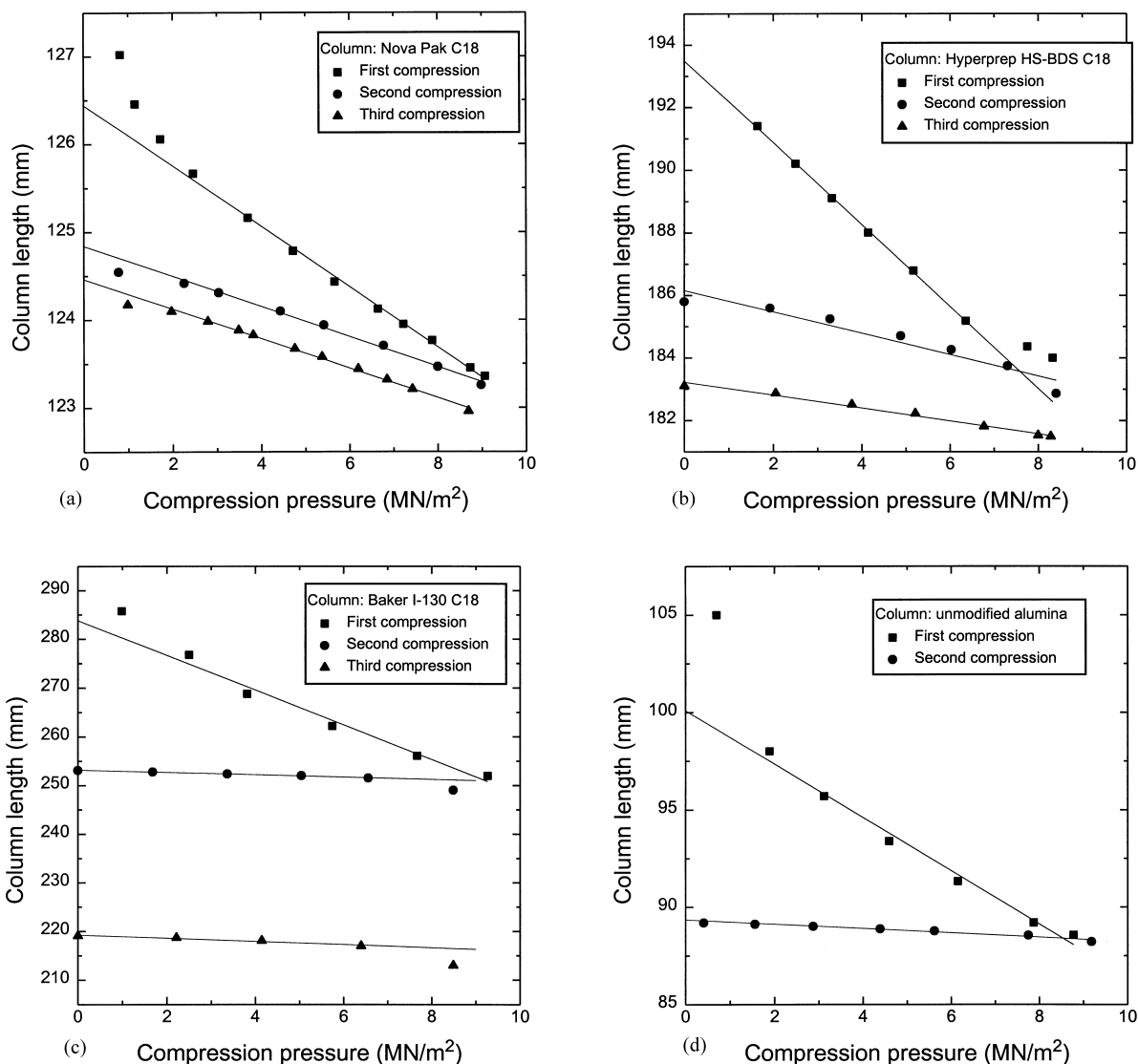
Fig. 5. Plot of the length of the consolidated column versus the compression stress: (a) NovaPak column; (b) Hyperprep column; (c) Baker I-130 column; (d) unmodified alumina column.

the decrease in axial compressibility of the column upon its consolidation is more significant with large and irregular materials [4].

