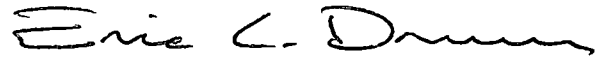


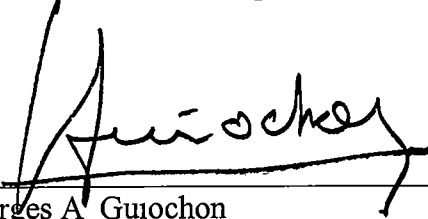
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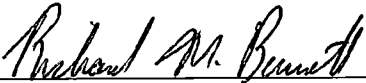


Eric C. Drumm, Major Professor

We have read this thesis
and recommend its acceptance.



Georges A. Guiochon



Richard M. Bennett

Accepted for the Council:



Associate Vice Chancellor
and Dean of The Graduate School

**Application of Soil Mechanics and
the Finite Element Method (FEM) to
High Performance Liquid Chromatography
(HPLC) Columns**

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Bee Gaik Yew

May, 2000

Dedication

This thesis is dedicated to my parents,

尤振成 陳秀蕊

Chin Seng Yew and Siew Looi Tan

my brothers,

尤榮德 尤榮財

Eng Teik Yew and Eng Chye Yew

and especially my soul mate,

鄭瑾謙

Chin Chien Tee

for all their support and encouragement.

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Abstract

The efficiency of High Performance Liquid Chromatography columns is often reduced due to radial variations of the density or void ratio of the silica packing material. This heterogeneity is due to wall friction effects during column preparation, and although the friction reduces the column efficiency, some friction is required to stabilize the bed during the chromatography process and ensure a leak-proof seal between bed and wall. To investigate the induced heterogeneity during the compaction process, concepts from soil mechanics were used to study the column preparation process. Laboratory tests were conducted to measure the relationship between permeability and void ratio. The coefficient of friction between a typical packing material and the stainless steel column wall was determined in the laboratory, and the volumetric response was modeled with a nonlinear elastic-plastic model. The effect of wall friction and piston shape on the radial distribution of void ratio was then investigated by numerical analysis. The effect of loading rate was investigated using a coupled mechanical-seepage model. The results suggest that the homogeneity of the packed bed can be improved by reducing the effects of wall friction, and increasing the rate at which the piston compacts the column.

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List of Symbols

A	cross-sectional area of the sample
A_t	base area of the block used in tilt tests
a	cross-sectional area of the graduated burette
C_c	compression index
C_s	swelling index
C_v	coefficient of consolidation
c	cohesion or cohesive strength of the material contact
D	sample diameter
d	yield function intercept on the q axis
d_{10}	grain size corresponding to 10% finer
d_{90}	grain size corresponding to 90% finer
d_{max}	maximum grain diameter
d_{min}	minimum grain diameter
E	Young's modulus of the porous material
e, e_v	void ratio of the packing material
e_0	initial void ratio
F	linear Drucker-Prager yield surface function
f	coefficient of pore shape used in Carman-Kozeny formula
G_s	packing materials specific gravity
g	gravitational acceleration.
H_0	initial height of the sample

H_1	measured vertical distance using caliper
H_2	depth of the shear box
H_3	height of the top cap
H_4	thickness of the filter paper
h	hydraulic head
h_f	elevation of methanol solvent in the standpipe above the discharge level at time t .
h_i	elevation of methanol solvent in the standpipe above the discharge level at time $t = 0$
h_0	initial height
h_t	height of plate
J^{el}	logarithmic measure of the elastic volume change
K	intrinsic permeability
K_g	bulk modulus of the solid grains
K_i	the permeability of the porous medium in the i direction, where $i = x, y, z$.
k	permeability coefficient or hydraulic conductivity
L	length of the sample
L_t	length of the plate used in tilt tests
M_d	mass of the dry sample
M_e	external mass occupied by solvent around the particles
M_i	internal mass occupied by solvent inside the particles
M_T	total mass of the packed bed
M_u	inaccessible mass occupied by the solids of the silica particles

m	mobile phase
N	normal load
n	number of elements
n	porosity of the porous medium
p	mean stress
p_0	initial value of the equivalent pressure or stress
p_t^{el}	elastic tensile strength of the material
q	Mises equivalent stress
R	resisting force against sliding
S	specific surface area
S_s	specified storage where the volume of fluid released from a unit volume of saturated porous medium for a unit decline in hydraulic head, h
s	stationary phase
T	shear force
t	time
U	degree of consolidation
U_z	axial displacement
UTOL	maximum pore pressure that was allowed to dissipate in each time increment
V	present volume
V_i	initial volume
V_e	external pores volume
V_i	internal pores volume
V_o	total volume occupied by solvent

$V_{particles}$	volume of silica particles, occupied by the volume inaccessible to the solvent and the internal pores volume
V_s	total volume of silica particles
V_T	total column volume
V_u	volume inaccessible to the solvent
$v_x, v_y, \text{ and } v_z$	the specific discharge (volume flow rate of permeating liquid per unit area) in the x, y, and z direction, respectively
v_w	the magnitude of the velocity of the pore fluid in Forchheimer's flow law
W	weight of phenolic block
α	angle between a plane surface to the horizontal surface
α_{pm}	compressibility of the porous medium
β	slope of the yield function in the p - q stress space
β_w	compressibility of the permeating fluid
β_F	the velocity coefficient in Forchheimer's flow law
Δh	vertical deformation due to axially applied load
Δl	a typical element dimension
Δt	time increment used in ABAQUS (1998)
δ	interface friction angle
ε_e	external porosity
ε_i	internal porosity
ε_T	total porosity
ε_v	volumetric strain

ε_z	axial strain
γ_w	specific weight of the wetting liquid or solvent
ϕ	internal friction angle
ϕ_p	peak friction angle
ϕ_r	residual friction angle
κ	logarithmic bulk modulus
μ	dynamic viscosity of the fluid
ρ_{d0}	initial dry density
ρ_{dry}	dry or apparent density of packed bed
$\rho_{particles}$	density of silica particles
ρ_u	density of silica solids
ρ_w, ρ	density of the solvent or fluid
σ	total or axially applied stress (normal stress)
$\sigma_{11}, \sigma_{22}, \sigma_{33}$	principle stresses
σ_y	normal stress
σ'	effective stress
σ'_p	pre-consolidation pressure
τ, τ_{xy}	shear stress
ψ	dilation angle

Chapter 1

Introduction

The chromatography process is used to separate nonvolatile chemicals from dilute solutions under a high velocity and large pressure drop across a vertical column consisting of porous silica, which is an absorbent, and a solvent such as methanol. The efficiency of the separation process conducted in High Performance Liquid Chromatography (HPLC) columns is strongly dependent upon techniques used to prepare or pack the column. During the preparation of the column, friction between the packing material and the wall of the column results in a nonuniform density across the radius of the column, which significantly reduces the efficiency of the separation process.

Since the silica packing material consists of small spherical or near spherical particles, the behavior of the silica during the packing process is likely to be similar to that of other particulate materials such as soils. Concepts from soil mechanics and numerical approximations using models developed for soils were utilized to investigate the mechanics of the chromatography column preparation process.

To investigate the mechanics of the packing process, specifically the distribution of stress and strain in the chromatography column and the role of wall friction on the particle density, a series of finite element analyses was conducted. To obtain parameters for the numerical analysis, several series of laboratory tests were conducted. These tests include interface direct shear tests and fixed ring consolidation tests incorporating falling head permeability tests. The goal of the study was to investigate the mechanics of packing process,

and perhaps to recommend alternative packing procedures such that more uniform columns may be assembled.

Chapter 2

Literature Review

Chromatography in the past twenty years has developed into one of the major preparative and analytical tools of the chemistry and biotechnology industries. The efficiency of the separation process conducted in High Performance Liquid Chromatography (HPLC) columns is strongly dependent upon techniques used to prepare the column. During the preparation of the column, friction between the packing material and the wall of the stainless steel column results in a nonuniform density across the radius of the column, which significantly reduces the efficiency of the separation process. In addition, the seepage forces imparted to or generated in the packing material as solvent is pumped through the system may also lead to nonuniform density in the column. To investigate the mechanics of the packing process, a review of the literature was conducted to survey published ideas related to the mechanics of HPLC column preparation process.

2.1 History of Chromatography and the Separation Process

To separate a mixture of talc powders and iron fillings, all that is needed is a magnet, which selectively removes the iron fillings from the mixture, leaving the talc powders unaffected. As the individual components of a mixture get more and more similar in physical or chemical properties, it becomes increasingly difficult to separate them. This is especially true in chemistry or biology, where it is frequently necessary to separate, isolate, purify, and identify the components of mixtures such as proteins. To achieve such a separation fairly rapidly, the chromatography process can be used (Abbott and Andrews, 1965).

Chromatography can be defined as that technique for the separation of a mixture of solutes, in which separation is brought about by the differential movement of the individual solutes through a porous medium under the influence of a moving solvent (Abbott and Andrews, 1965)

The Russian biologist, Tswett was the first person to appreciate the possibilities of such a method as long ago as 1906 (Guiochon *et al.*, 1994). The porous medium that Twett used consisted of finely powdered chalk packed into a long vertical glass column provided with an outlet at the bottom. Twett noticed that when a solution of green plant pigments was applied to the top of the column and then washed down with light petroleum, a series of horizontal bands of different pigments and colors began to separate from one another as they moved down the column (Guiochon *et al.*, 1994). The term “chromatography”, which literally means “color writing”, was coined to describe this phenomenon (Abbott and Andrews, 1965). In fact, the separation had nothing to do with the components being colored, but was simply due to the fact that the various pigments had different adsorptive affinities for the chalk: those least strongly adsorbed moved down the column more rapidly than those more strongly adsorbed. Twett’s experiment was the first demonstration of adsorption column chromatography.

The studies done by Tswett remained more or less a laboratory curiosity until Martin and Synge (1941) introduced partition column chromatography, which is particularly suitable for water-soluble compounds. However, with these “closed columns,” it was very difficult at the time to obtain a reliable identification of very small quantities of the separated substances. Later, in 1944, paper chromatography was discovered by Consden, Gordon, and Martin (Abbott and Andrews, 1965). With paper chromatography, quantities on the order of

a few micrograms of most of the compounds could be detected and identified in a dependable manner. This "open column" concept was carried further by the introduction of thin-layer chromatography, in which separations are carried out with thin layers of almost any material supported on glass plates. Later, in 1960's, gas chromatography was logically developed from column chromatography. In gas chromatography, gas replaces liquid as the solvent. It is particularly valuable for separating mixtures of gases, or volatile liquids or solids.

With the invention of sensors that transform the variations of physical and physicochemical properties into a current, and recorders that rendered the electric signal in 1950's, column chromatography has become a popular method used in fine chemical, pharmaceutical and biotechnology industries over the last thirty years (Guiochon *et al* , 1994).

2.2 High Performance Liquid Chromatography (HPLC)

Chromatography is a separation process in which the sample mixture is distributed between two phases in the chromatographic column. One phase is stationary while the other passes through the chromatographic column. The stationary phase is either a solid, porous, surface active material in small-particle form or a solid support covered with a thin film of liquid. The mobile phase is either a liquid or a gas (Meyer, 1988)

There are various types of liquid chromatography: liquid-liquid partition chromatography, adsorption chromatography, ion-exchange chromatography, ion-pair chromatography, size-exclusion chromatography, affinity chromatography, and reverse phase chromatography. The most popular method, Reverse Phase Liquid Chromatography (RPLC), is a form of High Performance Liquid Chromatography (HPLC) that involves a hydrophobic or low polarity stationary phase, which is chemically bonded to an inert solid

such as silica. The separation is essentially an extraction operation and it is used to separate and/or detect non-volatile chemicals in a mixture with a boiling point (b.p.) greater than 200-250 degrees Celsius. The process is conducted at a high velocity (which requires a rather high pressure drop) and thus the HPLC is sometimes referred to as "High-Pressure Liquid Chromatography" (Meyer, 1988).

HPLC is a vital separation technique used either for analytical or preparative applications. The former is used when the components of a mixture must be separated, identified and its relative concentrations determined. Because of the high sensitivity of detectors, only small amounts are used during the separation process. Since the amounts used are small, the detector signals are easier to handle. In preparative HPLC, some pure products are separated, collected and recovered for commercial sale. Thus, large amounts of the mixtures are often injected in order to obtain a significant amount of pure compounds. Important concentration effects must be taken into account, but this work is not concerned by them.

A preparative schematic of a HPLC instrument is shown in Figure 2.1. The chromatographic column is a polished stainless steel tube of various diameter (5-80 cm) and height (90-170 inches) depending on the desired column length (30-65 inches). The column that is used in this research is typically a 5 cm diameter and a column length of 80 cm. The column is polished such that the surface has an arithmetic mean roughness value (RA) of $2.0\mu\text{m}$ (Thomas and Drumm, 1998). The column is packed with a slurry to form the stationary phase. To achieve a length of 16 cm packed column, a slurry of 240g silica particles is mixed with 600 cm^3 solvent. The slurry is mixed for an hour such that all the particles are properly dispersed and wetted with the solvent. Then, the slurry is poured

carefully into the column, which is closed by a frit. The hydraulic jack (cylinder), which actuates the movement of the piston along the axial compression column, is piped to a pneumatic pump. The slurry is compressed into a bed while the solvent percolates through the compressed bed.

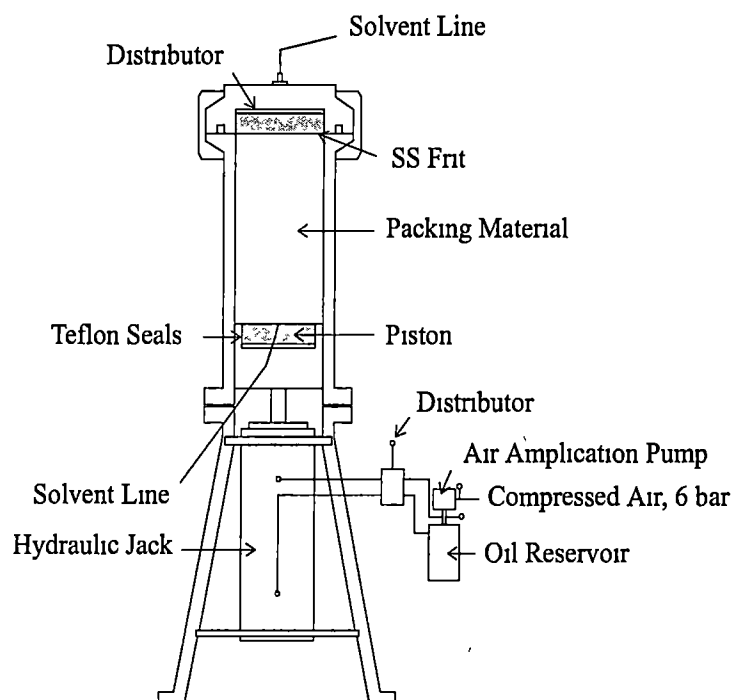


Figure 2.1 Schematic of a Preparative HPLC Instrument.

After the column is packed, then the separation process, or in chromatography terms the mobile phase, is started. The mobile phase is constantly flowing through the column as illustrated in Figure 2.2. Many mobile phases are made up of specific ratios of water, methanol and acetonitrile. As illustrated in Figure 2.3(a), when the sample (a mixture of two components, Δ and $\circ$) is injected into the solvent line from the left of the column, it is swept onto the column by the mobile phase. Since all chemicals are different, they will have different affinities (attractions) to both the stationary phase and the mobile phase, as illustrated in Figure 2.3(b), where the Δ component has a preference for the stationary phase

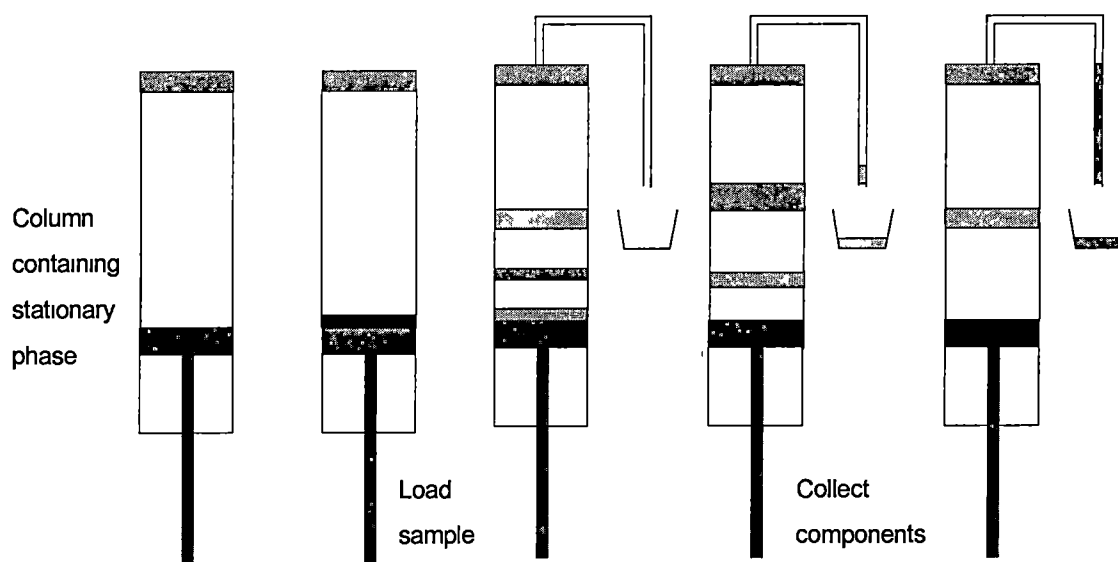


Figure 2.2 HPLC separation process.

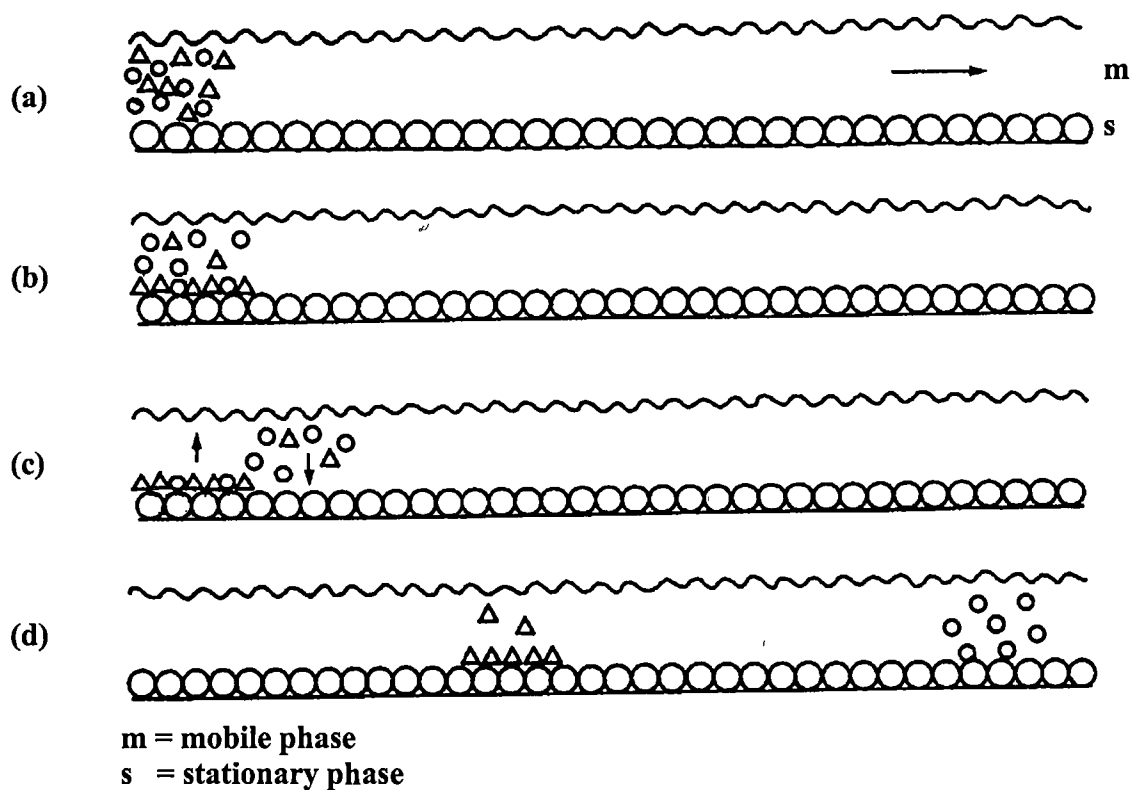


Figure 2.3 Representation of a chromatography separation (Meyer, 1988).

and the $\circ$ component has an affinity for the mobile phase. As a volume of feed is injected periodically the column, each component of a mixture equilibrates between the solvent and the adsorbent surface of the particles. The migration velocity of a band of compound is a direct function of the constant of this equilibrium. As illustrated in Figure 2.3(c), a new equilibrium follows the addition of fresh eluent (mobile phase): sample molecules in the mobile phase are partly adsorbed by the stationary phase surface, in accordance with their distribution coefficients, whereas those molecules which have previously been adsorbed appear again in the mobile phase. After repeating this process several times, the two components are finally separated. The $\circ$ component prefers the mobile phase and migrates more quickly than the Δ component, which tends to "stick" in the stationary phase (Figures 2.2 and 2.3(d)). If the experimental conditions are properly selected, the bands of each compound arrive successively at the outlet of the column where they are collected separately for further processing, as shown in Figure 2.2. When the compounds elute, they can be detected (measured) using a detector that is appropriate to the chemicals being measured (Meyer, 1988).

In short, HPLC permits the extraction or purification of desired compounds from mixtures of various origins, natural or synthetic, and is widely used in industrial, environmental, biological, clinical, and forensic analyses. HPLC plays the same role in the pharmaceutical industry as distillation plays in the petroleum industry. Although it is a very expensive process, it is the only available technique to achieve the strict purity specifications imposed by the regulators of the pharmaceutical industry. Four typical HPLC instruments that are used in the industry is shown in Figure 2.4. First, from the right, a solvent tank is providing the solvent to the small column on the white tripod. The compounds that have

been separated by the column are collected individually using collection tanks that are located beside the column. A larger column can also be used to separate the compounds (extreme left in Figure 2.4).

2.2.1 Properties of the Packing Material

Chromatography is based on the difference between the migration velocities of different compounds carried through a column of an appropriate packing material by a stream of fluid (usually a solvent) percolating through the bed. Unlike soils, the packing material used in Reversed Phase Liquid Chromatography (RPLC) is hydrophobic. This material is not wetted by water. The material to be purified is not or poorly soluble in water. It is soluble in certain solvents. Typical solvents used are methanol and acetone (density 0.79 g/cm^3). The packing material is made of fine particles, typically 3 to $20 \mu\text{m}$, with a very narrow particle size distribution, in which d_{90}/d_{10} of the packing material is typically less than 2, where d_{90} and d_{10} are grain size corresponding to 90% and 10% finer, respectively. The particles are porous, with particle pore sizes between 7 and 100 nm, and possess well-defined surface chemistry.

Two common packing materials that are used in this research are Zorbax spherical C18-bonded silica and Kromasil spherical C18-bonded silica particles shown in Figure 2.5. Note that the magnification of these two pictures are different. The average particle diameter for both materials is about $10 \mu\text{m}$, which is about the size of silt particles encountered in soil mechanics. Unlike Kromasil, Zorbax particles are not true spherical particles. They are an agglomerate of spherical particles, as shown in Figure 2.5(a).

2.2.2 Phase Relationship in Packed Chromatography Beds

The performance of systems of particles, such as packed chromatography beds,

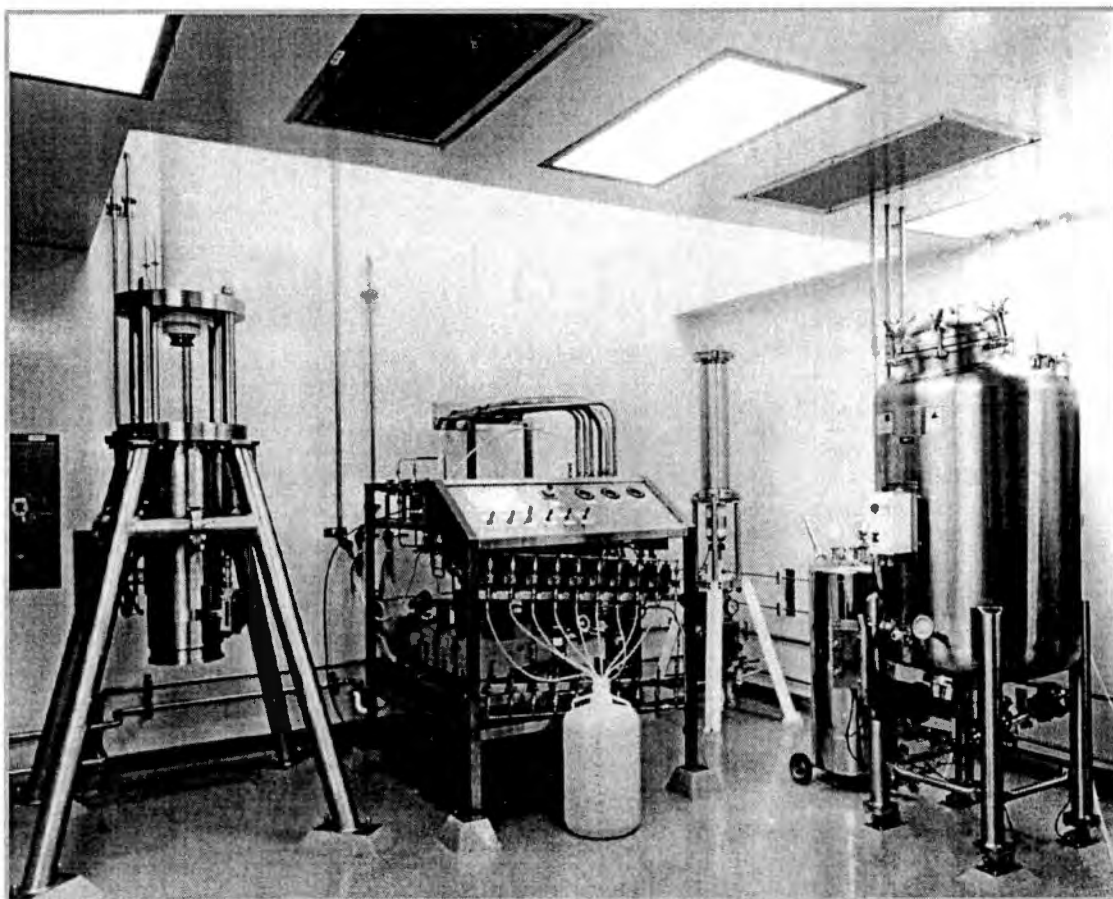
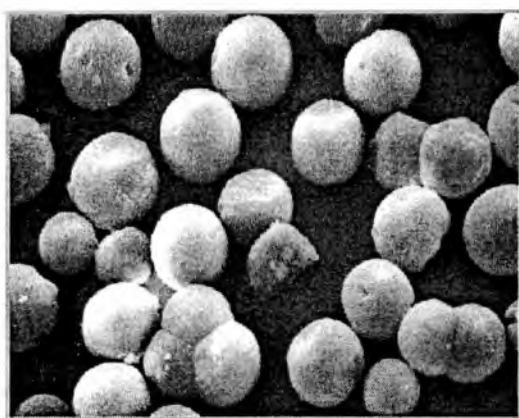
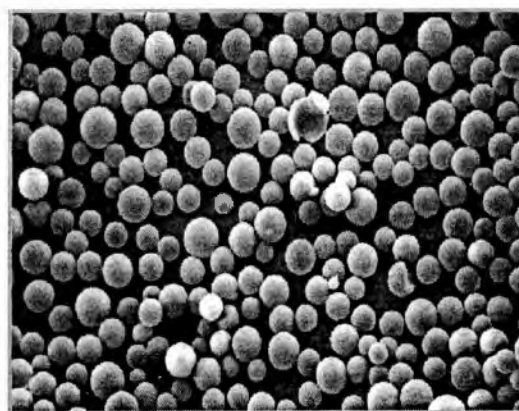


Figure 2.4 HPLC Instruments.