Consolidated NovaPak has the lowest compressibility of all three silica-based materials but consolidated alumina has a still lower compressibility. NovaPak and Hyperprep are also more elastic than the other two materials. This was expected from these fine and uniformly spherical materials. The

average pore size is also small and the internal pore volume is the smallest of the silica materials (Table 1). Hyperprep is more compressible and less elastic than NovaPak after the second compression but changes much more during the interval between the second and third compressions. This result may be explained by the slightly different physical properties shown in Table 1. However, these two materials do exhibit a similar consolidation behavior. Baker 1-

Table 2
Bed compressibility data

		Nova Pak	Hyperprep	Baker I-130	Alumina
Compressibility	First	343.8	1309.1	3561.2	1369.5
$(-\mathrm{d}L/\mathrm{d}P,$	Second	171.9	341.4	238.0	111.8
$cm^3/MN)$	Third	168.4	206.5	326.5	
Column length	First	126.44	193.49	283.78	100.08
at zero pressure	Second	124.84	186.15	253.15	89.35
$(L_0,$ mm)	Third	124.46	183.22	219.22	
Elasticity	First	367.8	147.8	79.7	73.1
$(E,$ MN/m^2)	Second	726.2	545.3	1063.7	799.2
	Third	739.1	887.3	671.4	
Bed porosity	All	0.376	0.409	0.469	0.485
(ε_e)					
Compressibility	First	44.648	120.388	266.240	300.138
coefficient	Second	22.342	31.590	18.000	24.613
$(a_v,$ cm^3/MN)	Third	21.941	19.252	28.868	

130, having much larger internal pore volume, average pore size, and average particle size, and having also irregular-shaped particles, exhibits quite a different behavior. Both its elasticity and its compressibility change dramatically after the first compression. The particles appear to be more seriously damaged by the second compression than by the first one, suggesting that, in actual practice, columns packed with irregular-shaped particles should never be decompressed and recompressed. Finally, the alumina material has a consolidation behavior similar to that of Baker I-130, although the alumina particles are twice smaller (but their pores are four times larger than those of Baker 1-130, Table 1). A further discussion of the physical characteristics of these materials and of their influence on the compressibility of the columns will be presented later, with the analysis of the porosity data.

3.2. Column pressure drop and permeability

The back pressure of each column was measured at different flow-rates. After all the measurements required by the study of each column had been completed, back pressure measurements were carried out on the instrument, without putting any packing material in the column. The column back pressure data, corrected for the back pressure of the column-less instrument, are plotted versus the flow-rate in Fig. 6. The amount of material used to pack each column was approximately 240 g for the three silica-based columns and 200 g for the alumina column. Because of important differences in the apparent density of the packing materials, columns of widely different lengths were obtained (Table 3). The packing density of the silica columns decreases with
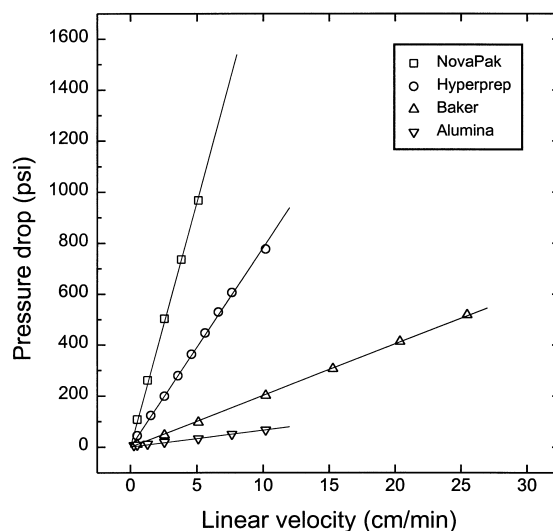

Fig. 6. Plot of the back pressure of the different columns versus the superficial velocity of the mobile phase. Solvent: methanol–water (40:60).