(a)



(b)

Figure 2.5 (a) Zorbax spherical C18 silica particles (x 1250);
(b) Kromasil spherical C18 silica particles (x 310).

granular construction materials, chemical reactors, gas chromatographic columns, and filtration systems depends significantly on the particle arrangement and density (Guan and Guiochon, 1996). A packed chromatography bed consists of two constituents: a dissolving solvent, such as methanol, and the silica particles. The relationships between the various constituents can be depicted in a phase diagram, Figure 2.6, much like is done in soil mechanics. Unlike soils, the silica particles are extremely porous with a surface area between $150 \text{ m}^2/\text{g}$ and $300 \text{ m}^2/\text{g}$, and this surface is “painted” with a monomolecular layer of alkyl chains, $\text{C}_{18}\text{H}_{37}$ bonded to the OH groups of the silica surface. This layer is inaccessible to the solvent, and corresponds to the inaccessible volume, V_u .

As illustrated in Figure 2.6, the total column volume V_T of the packed bed is the sum of the external pores volume V_e , the internal pores volume V_i , and the volume inaccessible to the solvent V_u . It is assumed that the packing material is saturated, such that no volume is occupied by air. The total volume occupied by solvent, V_o , is the sum of the external pores volume, V_e , and the internal pores volume, V_i . The inaccessible volume (inside the silica particles), V_u , consists of three components: the solid silica skeleton volume, the closed or

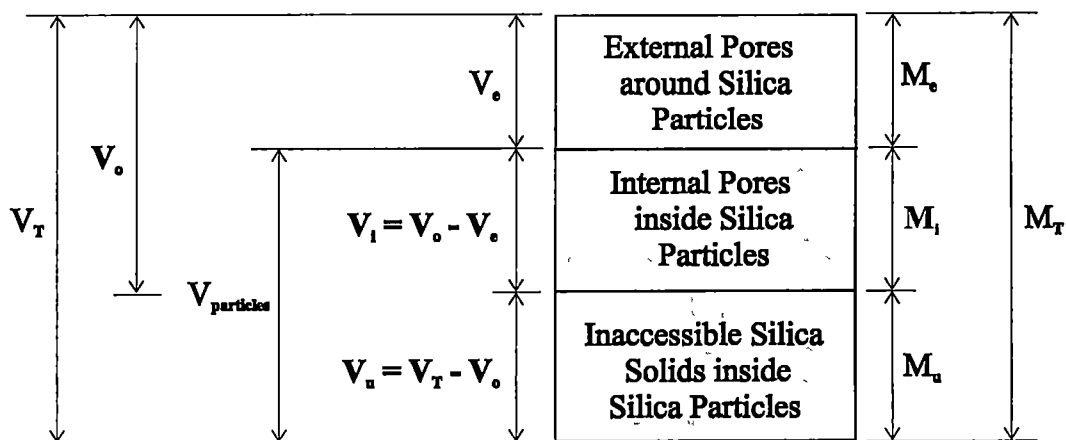


Figure 2.6 Phase diagram of a packed chromatography bed.

unconnected pores volume, and the volume of the layer of C_{18} bonded chains (alkyl). Typical solid volume fractions of 10 μm spherical Zorbax is 11.04 % carbon, 1.98 % hydrogen, and 86.98 % silica (Guan, *et al.*, 1996). The total mass of the packed bed, M_T , is the sum of M_i , M_e , and M_u , where M_i is the internal mass occupied by solvent inside the particles, M_e is the external mass occupied by solvent around the particles, and M_u is the inaccessible mass occupied by the solids of the silica particles.

Recently, the pore-size distribution and pore connectivity of stationary phases for High Performance Liquid Chromatography (HPLC) columns has been studied. According to Guan *et al.* (1996), the inaccessible volume, V_u , can be measured directly by the helium pycnometry method. Currently, there are three methods that can be used to determine the phase volumes of the packed bed: inverse size-exclusion chromatography (ISEC) (Guan and Guichon, 1996), mercury intrusion porosimetry (Guan-Sajonz, *et al.*, 1997), and nitrogen sorptometry methods (Guan-Sajonz, *et al.*, 1997). By employing these methods, an accurate estimate of the total volume occupied by the solvent in the column, V_o , and the volume of the external pores, V_e , (around the silica particles) can be measured. Subsequently, by knowing the total column volume V_T , and the internal pores volume V_i (inside the silica particles) containing a solvent, the inaccessible volume V_u can be obtained.

The properties of chromatography beds are often described in terms of porosity where:

$$\text{Internal Porosity} = \varepsilon_i = \frac{V_i}{V_p} \text{ (Chemical Engineering Definition)} \quad (2.1)$$

$$\text{Internal Porosity} = \varepsilon_i = \frac{V_i}{V_T} (\text{Chromatography Definition}) \quad (2.2)$$

$$\text{External Porosity} = \varepsilon_e = \frac{V_e}{V_T} (\text{Chromatography Definition}) \quad (2.3)$$

$$\text{Total Porosity} = \varepsilon_T = \frac{V_e + V_i}{V_T} = \varepsilon_i + \varepsilon_e (\text{Chromatography Definition}) \quad (2.4)$$

The void ratio, e , of packed bed can therefore be defined:

$$e = \frac{V_e}{V_{\text{particles}}} = \frac{\varepsilon_e V_T}{V_T (1 - \varepsilon_e)} = \frac{\varepsilon_e}{1 - \varepsilon_e} \quad (2.5)$$

Typical values of the internal porosity, external porosity, total porosity, and void ratio for 10 μm spherical Zorbax and Kromasil columns are summarized in Table 2.1 based on equations (2.1), (2.3), (2.4), and (2.5) above (Guan-Sajonz, *et al*, 1997).

Table 2.1 Typical properties for packing materials (Guan and Guiochon, 1996).

	Zorbax (spherical C18)	Kromasil (spherical C8)
Internal porosity, ε_i	33.8 % to 34.2 %	35.9% to 36.5%
External porosity, ε_e	39.5 % to 40.1%	36.6% to 38.3%
Total porosity, ε_T	57.3 % to 60.6%	58.0% to 60.8%
Void ratio, e	0.65 to 0.67	0.58 to 0.62

The density of the packed chromatography columns can be defined as:

$$\text{Density of Silica Solids} = \rho_u = \frac{M_u}{V_u} \quad (2.6)$$

$$\text{Density of Silica Particles} = \rho_{particles} = \frac{M_u}{V_{particles}} \quad (2.7)$$

$$\text{Dry or Apparent Density of Packed Bed} = \rho_{dry} = \frac{M_u}{V_T} \quad (2.8)$$

Based on the experiments conducted by Guan, *et al.* (1996), typical values for the density of silica solids, ρ_u are 1.80 g/cm³ and 1.57 g/cm³ for 10 µm spherical porous Zorbax and Kromasil silica particles, respectively. The solid density of the silica particles is 2.65 g/cm³ (Guan, *et al.*, 1996). The dry or apparent density of the packed chromatography beds ρ_{dry} ranges from 0.8 g/cm³ to 0.9 g/cm³ (Guan-Sajonz, *et al.*, 1997).

2.3 Band broadening inside HPLC bed

Band broadening is the result of a combination of processes, which makes the bands of feed components exiting the column wider than the injection pulse, and ultimately decreases the efficiency of the column, as illustrated in Figure 2.7 (Guiochon, *et al.*, 1994). It is important to understand the causes of band broadening so that the phenomenon can be minimized such that the efficiency of the column can be maintained. There are several causes for band broadening, but one of the major causes for band-broadening is the heterogeneity of the column.

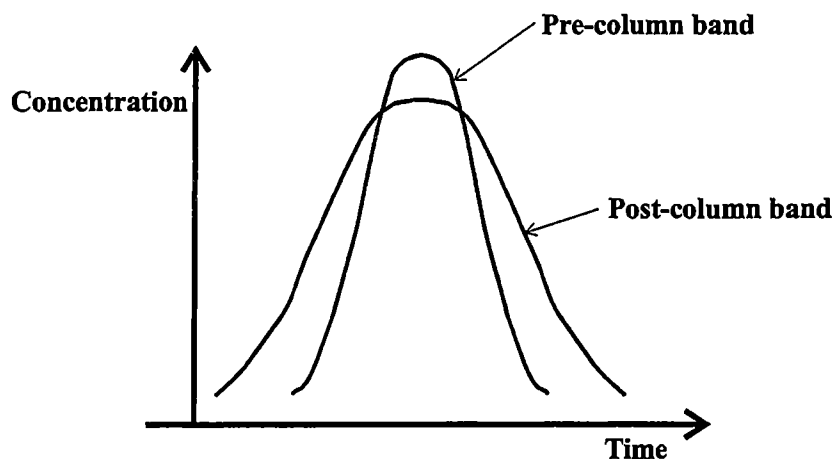


Figure 2.7 Schematic of band broadening inside HPLC bed.

Experimental evidence has shown that the packing in chromatography columns is heterogeneous. The experiments conducted by Knox and Parcher (1969), Knox *et al.* (1976), and Horne *et al.* (1966) suggested that there is a wall region in packed columns which is severely perturbed, extending about 30 particle diameters from the wall. Farkas, *et al.* (1994) found that the wall layer is thicker than that reported by Knox and Parcher (1969), Knox *et al.* (1976), and Horne *et al.* (1966) for wider bore columns, and suggested that the perturbed region is larger in large diameter columns. This is contrary to principles of soil mechanics, where the wall friction effects are often reduced by testing specimens with a ratio of diameter over height (d/h) greater than 3 (Cernica, 1995). The conclusion drawn by Farkas, *et al.* (1994) may be affected by factors other than the sample dimensions, since the measurements made by Knox and Parcher (1969), Knox *et al.* (1976), Horne *et al.* (1966), and Farkas, *et al.* (1994) on chromatography columns were indirect measurements of heterogeneity that took into account of other band-broadening effects.

The column core, on the other hand, appears to be much more homogeneous (Guiochon, *et al.*, 1994). Thus, if the sample is injected at the center of a wide enough

column in the mobile phase, the elution bands would never have time to reach the wall region and the column performance would be as almost good as if the column were entirely homogeneous. However, if the column is narrow, a significant fraction of the molecules in the mobile phase enter the wall region and propagate inside it. Consequently, the apparent efficiency of the column drops markedly when the band has access to the packing in the wall region, due to the heterogeneity.

Eon (1978) further confirmed that the band spreads in the direction of the flow velocity as the location gets closer to the wall. However, Little *et al* (1976) suggested that the radial compression may improve column performance markedly, presumably because it reduces the density difference between the wall and the core regions.

These experimental results were confirmed by Baur *et al.*(1988) and Farkas *et al* (1994), where these authors have shown that the distribution of the residence times of the molecules of a non-retained tracer in the exit cross-sectional area of a chromatographic column depends on the distance to the column center. Baur *et al.* (1988) also found that the retention time of a non-retained tracer along the axial direction varies with radial position, where it is minimum at the column center, and maximum at the wall. Farkas *et al.* (1994) also found 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 than in the core region. It was also shown that these experimental results cannot be explained by a non-planar injection (Farkas *et al.*, 1994). The difference between the results of Baur *et al.*(1988) and Farkas *et al* (1994) are due to a difference in the packing technology used

It is important to note that the velocity distribution observed by Baur *et al.* (1988) and

Farkas *et al.* (1994) is opposite that in the earlier works done by Knox *et al.* (1976) and Eon (1978). Knox *et al.* (1976) and Eon (1978) found that the velocity was minimum at the column center, while Baur *et al.* (1988) and Farkas *et al.* (1994) found that the velocity was minimum at the wall and thus a higher packing density exists along the column wall. This might be due to the fact that 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 pronounced 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.* (1988) and Farkas *et al.* (1994) cannot be accounted for by a systematic variation of the average particle size along the diameter. They suggested rather a nonhomogeneous density of the column packing.

Guiochon and Sarker (1995) have shown that the packing density of columns prepared with a given packing material is different depending on the type of column used: analytical columns, dynamic axial compression columns, or dynamic radial compression columns. Various independent observations suggest that the density of a packing material is not a physical property like the density of a solvent, but instead varies with packing procedures (Guiochon and Sarker, 1995).

In conclusion, a chromatographic bed is submitted to compression stress of various origins. In addition to axial or radial 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. Removing the exit frit and applying a high inlet pressure results usually in the expulsion of the packing material from the column. The friction of the bed against the column wall opposes the sliding movement of the bed. Finally, 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. 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. Consequently, the chromatography bed is heterogeneous since the density is not uniform.

2.4 Applications of Soil Mechanics

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. In the particular case of column packing, we deal with a system of particles, which has no proper shape, like a liquid, and can deform almost as freely. The structure of the packing material 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 depends on the nature of the surface of the particles and on their size. Spheres with a glassy surface will interact the least. Spheres with a rough surface will interact somewhat more. Irregular-shaped particles will interact the most. Small particles will interact more strongly than large particles of the same physical and chemical properties. These interactions will have an important role when the bed consolidates or reacts physically under compression.

A bed of packing material behaves in an inelastic manner. 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 will deform. Depending on the rigidity of the particles, widely different results may be observed. The packing material in a chromatography 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 (described in Section 2.2.2) of the packing is not a constant with position. 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.

There are two distinct consolidation processes used in the packing of chromatographic columns (Guiochon and Sarker, 1995). Analytical columns are consolidated under the influence of the hydraulic gradient applied to the particles by the solvent stream percolating through them (Guiochon and Sarker, 1995). This stress is equivalent to the stress afforded by an intense gravity field acting parallel to the column axis in the direction of fluid flows. Dynamic compression columns are consolidated under the influence of mechanical compression of the bed by a compression stress applied through a piston (axial compression), or column wall (radial compression). In dynamic radial compression, the stress is not distributed along the entire column as in the dynamic axial compression, but conveys from the surface toward the inside of the packing (Guiochon and Sarker, 1995).

Because of friction between particles and between the packing bed and the wall, the distribution of stress inside the column bed is not homogeneous. As 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 the packing material is subjected to small stresses because the liquid's compressibility is small. On the other hand, if the container is open, as in a chromatography column, the liquid can flow out and is under very small stress, unless there is an induced flow due to additional pressure (Guiochon and Sarker, 1995).

The packing material is under the mechanical compression stress, which varies through the bed. In the case of a dynamically compressed chromatographic column, the viscous stress due to the local flow velocity (or rather the pressure gradient) which is described above adds to the mechanical stress (Guiochon and Sarker, 1995).

Many aspects of the behavior of packing material and soil are similar. If a given mass of packing material 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 (Sarker, *et al.*, 1996). For silica-based phases, the contribution of the first phenomenon is negligible and it is accurate enough to consider only the fourth one (Sarker, *et al.*, 1996). The process in which the saturated bed responds to the external compression and settles is called consolidation, and the extent of consolidation depends on the compression pressure applied. The phenomenon is not instantaneous. The interactions between the packing material and the mobile phase are important in any study of packed bed stability. If the packing is strongly consolidated, there will be little change in its density, unless the stress becomes strong enough to break some particles (Sarker, *et al.*, 1996). If the packing is only weakly consolidated, a concentration gradient, 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 stress level, the bed should remain stable under the experimental conditions used (Sarker, *et al.*, 1996). When the stress is reduced, there is little rebound or volume increase since the bed of packing material has little elasticity. In other words, the particles cannot bounce back to their original position.

Sands are the types of soil closest in properties to packing materials for chromatography. The main difference between sands and packing materials is the particle size distribution. Most sands are very heterogeneous, with a range of particle sizes extending over several orders of magnitude, with particle diameters ranging from a few μm to less than 1000 μm (Lambe and Whitman, 1969). As a consequence, their porosity in compressed beds can be as low as 27 %. They are also nonporous and stronger than the porous silica particles used in HPLC columns. In soil mechanics, the volume of material involved is many times larger than in chromatography, the time scale is similarly much longer (typically years), and the pressure gradients and the flow velocities are typically much lower.

The time lag during compression of sands and 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 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 (Lambe and Whitman, 1969). 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 but increases

with increasing bed volume.

Two phenomena explain the finite rate at which a bed of sand or the packing of a chromatographic column consolidates. 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 solvent pressure applied to the top of the bed (the inlet pressure). Thus, consolidation is expected to be slower with irregular particles than with spherical and smooth particles. The second phenomenon 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 (Sarker, *et al.*, 1996). 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 the average diameter of the packing material is much larger than the finest sand grains found in nature, so the rate of consolidation appears to be faster (Guiochon and Sarker, 1995).

The theory of kinetics of consolidation of Terzaghi (1925) 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 the experimental data are better fitted by a logarithmic pressure dependence. When the pressure applied to the sample is increased, 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 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.

The Terzaghi theory applied to packing material makes the following assumptions: (i) the bed is homogeneous; (ii) the bed is completely saturated with the mobile phase (no residual gas); (iii) the compressibility of the mobile phase and of the particles are negligible; (iv) the compression and the flow are unidimensional and parallel; (v) Darcy's law is valid; (vi) the parameters considered are independent of the pressure. All these conditions are fully fulfilled in HPLC columns (Guiochon and Sarker, 1995). The Darcy's law is valid in a porous medium as long as the Reynolds number is lower than 1. Typical values of Reynolds number in liquid chromatography are lower than 0.01 (Farkas, *et al.*, 1999). As long as the bed is in the process of consolidation, the permeability is not constant along the column with position.

In soil mechanics, two steps are recognized during the consolidation of a material. The primary consolidation is controlled by the permeability of the bed. The pore pressure will be dissipated by the end of the primary consolidation. During the secondary consolidation, or plastic time lag deformation, the rate of consolidation is much lower than during primary consolidation such that the escape of water takes place freely and the kinetics is controlled by plastic resistance (Lambe and Whitman, 1969). 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. The plastic time lag depends on the energy of particle-particle interactions. Thus, a higher plastic time lag exists for the irregular particles than spherical particles due to stronger interactions between its particles during consolidation. On the other hand, such differences could be explained by the narrow size distribution of the particles used in chromatography. The particle size distribution results in

a much larger average volume of the cavities between neighbor particles in columns than in sand beds.

2.5 Mechanics of Particle Packing

A review of the literature from other fields was conducted. These problems include compacted powder (Train, 1957), compacted ceramics (Aydın, *et al.*, 1998; Brekelmans, *et al.*, 1991) and metal powders (Krezalek, *et al.*, 1995). These applications, which are similar to HPLC in several respects, yield experimental and numerical solutions which were studied and compared to the numerical results obtained by HPLC columns.

2.5.1 Compaction of Powders – Train’s Experiment

An experimental investigation of the mechanisms governing powder compaction was conducted by Train (1956 and 1957). These experiments investigated the mechanisms by which a mass of powder was compressed into a coherent tablet or pellet. This investigation was from the perspective of the pharmaceutical industry, and focused on the transmission of forces through the compacting powder and the effects of these forces within the powder (Train, 1956).

2.5.1.1 Experimental Setup

A horizontally split die was designed, Figure 2.8 The split die consisted of eight segments in which each segment has a depth of 2.5 cm resulting in a maximum compact fill of 13.5 cm. All segments were made of Grade K.9 steel but were not hardened. They were located and clamped together to form a die by means of three studs screwed into the bottom segment. The upper punch was made of Grade K.9 steel, and was a sliding fit in the die. The punch had a diameter of 5.32 cm and a length of 20 cm. The base plate and bottom punch

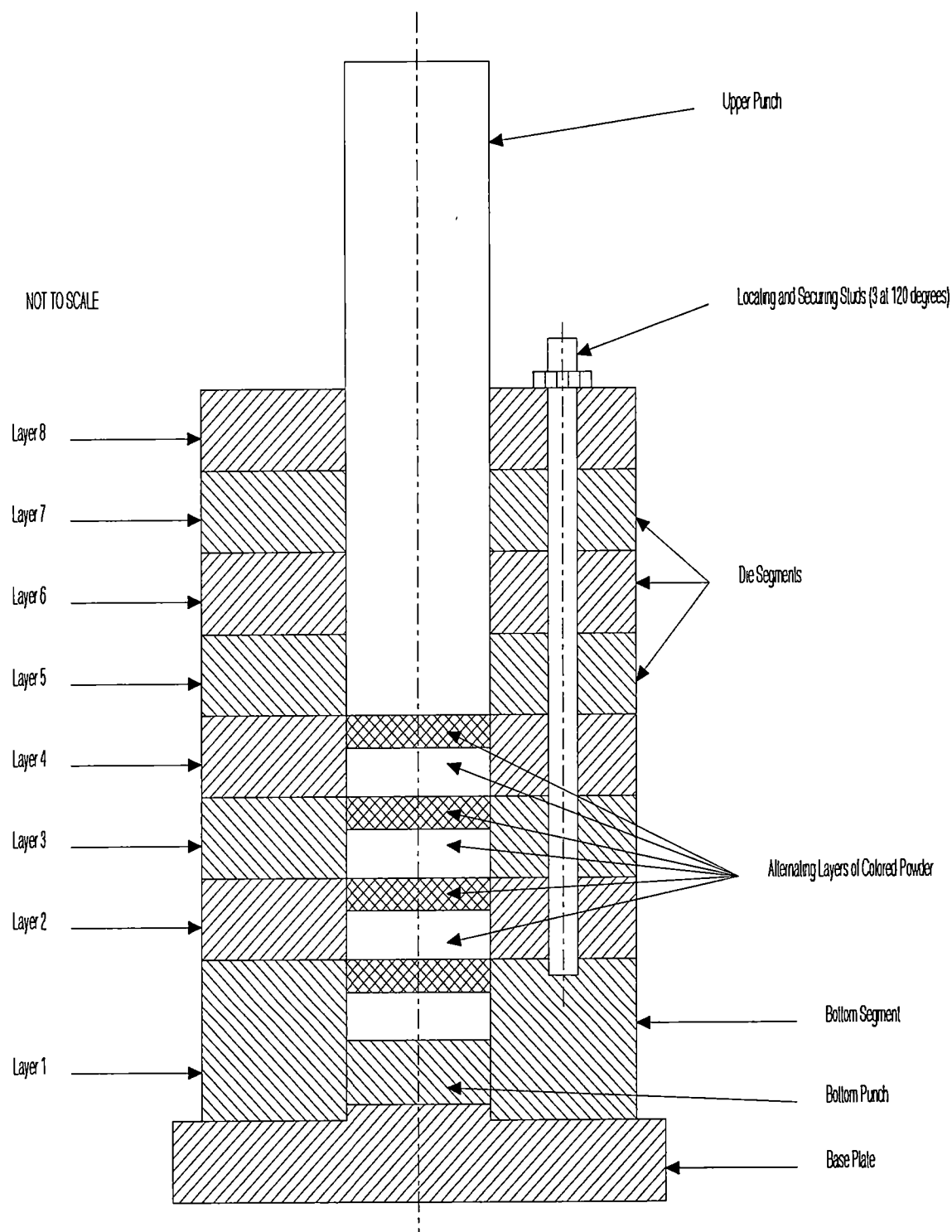


Figure 2.8 Split-die assembly for preparative of powder compact (Train, 1956).

were made of mild steel. A location slot was milled in the base plate in order to prevent relative movement between the base, die and lower punch. This die-set was used between the platens of a 50-ton hydraulic press to give a maximum punch pressure of more than 2000 kg/cm².

A sample of Heavy Magnesium Carbonate, with a mass of 160 g was used as a powder fill. The fill was made up of eight alternatively contrasting color layers which were packed in predetermined levels in the split die. Heavy Magnesium Carbonate was selected as the powder fill because it has constant powder characteristics of shape and size, and it coheres when compressed so that the resultant compact could be taken intactly from the die for subsequent measurements. The walls of the die were lubricated with a layer of colloidal graphite (Train, 1956).

To measure hydrostatic pressures at selected points within the powder fill, stress gauges made of a manganin wire were used. The manganin gauges were located at twenty different points in the vertical half-section of the compact and these points were given the reference numbers as shown in Figure 2.9. As illustrated in Figure 2.9, position A indicates the centerline of the compact, and circles indicate the positions of manganin gauges. The gauge consisted of an 80 mm length fine coil of 48 Standard Wire Gauge (s.w.g.) enameled manganin wire brazed to 45 s.w.g. copper leads. The joints were insulated with a suitable silicone and the assembly was annealed. The wire was protected by enclosing it in a small bulb of 5 mm diameter glycolatin. When tested hydrostatically against a dead weight pressure tester, a typical gauge gave a linear response of change of resistance to change of pressure over a range of 0-1000 kg/cm² with a standard error of ± 2.5 kg/cm². This was a

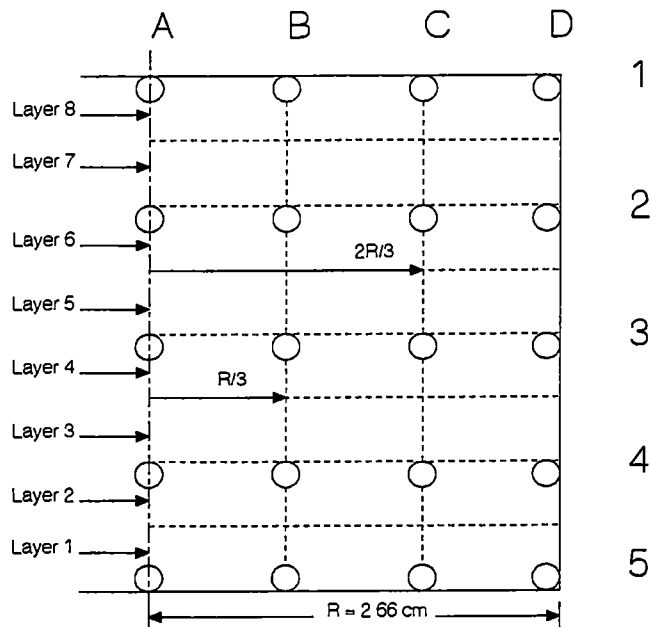
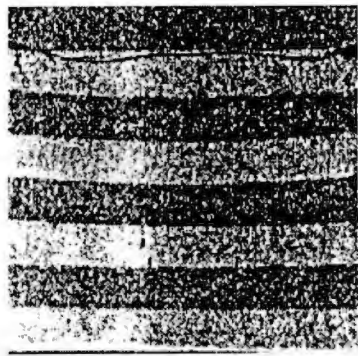


Figure 2.9 Stress measured in powder compact (Train, 1957)

desirable gauge because it did not affect the forces transmitted through the system appreciably, and the reaction induced in the gauge by any change in the magnitude of the forces could be measured (Train, 1956)