Table 3
Column density and permeability

	NovaPak	Hyperprep	Baker I-130	Alumina
Dry mass (g)	238	240	240	200
Column length (cm)	12.3	18.3	22.4	8.8
Density (g/cm^3)	0.985	0.668	0.546	1.157
to $\Delta P/\Delta u_0$ (p.s.i. min/cm)	192.324	78.254	20.189	6.600
Permeability (cm^2)	1.341×10^{-10}	4.905×10^{-10}	2.327×10^{-9}	2.796×10^{-9}

increasing internal pore volume (Table 1). The alumina packing material has a higher density than the three silica materials, even than the NovaPak one. This is a result of the specific density of alumina being higher than that of silica. A meaningful comparison of the hydraulic resistances of the different columns requires proper correction for the effects of their lengths and particle diameters. The high hydraulic resistances of the columns packed with NovaPak and Hyperprep were expected, given their small average particle sizes. The fact that the alumina column has a lower resistance than the Baker I-130 column while its average particle size is twice smaller results in part from the shorter length of the alumina column (8.8 cm against 22.4 cm for the Baker 1-130 column, Table 3). It is also a result of the important degree of particle breakage exhibited by the Baker I-130 material during its consolidation.

The permeability of the columns was calculated from Darcy's law, using the back pressure data (Table 3). Assuming constant bed porosity (or external porosity), the permeability is proportional to the square of the particle diameter. The values reported in Table 3 show that, indeed, the permeability of the Hyperprep column is approximately 4 times higher than that of the NovaPak column, in excellent agreement with the average size of the Hyperprep particles, twice larger than those of NovaPak (Table 1). The permeability of the Baker I-130 column, however, is only 20 times larger than that of the NovaPak column, while the average size is slightly more than 20 times larger. This means that the effective or hydraulic particle size of the packing material in the Baker I-130 column after its consolidation under 90 kg/cm^2 is approximately 4.5 times lower than its nominal size, confirming the intense particle breakage under this high compression stress.

Interestingly, the alumina column has a 20% higher permeability than the Baker I-130 column. Compared to the permeability of the NovaPak and Hyperprep columns, the alumina packing material has a hydraulic radius of approximately 30 μm, 40% lower than its nominal size. The difference could certainly not be explained by the external porosity of the alumina column being slightly higher than that of these two silica-based materials (see Section 3.3 Table 4).

3.3. Inverse size-exclusion data, external and internal bed porosity

In ISEC, authentic samples of polymers having a high and narrow molecular mass and a narrow molecular-mass distribution are injected into a column and the molecular mass of the sample is plotted versus its retention volume [15]. For all the packing materials, polystyrene, a nonpolar polymer, was used with methylene chloride as the mobile phase. It is not retained either under these conditions. Benzene was used as the tracer. To minimize the amount of chlorinated solvent used, these measurements were made on analytical-size columns. It has been shown that analytical columns prepared by slurry packing have a lower packing density and a higher external porosity than columns packed under compression [6] and undergo a lower degree of particle breakage. However, the internal porosity of the packing material is independent of the column and of the degree of consolidation of the bed. The external porosity of any column is easily derived from its total porosity (determined from the retention volume of a tracer) and the weight and internal porosity of the packing material used. Finally, we should note that the pores of the alumina material are two orders of magnitude

Table 4
Inverse size-exclusion chromatography (ISEC) data

	NovaPak	Hyperprep	Baker I-130	Alumina
Column type and size (length×diameter)	Preparative (DAC), 12.5×5 cm	Analytical, 10×1 cm	Analytical, 25× 0.4 cm	Analytical, 10× 0.46 cm
Sample	Dextran	Dextran	Polystyrene	Polystyrene
Mobile phase	Methanol–water (40:60)	Methanol–water (40:60)	Methylene chloride	Methylene chloride
Critical M_r [a]	28 459	22 422	32 076	2 519 179
Critical bed [a] vol.	92.180	3.216	1.949	0.805
External porosity	0.376	0.409	0.469	0.485
Total porosity	0.542	0.593	0.723	0.747
Internal porosity	0.267	0.311	0.478	0.509

[a] Cross point of the two straight lines for each ISEC data in Fig. 7a–d.

larger than those of the silica materials, which have all pores of similar sizes.