2.5.1.2 Typical Results and Discussions

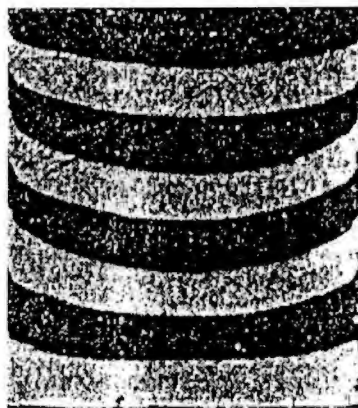
Figure 2.10 shows the cross-sections of the compact subjected to compaction pressure under different lubrication conditions (Train, 1956). As illustrated in Figure 2.10(b) and (d), for the unlubricated compacts, there are differences in relative displacement of the layers of material when compacted to the same level of pressure. Train (1956) suggested that the differential displacement of the compacts is caused by greatly increased frictional forces occurring at the face of an unlubricated die wall, opposing the movement of the adjacent compact material which tends to move as a result of the thrust from the top punch. On the other hand, Train (1956) further suggested that the material at the center is relatively free to



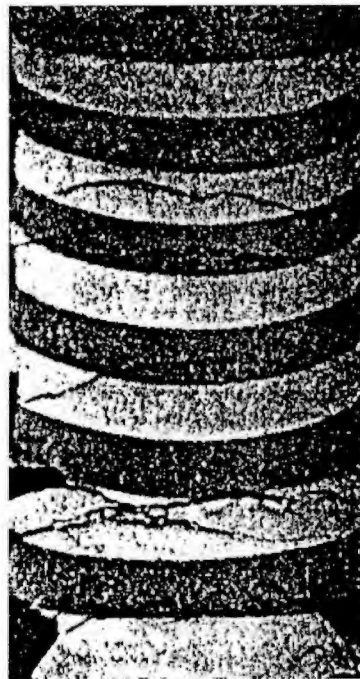
(a)



(c)



(b)



(d)

- (a) 160 g subjected to 2040 kg/cm^2 in lubricated die
 (b) 160 g subjected to 2040 kg/cm^2 in unlubricated die
 (c) 80 g subjected to 2040 kg/cm^2 in lubricated die
 (d) 240 g subjected to 1358 kg/cm^2 in unlubricated die

Figure 2.10 Cross sections of compact after ejected from die (Train, 1956).

move, and therefore it only subjected to normal inter-particulate friction. Consequently, the layer unevenly displaced in the manner shown in Figure 2.10 (b) and (d).

To estimate the density distributions inside the column bed, Train (1956) cut the compact in radial and lengthwise directions with a lathe. The compact was carefully measured before and after cutting, and the material parted off was collected and weighed. From this data, it was possible to calculate the apparent density of the compact fill (Figure 2.11(a)). To confirm the results obtained in Figure 2.11(a), Train (1956) traced the boundaries between the colored layers in the compact fill during cutting, and then constructed a complete picture of the apparent density inside the compact fill in its compressed state, as shown in Figure 2.11(b).

Figure 2.11(a) shows the apparent densities obtained by measuring and weighing. The results are subject to an error of about $\pm 0.4\%$ when allowance is made for the uncertainty in measurements and possible loss of powder (Train, 1956). The apparent density as percentage solid is shown on the left of the figure, while contours of equal apparent density are shown on the right of the figure. Figure 2.11(b) shows the results obtained by measuring the position of the boundaries between the colored layers subjected to error of about $\pm 0.5\%$. Comparing Figures 2.11(a) and 2.11(b), Train (1956) concluded that there is a close agreement between the two methods, and thus the results presented in the figures are valid.

Figure 2.12(a) shows the pressure distribution inside the compact, corresponding to the apparent density as percentage solid (Figure 2.12(b)) subjected to a punch pressure of 2040 kg/cm^2 . As illustrated in the figure, there is no significant radial movement of the particles compared to axial movement in the compact (Train, 1956). Therefore, it is

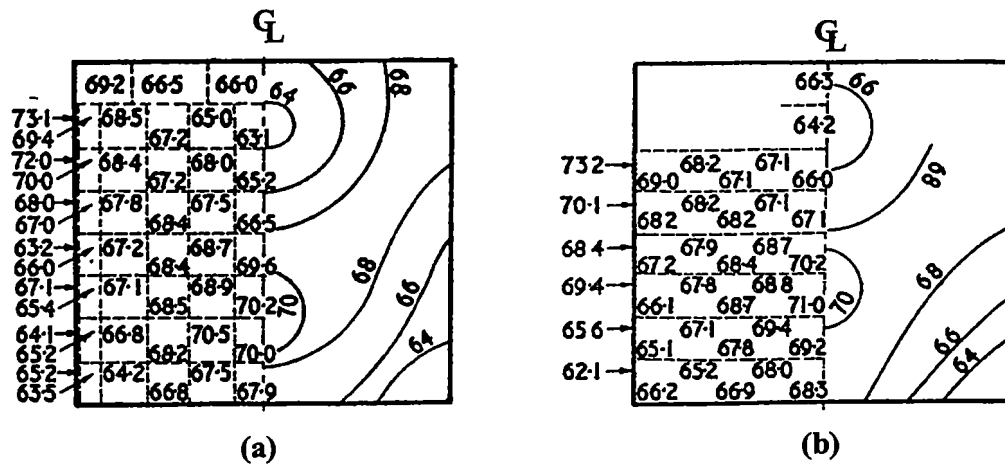


Figure 2.11 Apparent density measurements (a) Turning measuring and weighing method, (b) Tracing boundaries method (Train, 1957).

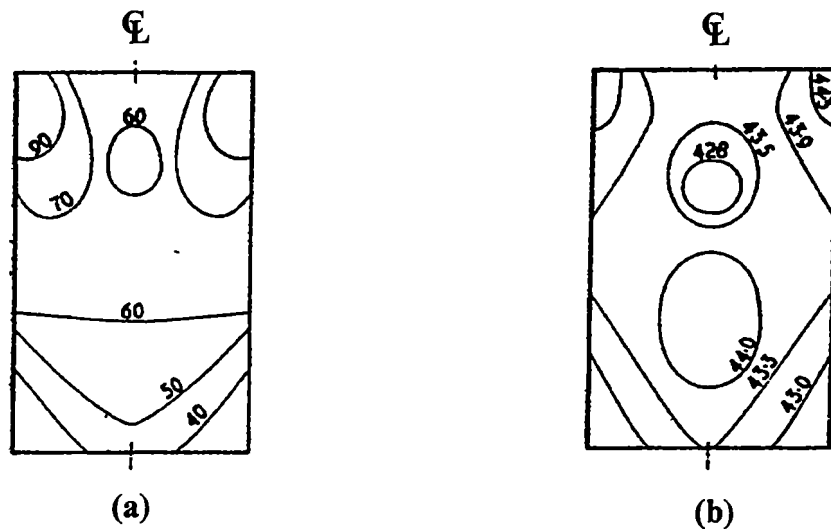


Figure 2.12 Reactions in compact when pressed under 90 kg/cm^2 (a) Pressure contour levels in kg/cm^2 , (b) Apparent density contours levels represent percent solid present (Train, 1956).

appropriate to calculate the degree of compaction at various regions of the compact based on the measurements of the vertical heights using half of the compact due to axisymmetric nature of the compact.

As shown in Figure 2.12(a), there are high pressure wedges developed near the corners on top of the compact, corresponding to a higher apparent density. There is also a high pressure region at the mid-lower center of the compact.

2.5.2 Compaction of Powders – Others

Results obtained from experimental, analytical and numerical studies on the powder movement during the unlubricated die compaction of metal powders (Krezalek and Sivakumar, 1995; Brekelmans, *et al.*, 1991) and ceramic powders (Aydin, *et al.*, 1997a; Aydin, *et al.*, 1997b; Briscoe and Rough, 1998) showed agreement with Train's experimental results, except they did not observe a high pressure region at the mid-lower center of the compact.

Further investigation was done by Hirai and Okada (1981) on the stress and strain distributions in a compressed powder bed of potassium chloride lubricated with magnesium stearate, based on the theory of limiting equilibrium states specified by the Mohr criterion. Compared to results obtained using unlubricated powder bed (Fukumori and Okada, 1976), Hirai and Okada (1981) concluded that a more uniform pressure distributions on the boundary surfaces and within the powder bed appeared in the lubricated system. This is consistent with Train's observation.

Dimilla and Reed (1983) also studied the stress transmission through the compact, die wall friction, and the radial/axial stress ratio using a spray-dried alumina powder and an unlubricated/lubricated steel die for pressing. Similar studies were done by Briscoe and

Evans (1991), with single-sided uniaxial cylindrical compaction of zirconia and alumina powders. The die walls were lubricated with an established wall lubricant: calcium stearate powder. Their results further confirmed Train's findings, in which a more uniform compact was achieved by using lubricant.

2.6 Compaction of Powders – Punch Tip Geometry

To investigate the effect of punch shape on powder compression, Sixsmith (1980) prepared four different punch faces: flat faced, bevelled, concave, and deep concave to be used in his experiments with Avicel PH101 powder. According to Sixsmith (1980), as the punch curvature increased, there was a decreased tendency to decrease tablet porosity such that zero porosity would theoretically be achieved at the following compressional forces: flat faced 167 kN; bevelled 206 kN; concave 550 kN; deep concave 1670 kN, respectively. The effect of the variation of sample height/diameter (h/d) ratio was studied using concave and deep concave punches, and Sixsmith (1980) found that for tablets that were prepared using deep concave punches, a decrease in the h/d ratio by a factor of 2 would cause an increase in the theoretical force to produce zero porosity from 1670 kN to 2550 kN. This effect is contrary to what one would expect, as a decrease in h/d ratio would decrease total die wall friction, which should lead to a decrease in the resistance to compression.

This counter intuitive effect might be due to a large proportion of the total tablet volume that was enclosed within the punch tip and thus a decrease in the h/d ratio would increase the proportion within the punch tip (Sixsmith, 1980). As suggested by Train (1957), who used a flat faced punch, particles adjacent to the moving punch face were relatively protected during the compression process. Thus, based on the same analogy, Sixsmith (1980) expected that a similar situation would exist during his investigation, and the material

enclosed within the moving punch tip would remain relatively protected until the main body of the tablet was compacted to a relatively low overall value of porosity. Sixsmith (1980) further suggested that at this point, the high density main body of the tablet might act as a secondary punch face causing compression of the material enclosed within the punch tip. In addition, Shaxby and Evans (1923) suggested based on similar testing that as the compressional force died away exponentially from the point of compaction, a decrease in the h/d ratio by increasing the relative proportion and thus relative height in the punch tip would require greater forces to be exerted to compact the material within the punch tip.

Further investigations were later conducted by Sixsmith and McCluskey (1981), where the axial and radial powder movements were studied during the tableting process using various punch tip geometries. Sixsmith and McCluskey (1981) observed that alteration of punch tip geometry affected both axial and radial powder movement, to the extent that depended on the relative curvature of the punch tip. Moreover, addition of the lubricant decreased relative axial movement but had little effect on radial movement (Sixsmith and McCluskey, 1981).

2.7 Micromechanics

Developments in the field of micromechanics can be used to further investigate the side wall friction effects on the HPLC columns, because the packing materials inside the columns are an assemblage of silica particles, and they are more or less isotropic and homogeneous. Lannutti (1997) investigated the microstructure and properties of a ceramic component during the manufacturing process using micromechanics. The application of micromechanics to the conditions in HPLC columns may provide additional insight to the mechanics of the packing process, but is outside the scope of this work.

Chapter 3

Characterization of HPLC Packing Materials

To further understand the stress distribution within the packing material inside the HPLC columns, numerical modeling was used. Laboratory testing was conducted to investigate the response of the packing material and determine the material properties for use in the numerical analysis. These material properties include the elastic stress-strain-volume relations, the internal coefficient of friction, the interface coefficient of friction, and the permeability of the packing material. Muhlbachler *et al* (1998) measured the internal friction of the packing material and determined the internal friction angle, $\phi = 36^\circ$ and 23° for Pro 10 Sil and Kromasil NP 10, respectively. The cohesion, c , of Pro 10 Sil and Kromasil NP 10 was found to be 1.1 kPa and 0.8 kPa, respectively. Therefore, no laboratory testing will be conducted to determine the internal coefficient of friction of the packing material. In the numerical analysis described in Chapter 4, the values of $c = 1.1$ kPa and $\phi = 36^\circ$ were used to represent the packing material.

3.1 Consolidation Testing of Packing Material

When saturated fine-grained soils, or particulate materials such as packing material, are subjected to changes in mechanical load, they deform in a way different from that of liquids or solids. Their deformation takes place not only at the time of the load application, but also continues with time. The long-term settlement of a fine-grained soil layer is primarily controlled by consolidation, a physical process in which the interstitial water that is under excess pressure slowly diffuses through the compressible matrix of the soil particles.

After the excess pore pressure has completely dissipated, fine-grained soils can also deform due to their viscous nature. The properties that characterize the amplitude and rate of deformation for soils are determined in the consolidation test.

3.1.1 Loading, Unloading and Reloading Processes

Figure 3.1 shows the consolidation curve of a typical fine-grained material. The relation between void ratio, e and effective stress, σ' is nonlinear and irreversible. The material behaves differently during loading (A to C, or D to E) and unloading (C to D, or E to F). The material response of Figure 3.1 is not elastic, but is elastoplastic.

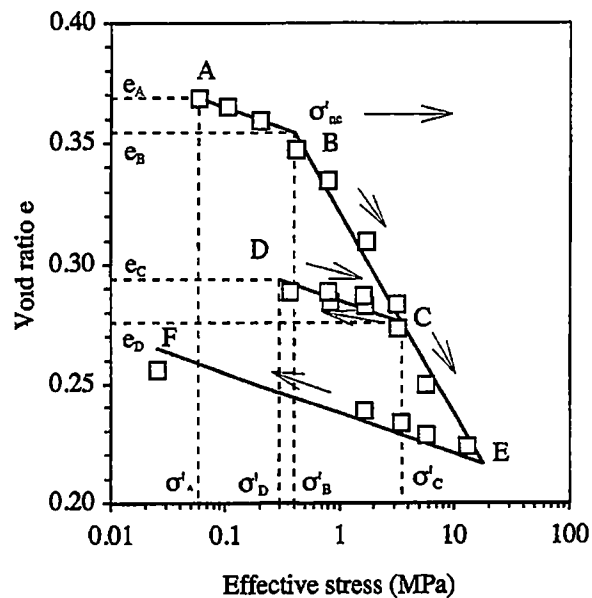


Figure 3.1 Idealized representation of stress-strain response (Bardet, 1997).

As illustrated in Figure 3.1, starting from point A, the void ratio, e varies linearly with $\log \sigma'$ when σ' is increased from σ'_A to σ'_B .

$$e = e_A - C_s \log \frac{\sigma'}{\sigma'_A} \quad (3.1)$$

where C_s is the swelling index, e_A is the void ratio at point A, and σ'_A is the effective stress at point A. Equation (3.1) is valid until σ' reaches stress σ'_B , at which point the e - σ' curve abruptly becomes steeper than the branch AB. When $\sigma' > \sigma'_B$, the void ratio, e varies again linearly with $\log \sigma'$ but with a steeper slope:

$$e = e_B - C_c \log \frac{\sigma'}{\sigma'_B} \quad (3.2)$$

where C_c is the compression index, e_B is the void ratio at point B and σ'_B is the effective stress at point B. When σ' is decreased from σ'_C to σ'_D , the point (e - $\log \sigma'$) follows the unloading branch CD, which is parallel to AB and has a slope equal to the swelling index. But, equation (3.1) is now referenced about C instead of A:

$$e = e_C - C_s \log \frac{\sigma'}{\sigma'_C} \quad (3.3)$$

When σ' is increased again, the point (e - $\log \sigma'$) follows the branch DC in the opposite direction and moves toward E on the branch that extends BC. When σ' is finally decreased from E to F, the point (e - $\log \sigma'$) follows the branch EF parallel to AB and DC. The branch BCE is called the virgin compression line (VCL). The branches AB, DC and FE are

swelling lines. A particular material has only one virgin consolidation curve, but an infinite number of swelling branches. The swelling branches are always to the left of VCL. The point (e -log σ') cannot go to the right of VCL.

The stress-strain relations specified by equations (3.1) to (3.3) are nonlinear because e is a logarithmic function of σ' . They are also irreversible because it is not possible to return to point A once σ' has exceeded σ'_B . The threshold of irreversibility is defined by the largest effective stress applied, which is also referred to as the pre-consolidation pressure, σ'_p . When the stress state is smaller than σ'_p , the response is described by a swelling branch. When stress state is equal to σ'_p , the response follows the VCL for the loading and a swelling line for unloading. The pre-consolidation pressure, σ'_p , either increases or remains constant but never decreases. During the loading ABC of Figure 3.1, σ'_p moves from σ'_B to σ'_C . σ'_p is constant during the unloading CD and reloading DC but increases again during the loading CE.

3.1.2 Experimental Setup

The consolidation (oedometer) test is used in soil mechanics to determine the compression index, C_c , swelling index, C_s , the preconsolidation pressure, σ'_p , which define the soil compressibility, and the coefficient of consolidation, C_v , which characterizes the rate of primary compression. Consolidation tests on the packing materials may be used to develop a mathematical model of the nonlinear stress-strain response.

A series of consolidation tests was conducted on the packing materials using a 2.5 inch diameter consolidation ring. The basic setup of a one-dimensional consolidation test is shown in Figure 3.2. The oedometer is a stiff ring, which limits the lateral expansion, with

the sample loaded between two porous stones, which allow drainage of the pore methanol. The slurry of packing material with methanol solvent is stirred for approximately an hour to ensure that all the particles have been properly dispersed and wetted. Then, the slurry was poured carefully into the oedometer. The slurry sample was allowed to settle and excessive methanol was decanted using a syringe. Then, filter papers were placed between the porous stone and the sample to separate the silica particles from the porous stone. The top cap was placed on the porous stone and sample was then completely immersed in methanol and remained fully saturated during the test.

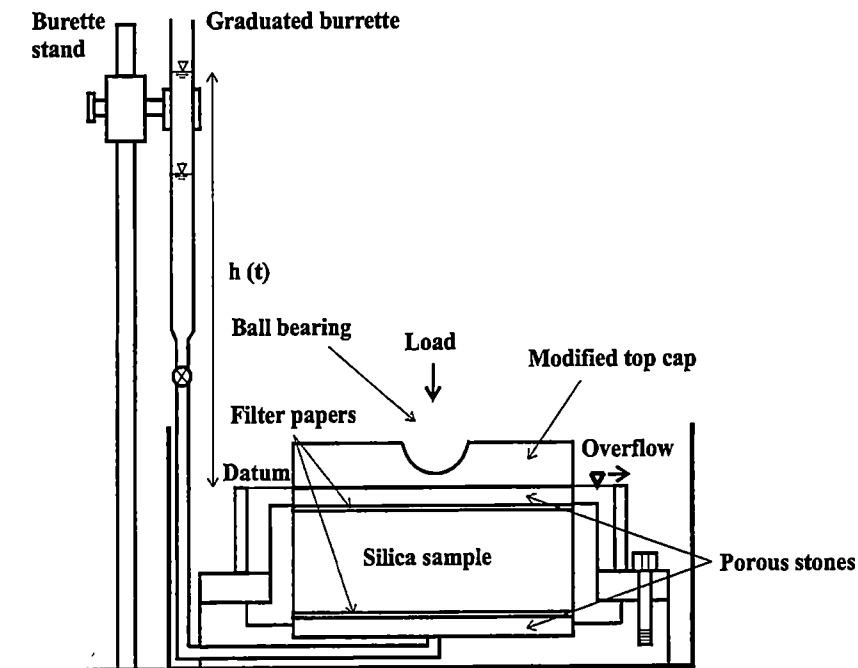


Figure 3.2 Fixed-ring consolidation cell with burette for permeability measurements

The loading sequence of the consolidation test depends not only on the materials tested, but also on the engineering application. The duration of each load application depends on the rate of consolidation of the soil. Ideally, the load should only be changed after the degree of consolidation, U , reaches 100%. In practice, the load is changed at convenient

times provided that U exceeds 90%. In the tests on the packing material, the load was applied to the sample every 24 hours, which was consistent with the laboratory observation that after 24 hours, all the primary consolidation of the sample was completed. A dial indicator with a range of 0.5 inch (12.7 mm) and an accuracy of 0.0001 inch (2.54 μm) was attached on top of the modified cap to measure the vertical displacement of the sample. A beam-and-counter weight mechanism loading device was used to apply and maintain the axial load to the specimen.

3.1.2 Parameter Determination and Discussion of Results

When the axial stress, σ , is applied, the sample of initial height, h_0 , deforms vertically with time. It ultimately settles an amount Δh when the excess pore methanol pressure is completely dissipated. In other words, consolidation is complete when the internal effective stress, σ' , equals to the externally applied stress, σ . The corresponding axial strain, ε_z can be determined:

$$\varepsilon_z = \frac{\Delta h}{h_0} \quad (3.4)$$

Since the stiff ring prohibits lateral strain (i.e., $\varepsilon_x = \varepsilon_y = 0$), the volumetric strain, ε_v is thus given by:

$$\varepsilon_v = \varepsilon_x + \varepsilon_y + \varepsilon_z = \varepsilon_z = \frac{\Delta h}{h_0} \quad (3.5)$$

The volumetric strain, ε_v , is also:

$$\varepsilon_v = \frac{V_I - V}{V_I} = \frac{\frac{V_I}{V_s} - \frac{V}{V_s}}{\frac{V_I}{V_s}} = \frac{e_0 - e}{1 + e_0} \quad (3.6)$$

where e is the present void ratio, e_0 is the initial void ratio, V is the present volume, V_I is the initial volume, and V_s is the total volume of silica particles. Therefore, e is related to Δh through:

$$e = e_0 - \varepsilon_v(1 + e_0) = e_0 - \frac{\Delta h}{h_0}(1 + e_0) \quad (3.7)$$

The initial dry density, ρ_{d0} , and initial void ratio, e_0 , of the materials can be calculated through.

$$\rho_{d0} = \frac{M_d}{V_1} \text{ and } e_0 = \frac{G_s \rho_w}{\rho_{d0}} - 1 \quad (3.8)$$

where M_d is the mass of the dry sample, $V_1 = \frac{\pi D^2 h_0}{4}$ is the initial sample volume, D is the

sample diameter, h_0 is the initial sample height, G_s is the packing materials specific gravity, and ρ_w is the density of the solvent.

Figure 3.3 shows experimental results that are representative of the response of

Kromasil C8 spherical silica particles with methanol solvent subjected to a loading-unloading-reloading cycle in the consolidation test. The compression index, C_c , and swelling index, C_s , which define the soil compressibility for the tests were calculated and are summarized in Table 3.1. Therefore, the packing material (Kromasil) used in HPLC column has a very low plasticity based on Table 3.1.

3.2 Permeability of the Packing Material

The packing materials inside HPLC columns are permeable to solvents such as methanol because the voids between silica particles are interconnected. The degree of permeability is characterized by the permeability coefficient, k , also referred to as the hydraulic conductivity. It depends on both the properties of packing material and the pore fluid and has a unit of length per time (Coduto, 1999). The intrinsic permeability, K , which primarily used by hydrogeologists, depends only on the packing material (Coduto, 1999). It has units of length², and is related to coefficient of permeability by (Freeze and Cherry, 1979):

$$K = k \frac{\rho_w g}{\mu} \quad (3.9)$$

where ρ_w is the density of the fluid, μ is dynamic viscosity of the fluid, and g is the gravitational acceleration

In order to obtain k for the packing material, laboratory testing can be performed by using either a falling head test or consolidation test, since the packing material has an intermediate to low permeability.

Table 3.1 Compression and swelling indexes for Kromasil with methanol.

Sample	Compression Index, C_c	Swelling Index, C_s
KMSample1	0.0035	0.0013
KMSample2	0.0056	0.0022
KMSample3	0.0232*	N/A
KMSample4	0.0166*	N/A
Average of KMSamples	0.0046	0.0018
Poorly Graded Sands*	0.055	0.010
Clay Till**	0.08	N/A
Very Low Plasticity Soils***	0.024	N/A

* C_c of these samples do not take into account on the average C_c for Kromasil samples due to loss of materials during permeability tests

* As summarized by Holtz and Kovacs (1981)

** As summarized by Bardet (1997)

*** Based on empirical equation: $C_c = 0.75(e_0 - 0.50)$ by using $e_0 = 0.5319$ (Holtz and Kovacs, 1981)

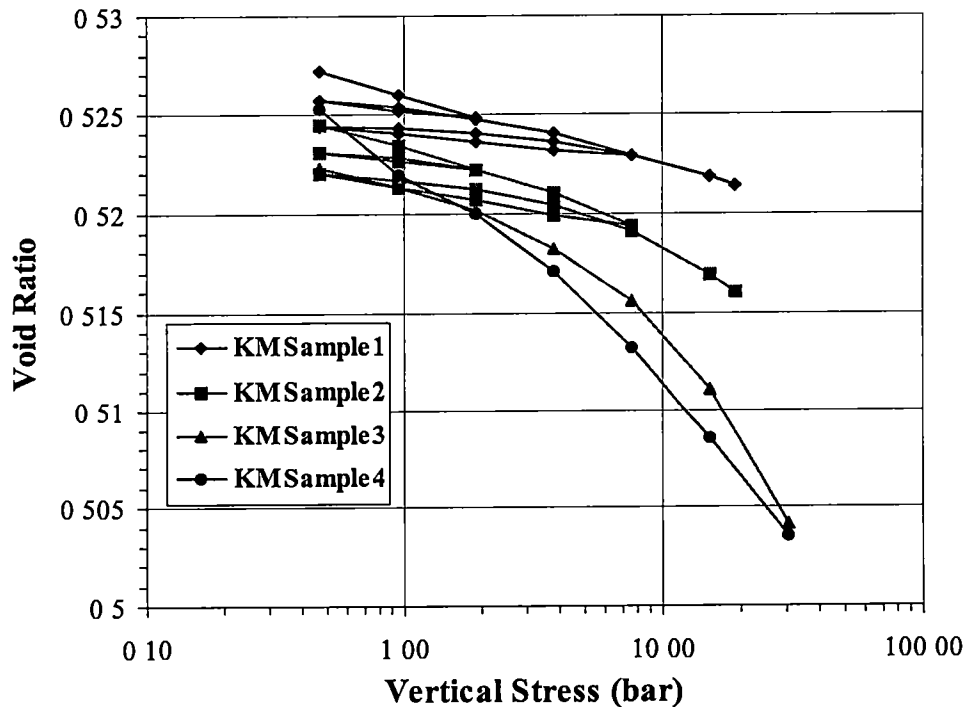


Figure 3.3 Typical void ratio vs. vertical stress responses.
(Loss of material in KMSample3 and KMSample4 during the permeability tests).

3.2.1 Empirical Relationships for Hydraulic Conductivity

The Kozeny-Carman formula (Kozeny, 1927, Carman, 1939) is an empirical expression that can be used to estimate k based on the void ratio (Bardet, 1997):

$$k = \frac{\gamma_w}{5f\mu S^2} \frac{e^3}{1+e} \quad (3.10)$$

where e is the void ratio, and μ is the dynamic viscosity of the fluid. The coefficient f depends on pore shape: $f=1.1$ for rounded grains, $f=1.25$ for subrounded grains, and $f=1.4$ for angular grains (Loudon, 1952). The specific surface area, S (i.e., the surface area per unit volume of grains) can be determined (Bardet, 1997):

$$S = \frac{6}{\sqrt{d_{\max} d_{\min}}} \quad (3.11)$$

where $d_{\max}$ is the maximum grain diameter in mm and $d_{\min}$ is the minimum grain diameter in mm.