The plots of the molecular masses of the polymer versus their retention volumes, in semilog coordinates, are shown in Fig. 7a–d, for the different materials studied. The data were corrected for the equipment contribution to the dead volume. All the plots show a sharp transition or critical point, the molecular mass exclusion limit. This limit is such that, at higher molecular masses, the polymer molecules have no longer access to any part of the internal pore volume while at lower molecular masses they have access to a part of this internal pore volume which increases with decreasing molecular mass of the polymer probe. From the coordinates of this point, we can derive the external porosity of each analytical column [15]. The internal porosity was obtained from the external and the column total porosity (itself obtained from the retention volume of the tracer). All these results are summarized in Table 4. The internal porosity of the four materials increases in order of increasing average pore size (Table 1). NovaPak and Hyperprep have close values for their internal and external porosities. Their internal porosities are close and rather small, near 0.3, a result which contributes to their strong mechanical resistance. The internal porosities of Baker I-130 and alumina are higher, near 0.5. The external porosities of the preparative

columns made with these two materials are relatively high, near 0.47.

3.4. Column efficiency

The efficiency of all the columns was determined using uracil at different flow-rates. In all cases, the mobile phase was a methanol–water (40:60, v/v) solution. The column efficiency was derived from its conventional relationship with the retention time and the peak width at half height. In Fig. 8, the number of theoretical plates for each column is plotted against the mobile phase linear superficial velocity. Although this plot format is not conventional in chromatography, it was preferred to the conventional height equivalent to a theoretical plate (HETP) plot (see later) because it illustrates an important, often overlooked, property of a stationary phase for preparative chromatography. Note that all the columns studied were packed with nearly the same mass of packing material but that their lengths are not the same, as explained earlier. The long Hyperprep column has by far the largest number of theoretical plates. This means that this material can perform a given separation with a shorter column, using a lower amount of packing material. This could suggest a higher productivity and a lower production cost, although the retention of the feed components, their separation factor, and the curvature of their
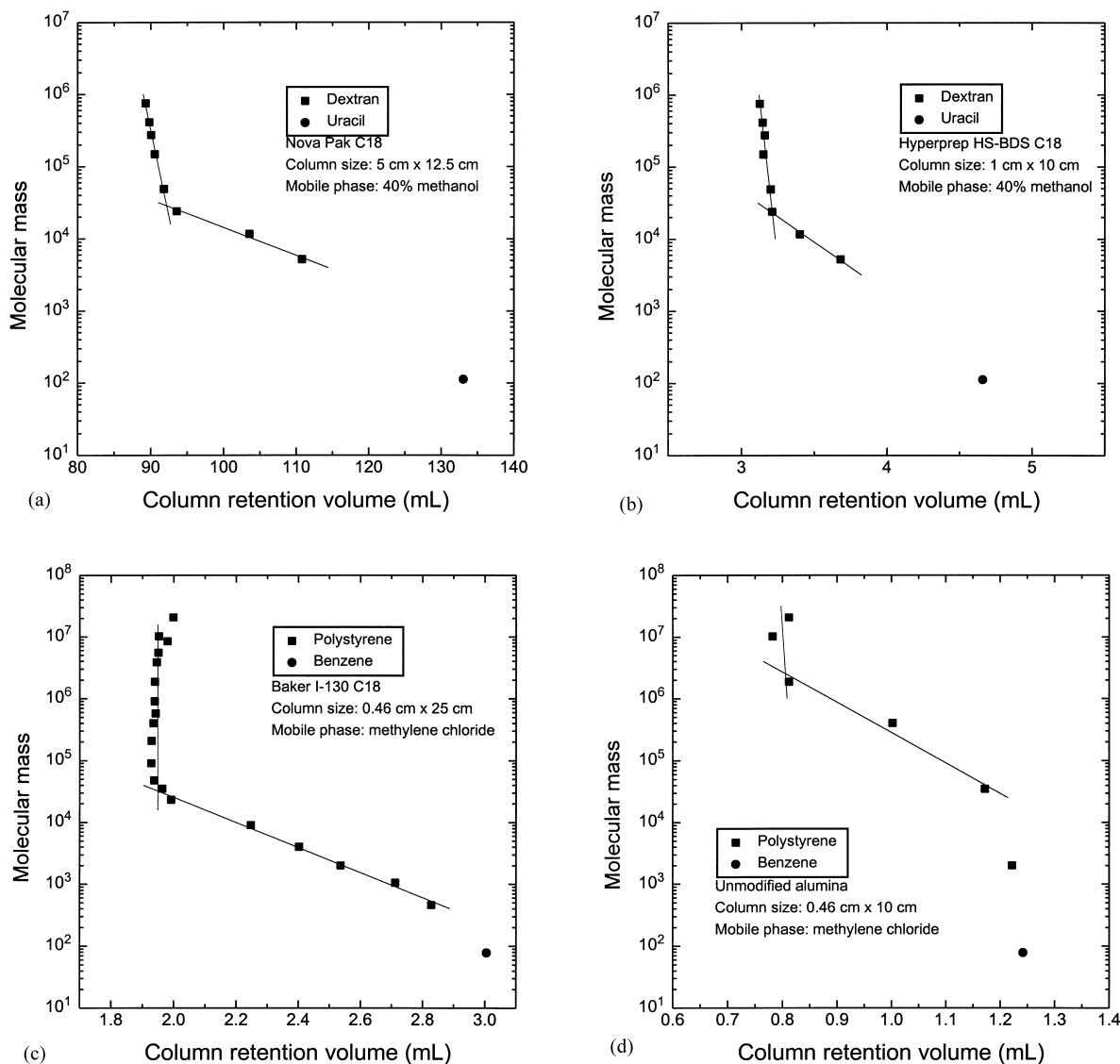
Fig. 7. Determination of the external porosities of the different columns by ISEC: (a) Semilog plot of the molecular mass of the polymer sample versus its retention volume on the NovaPak column; (b) semilog plot of the molecular mass of the polymer sample versus its retention volume on the Hyperprep column; (c) semilog plot of the molecular mass of the polymer sample versus its retention volume on the Baker I-130 column; (d) semilog plot of the molecular mass of the polymer sample versus its retention volume on the unmodified alumina column.

equilibrium isotherms play also a significant role in determining the productivity. These factors, which are very much problem specific, could not be studied here. The NovaPak column was slightly less effi-

cient. The Baker I-130 column has a much lower efficiency than the other three columns. Although shorter, the alumina column has a higher efficiency than the Baker I-130 column. The problem with the
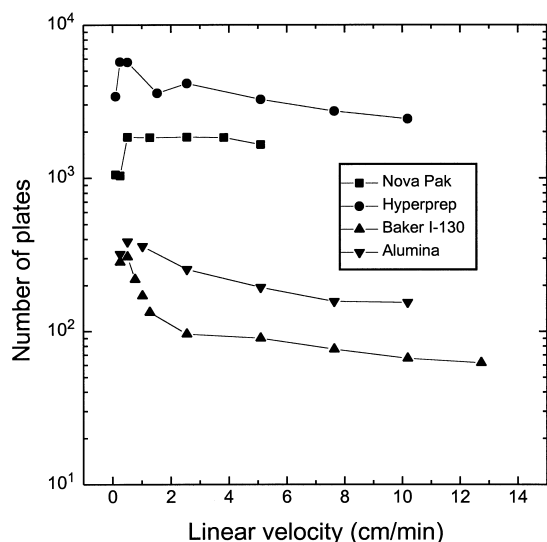
Fig. 8. Plot of the total number of plates of the different columns versus the mobile phase linear velocity.