3.2.2 Experimental Setup

The permeability of the packing materials also can be calculated from the rate of settlement during the consolidation test, or by conducting a falling head permeability test at the end of a loading increment. The latter method was used to measure the permeability of the packing materials during the consolidation tests.

Figure 3.4 shows the falling head permeability test during a consolidation test. The sample in the rigid container is squeezed by a constant vertical load. The standpipe is

attached to the consolidation cell and forces methanol solvent through the sample from the bottom. The sample is subjected to falling head test after being consolidated, thus allowing the determination of k as a function of e . The coefficient of permeability, k can be calculated:

$$k = \frac{aL}{At} \log \frac{h_i}{h_f} \quad (3.12)$$

where a is the cross-sectional area of the graduated burette, A is the cross-sectional area of the sample, L is the length of the sample, h_i is the elevation of methanol solvent in the standpipe above the discharge level at time $t = 0$, and h_f is the elevation of methanol solvent in the standpipe above the discharge level at time t .

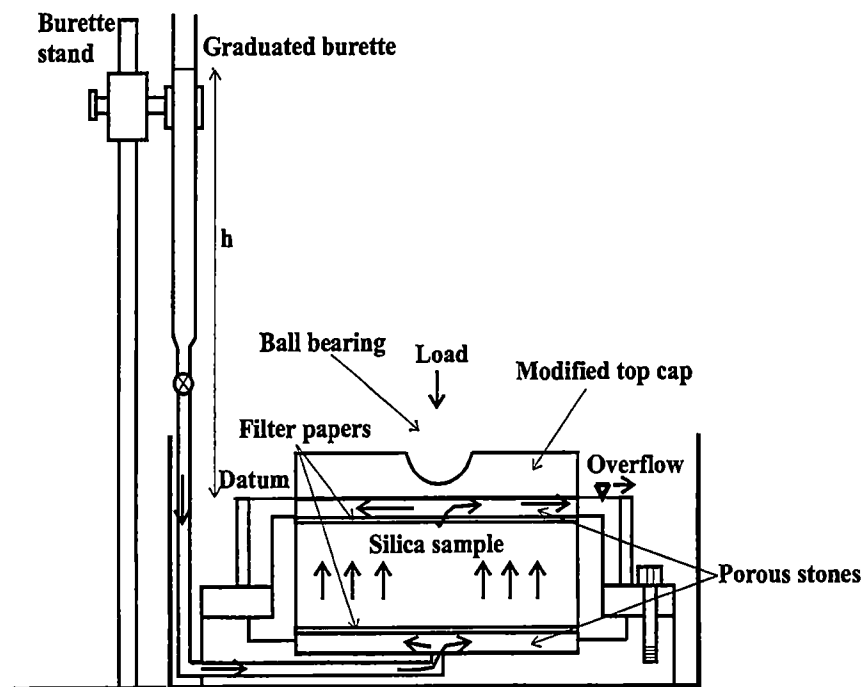


Figure 3.4 Falling head permeability test during consolidation test.

3.2.3 Parameters Determination and Discussion of Results

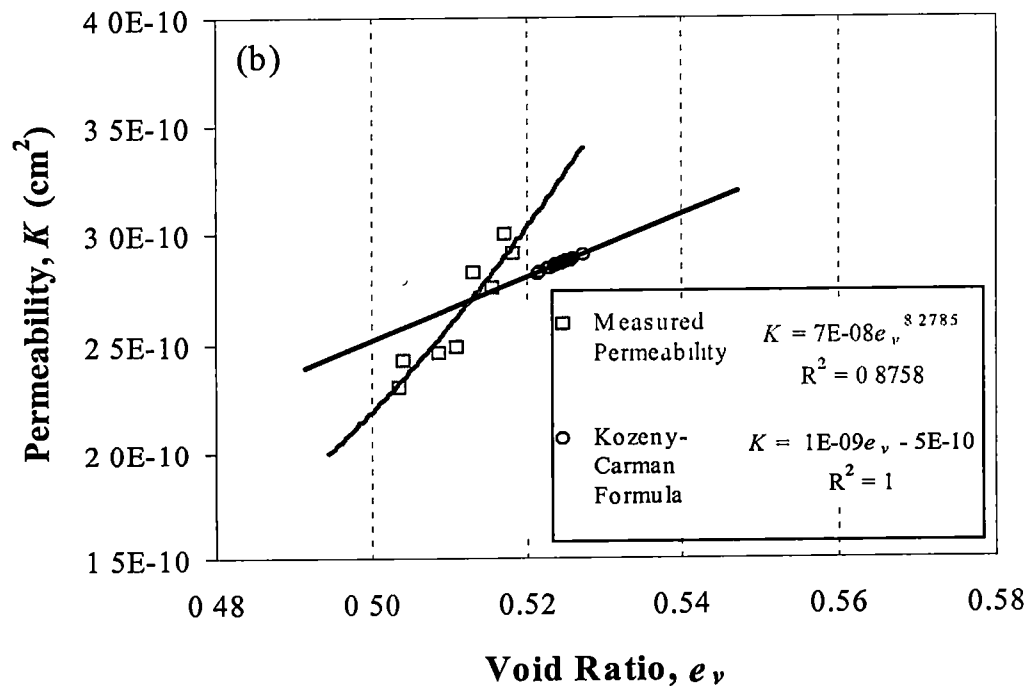
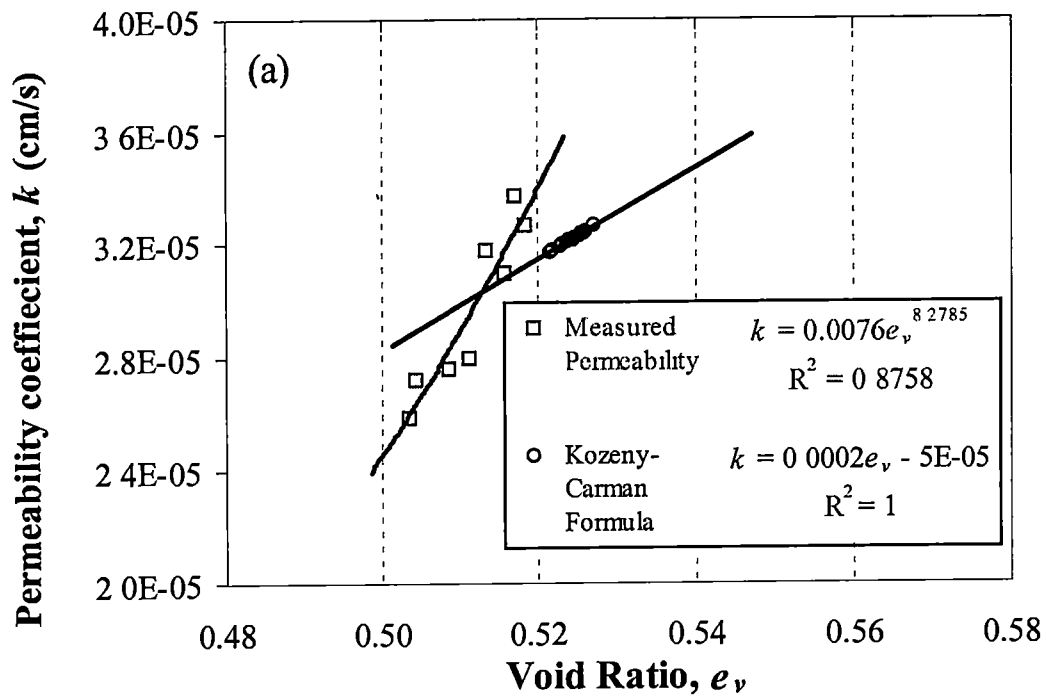
Typical coefficient of permeability response (Figure 3.5(a)) and permeability response (Figure 3.5(b)) for Kromasil C8 silica particles with methanol solvent is shown in Figure 3.5. As expected, the permeability decreased with decreasing void ratio. For comparison, the permeability values obtained using the Kozeny-Carman formula are also shown in Figure 3.5(a) and (b). The Kozeny-Carman formula appears to be a reasonable approximation of the relationship between the laboratory measured permeability and the void ratio. Regression analysis was performed on the data, and a power relationship as indicated in Figure 3.5 was found to provide a good approximation to the measured response. The permeability coefficient of the packing material ranges from 2.6×10^{-5} to 3.4×10^{-5} cm/s, which is a typical value for silty sand (10^{-5} cm/s) reported by Freeze and Cherry (1979).

3.3 Shear Strength of the Packing Material/Steel Interface

Silica, like any other material, fails at some point when it is subjected to increasing shear stresses. Silica cannot withstand a shear stress larger than its shear strength and deforms extensively when the applied shear stress approaches its shear strength. Likewise, when the shear stress along the packing material/steel wall contact equals the strength, slip will occur. As long as the stresses remain below this value, there can be no slip or movement. Thus, the strength or coefficient of friction between the packing material and column wall is important to the packing process.

3.3.1 Interface Friction Angle

Laboratory tests were conducted to measure the coefficient of friction between the packing material and the stainless steel HPLC column wall, and to measure the volumetric



Note: e_v is used for void ratio to avoid confusion with e for exponential function

Figure 3.5 Measured (a) coefficient of permeability, (b) permeability for Kromasil as a function of void ratio

response of the packing material. The results of these tests were then used for the estimation of the material constitutive parameters in the numerical analysis. Direct shear tests were conducted to directly measure the coefficient of friction, and tilt tests were performed to qualitatively investigate the effectiveness of several lubricants.

3.3.1.1 Direct Shear Test

The oldest form of shear test for soil is the direct shear test, first used by Coulomb in 1776. The direct shear test affords the easiest way to measure the friction angle of dry particulate materials. It is also very useful, however it is not as widely used, for testing materials that contain water due to the difficulty in controlling the drainage of the sample. The geometry of the direct shear test is also well suited for measuring the strength of soil structure contacts or interfaces.

3.3.1.1.1 Experimental Setup for Zorbax with Methanol

A comprehensive series of laboratory direct shear tests was performed on the contact surface between the packing material (Zorbax spherical 10 μ m C18-bonded silica and Kromasil spherical 10 μ m C18-bonded silica) and the polished stainless steel column wall material. Tests were conducted under a range of normal stresses with two solvents (both methanol and acetone). The results of a total of approximately 25 tests were reported.

A direct shear apparatus was used, with sample diameter of 63.5 mm in contact with a polished stainless steel plate. 50 grams (g) of silica packing material (solids density of 2.65 g/cm³) was weighed and mixed with 125 milliliters (ml) of methanol (density of 0.79 g/cm³) to form a slurry. The slurry was stirred for approximately one hour so that the spherical particles of silica were properly dispersed and wetted. Then, the slurry was poured slowly

and carefully into the shear box to allow the silica sample to settle. The settlement occurred due to a higher density of the silica particles relative to a lower density of methanol. Excessive methanol on top of the silica sample was then decanted using a syringe. Filter papers were placed between the silica sample and the modified cap and ball bearings. The filter papers would detain silica from flowing out of the shear box while the methanol pressure dissipated from the sample through the tubes on top of the cap as illustrated in Figure 3.6.

Typical initial sample height was about 10 mm. The initial height of the sample, H_0 , was calculated by measuring the depth of the shear box, H_2 , the height of the top cap, H_3 , the thickness of the filter paper, H_4 , and the distance H_1 (Figure 3.6) with a caliper:

$$H_0 = H_1 + H_2 - H_3 - H_4 \quad (3.13)$$

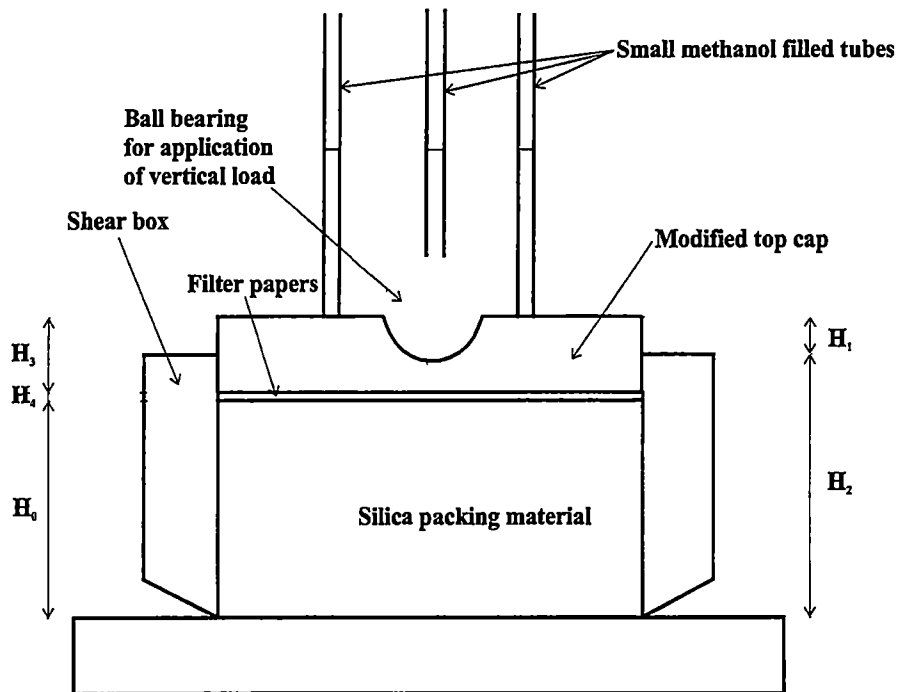


Figure 3.6 Schematic of direct shear tests of packing material-steel contact.

The dial gages that measure lateral and vertical displacements were then attached and the initial reading was recorded. The normal stress was applied to the sample at a rate of about 100kPa (one bar) per hour, and the vertical displacement of the sample was recorded. This rate assumed that the primary consolidation of the sample was completed after one hour, which was consistent with the observation of change in sample height with time. Methanol was added to the sample box surrounding the sample to prevent the methanol inside the shear box from evaporating after the initial normal pressure was applied.