Fig. 9. Plot of the reduced plate height of the different columns versus the mobile phase reduced velocity.

alumina material studied is its low specific surface area and the very low retention factors. To achieve some retention, hence a modicum of resolution, a water-rich eluent must be used, limiting the mobile phase capacity.

Fig. 9 shows the plots of the reduced HETP of the four columns versus the mobile phase reduced velocity. The reduced velocity is plotted in a logarithmic scale because the HETP determinations were done in nearly the same range of mobile phase flow-rates, which corresponds to widely different ranges of reduced velocities on the four columns. The plots obtained belong to the general Van Deemter type. The best efficiency is obtained at a reduced velocity slightly above 1 for NovaPak and Hyperprep and at a reduced velocity of the order of 3 for the alumina material. For the Baker I-130 material, the measurements were all carried out at too high velocities to estimate the optimum flow velocity for maximum efficiency. The lowest value of the reduced HETP is approximately 2.5 for Hyperprep, a very good result. Both the Baker I-130 and the alumina columns have smallest reduced plate heights approximately equal to 5, which is fairly good, especially for the Baker material for which the
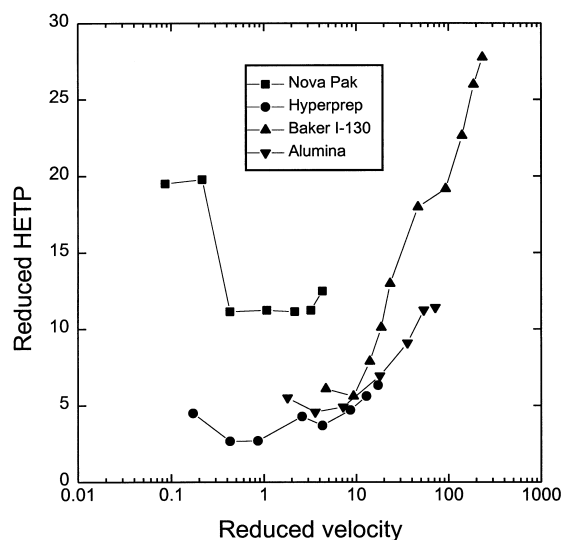
measurements were not made in a low enough range of flow-rates. The NovaPak column gave surprisingly large values of the reduced HETP, with a minimum around 10 which is unusually flat. For this reason, further studies of the efficiency of NovaPak columns were carried out by packing more columns in different ways and using different UV cells to monitor the elution.

The results of these investigations are summarized in Fig. 10. The first column is the one discussed above, compressed step by step, as was done with the other materials. The second column was compressed by raising the applied stress directly from zero to 60 kg/cm² , the most typical operating pressure of this dynamic axial compression column for strong silica-based packing materials (i.e., a material of medium porosity, having small pores, and made of spherical particles). There are practically no differences in efficiency between the first and the second column. This indicates that the low efficiency was not related to the use of a progressive compression procedure. The third column was compressed directly from zero to 50 kg/cm² , but, before packing this new column, the column frits were carefully cleaned with ammonium bifluoride and nitric acid
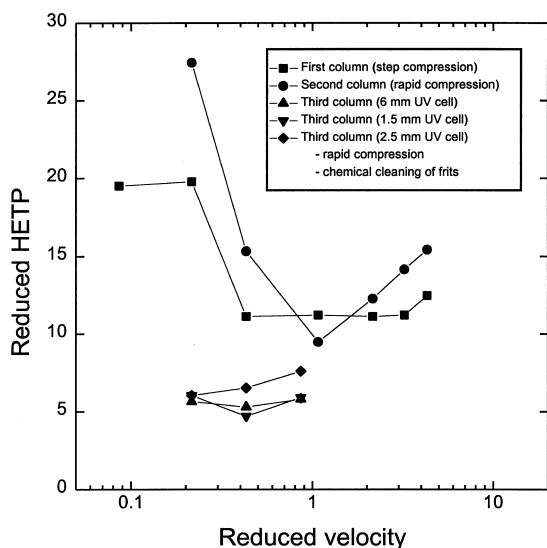
Fig. 10. Plot of the reduced plate height of the NovaPak columns versus the mobile phase reduced velocity. (1) ■ first column, step compression to 80 kg/cm^2, (2) ● second column, rapid compression to 60 kg/cm^2, (3) ▲ third column, rapid compression to 50 kg/cm^2, after chemical cleaning of the frits, using the analytical UV cell with a 6-mm long path length, (4) ▼ the same third column, using the preparative UV cell with a 1.5-mm long path length, and (5) ♦ the same third column, using the preparative UV cell with a 2.5-mm long path length.

[1]. Before packing all the other columns, the frits were merely cleaned mechanically, in an ultrasonic bath, as usual. A marked improvement of the performance is observed, the minimum reduced plate height decreasing to slightly less than 5 (Fig. 10). Finally, two different, smaller UV cells were used with this third column, to check whether the detector dead volume could have any influence on the band broadening. Obviously, there are no differences between the peak widths and the column efficiencies obtained with any of the three detector cells. The chemical cleaning of the frits enhanced the column efficiency to the level of the other column materials. Columns packed with NovaPak require more careful maintenance than the other columns in order to achieve a satisfactory efficiency. This phenomenon has not been observed yet with any of the packing materials investigated in our group so far. The reason is probably in some very fine particles which would become trapped in the column frits and partially obstruct the flow passage.

3.5. Particle size distribution and particle breakage

Samples were collected during the unpacking of different columns and their particle size distributions were determined as explained in Section 2. The experiments were carried out only with NovaPak and Baker 130-I. In both cases, samples were collected from the top, the center, and the bottom of the column. The same measurements were also carried out for samples of virgin material. The samples were collected from columns which had been consolidated under a stress of 55 kg/cm^2 for NovaPak and 23 kg/cm^2 for Baker 130-I [14]. The results obtained are plotted in Fig. 11a (Baker 130-I) and b (NovaPak).

As shown in Fig. 11a, even for a column compressed only at 23 kg/cm^2, the particle size distribution of the Baker I-130 material is significantly different whether collected in the regions at the column top and center or at the bottom (i.e., against the piston). When collected at the column top or center, the particles have nearly the same size distribution as that of the virgin material, except for a slight decrease of the volume fraction of the particles beyond 180 μm and an increase of the fraction of particles between 120 and 160 μm. This difference is possibly explained by a segregation taking place inside the container. The comparison between the distributions of the virgin material and those of the top and center samples suggest that there is little or no particle breakage in the two samples from the column. The distributions are nearly identical in the low particle size range (20 to 100 μm). By contrast, in the sample collected at the column bottom, there is a considerable increase of the volume fraction of the small particles (below 100 μm) and an important decrease of the volume fraction of the large particles (above 120 μm). This result is in agreement with the findings by Train [16] that the stress inside a compressed bed of particles is highest close to the moving boundary (here, the piston, at the bottom of the cylinder) and lowest against the opposite boundary (the top). In between, the stress varies slowly with the vertical position in the higher three quarters of the column and increases steeply close to the piston. This result is also in agreement with previous similar ones [4]. In the case
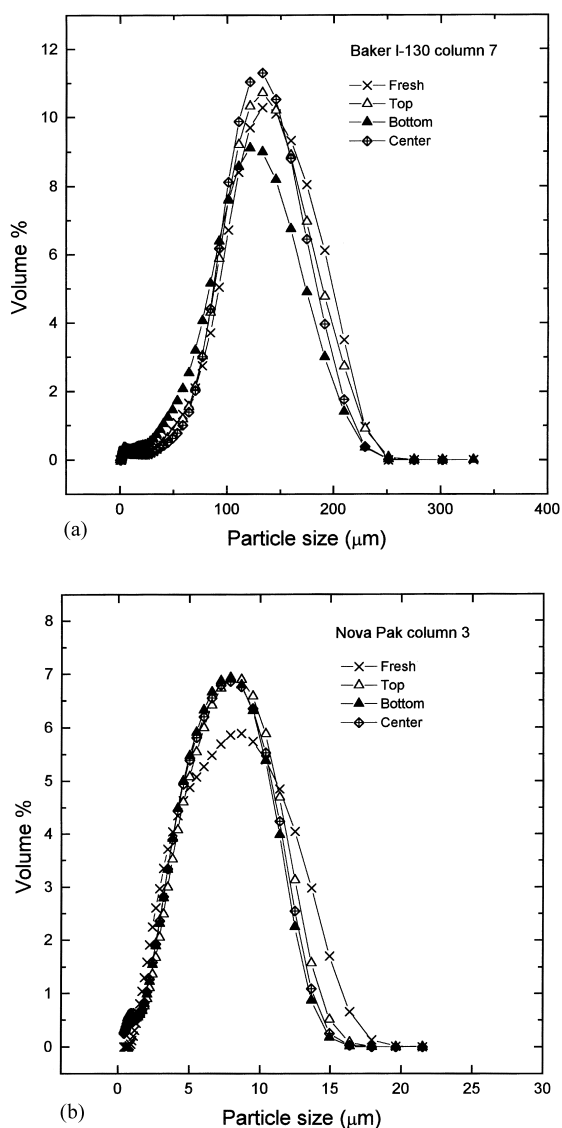
Fig. 11. Differential particle size distribution of the virgin material and of samples collected at the top, center and bottom of the column when unpacking it; (a) Baker 130-I; (b) NovaPak.

of a column consolidated under 65 kg/cm^2, the results of the determination of the particle size distribution showed an important particle breakage in the column center and a considerable breakage of the particles at the bottom (results not shown).

Fig. 11b shows that there is little particle breakage in the NovaPak samples collected during the unpacking of the column. Whether the material was located in the top, center, or bottom of the column, the size distribution obtained is nearly the same. However, in all three cases, there is a little amount of very fine particles (in the range 0 to 2 μm) which is not present in the virgin material. The distribution of the virgin material in the high particle size range is quite different from that of the three samples collected from the column packing. This is explained by the presence of aggregates (mainly dimers) which were dissociated during the preparation of the slurry (sonication step) but were not during the suspension of the virgin sample for particle size analysis (which were not sonicated).

The results of the particle size analysis are in agreement with the other observations and with the column properties. Irregular-shaped, large particles are more easily broken under high stress than small, spherical ones. Particle breakage is more severe near the piston of the DA than a few cm from it.

4. Conclusion

Our results show that different packing materials can behave very differently in a dynamic axial compression column. Fine spherical or nearly spherical materials can withstand relatively high compression stress, giving stable beds with reasonable values of the bed external porosity and permeability. This observation was reported previously with Kromasil, YMC, and Zorbax [3,4] and is observed here with NovaPak and Hyperprep. However, some unusual difficulties were encountered with NovaPak. The column efficiency was lower than with the other similar materials unless the column frits were very carefully cleaned before packing a new column. Obviously, the frits must also be cleaned most carefully after the unpacking of a column to avoid similar difficulties with the new packing material. Other silica-based materials, especially those which have irregular-shaped particles, are brittle, chip and fragment easily. They should not be subject to the same high compression stress. This stress causes particle breakage, a considerable decrease in the column permeability and, probably, a large increase in the polarity of bonded phases. On the other hand, when properly handled, irregular-shaped, large particles such as those studied here could give columns

with an extremely high permeability, which could be useful when a low column efficiency is deemed satisfactory. Whether the better efficiency obtained with the Hyperprep material is related to the smaller amount of fine particles was not elucidated.

Acknowledgements

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