The volumetric response of the packing material was measured during the application of the normal stress. Then, the displacement controlled direct shear tests were conducted, where the shear box was laterally pushed at a rate of approximately 1.3 mm/minute (Bardet, 1997) and the resulting shear resistance of the interface was measured. Displacement-controlled tests are preferred because they yield the residual shear strength, or post peak shear stress. The shear force and vertical and displacement were measured and recorded at every 0.05 mm of lateral displacement (Bardet, 1997). The test was continued until the shear force became constant. The tests were performed at normal stresses of 250 kPa, 500 kPa, 1000 kPa, 2000 kPa, and 3000 kPa, and several replications were obtained at most normal stresses.

3.3.1.1.2 Results for Zorbax with Methanol

The direct shear test is used to determine the shear strength of the material on predetermined failure surfaces. In the direct shear test, the material response is reported versus shear displacement instead of shear strain because it is not possible to evaluate shear strain since the strains are never uniform in the direct shear test. Thus, it is not suited for studying the stress-strain relationships of the sample. Figure 3.7(a) shows a typical response

of the Zorbax spherical C18-bonded silica samples (with methanol solvent) subjected to direct shear loading. In Figure 3.7(b), the shear stress response normalized with respect to the applied normal stress is shown. The variation of shear stress with horizontal displacement is shown in Figure 3.8(a), and the corresponding normal displacement is shown in Figure 3.8(b). The tests were performed at various normal stresses, and several replications were obtained at most normal stresses. With increasing shear (horizontal) displacement, the void ratio and vertical displacement increase until it becomes critical, after which the shear stress decreases and gradually approaches the residual shear strength, as shown in Figure 3.8. The peak failure is characterized by the peak friction angle, ϕ_p , and the residual failure is characterized by the residual friction angle, ϕ_r . Based on the peak failure value, the Mohr-Coulomb envelope could be plotted

The principles of the direct shear test are illustrated in Figure 3.9. The silica sample confined inside the rigid sample box is subjected to the normal load, N , and is sheared by the shear force, T . If A is the area of the contact surface along plane CD, the shear stress, τ_x , acting on the contact surface is equal to T/A , and the normal stress, σ_y , is equal to N/A . For a cylindrical box, $A = (\pi D^2) / 4$, where D is the diameter of the sample. The silica sample shear strength is the shear stress, τ_x , that causes the sample to slip along plane CD (horizontal surface). The shear stress at failure can be defined by Mohr-Coulomb theory:

$$\tau = c + \sigma \tan \delta \quad (3.14)$$

where c is the cohesion and δ is the interface friction angle

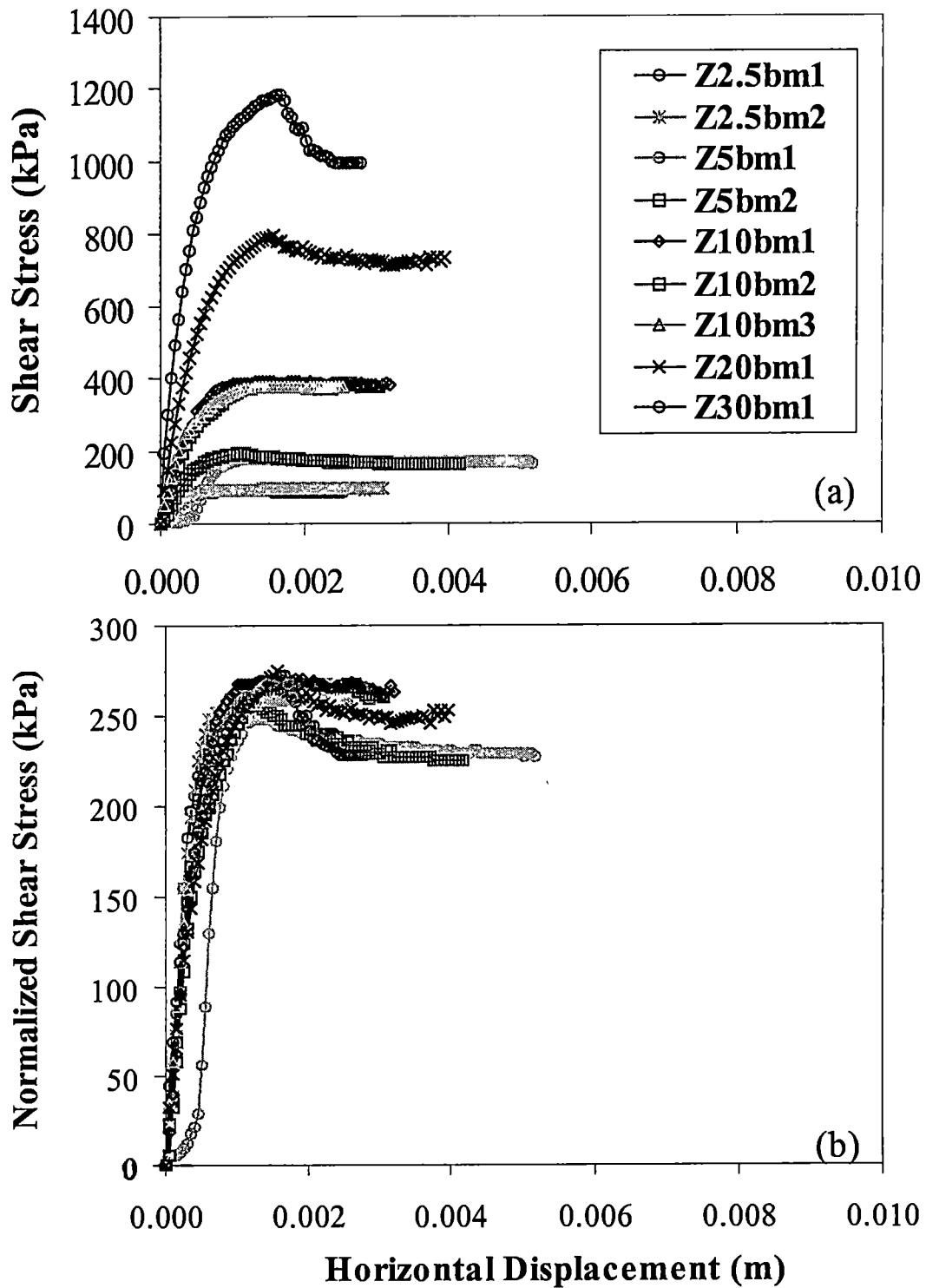


Figure 3.7 A typical result for Zorbax with methanol (a) Shear stress vs. horizontal displacement response, (b) Normalized shear stress vs. horizontal displacement response.

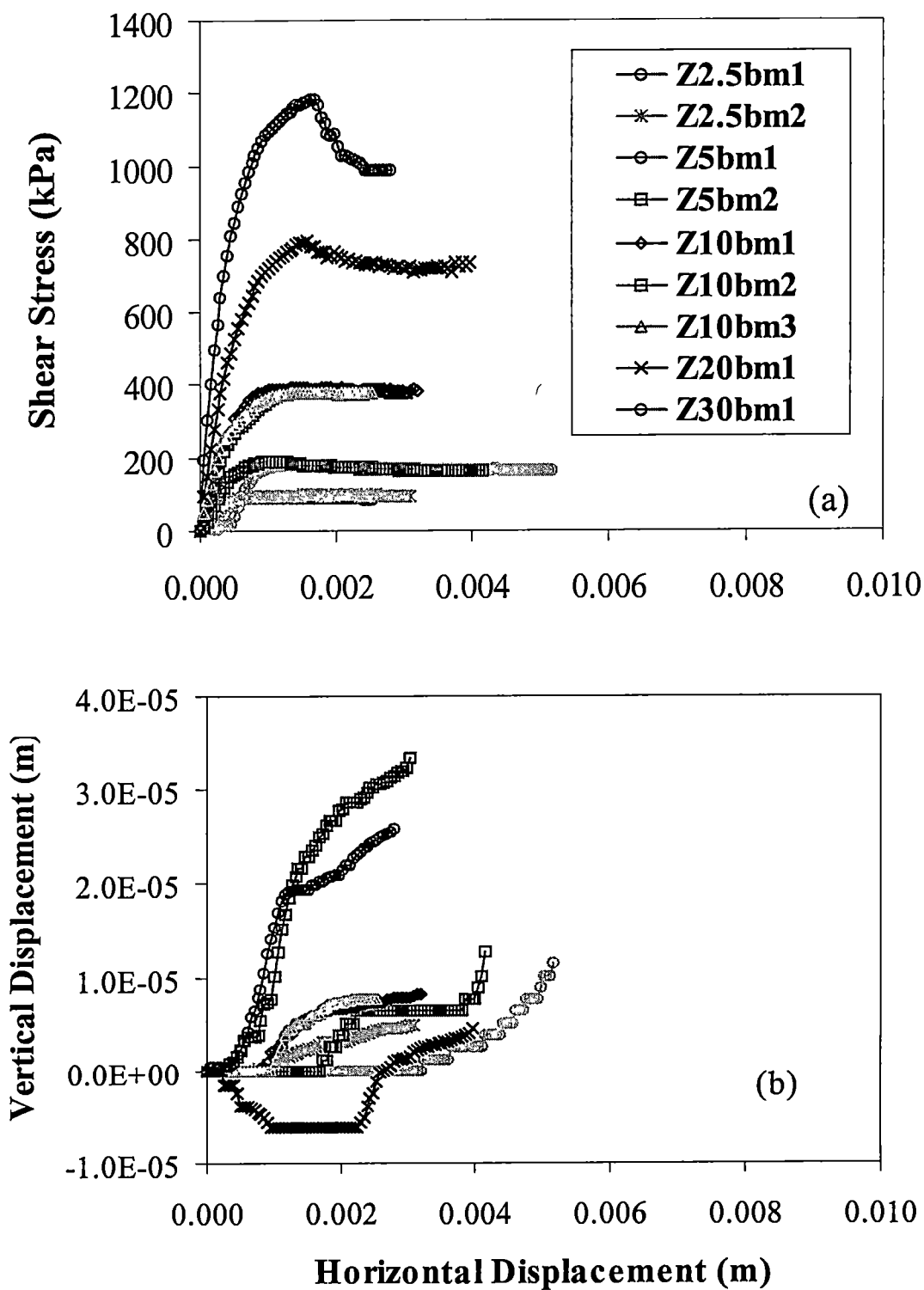


Figure 3 8 A typical result for Zorbax with methanol (a) Shear stress vs. horizontal displacement response, (b) Vertical displacement vs horizontal displacement response.

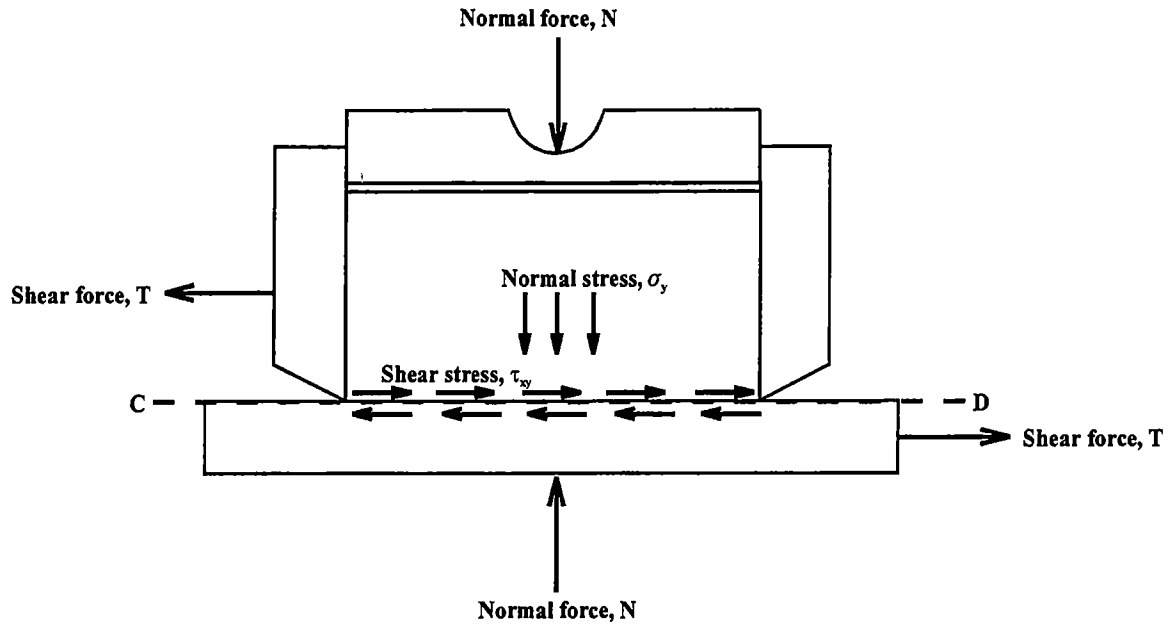


Figure 3.9 Silica sample in direct shear box.

During the direct shear test, the stress state is not completely defined: σ_y and τ_{xy} are known only on the horizontal surface, but the stresses are unknown on all other planes. The stresses on the horizontal plane at failure are represented by point M in Figure 3.10. If the stresses on the horizontal plane are measured at another value of normal stress, as shown by M', then the linear failure envelope A-M-M' can be drawn. Adoption of Mohr-Coulomb failure criterion assumes that the Mohr circle is tangent to the failure surface, and the point of tangency corresponds to the stresses on failure plane at failure. This allows the construction of the Mohr circle at failure. Thus, the Mohr circle can only be drawn at failure, assuming that the failure plane is horizontal and the stress state is uniform. As shown in Figure 3.10, point M represents the stress on the horizontal surface, and point N represents the stress on the vertical surface. Point P, referred to as the "Pole", is on the same horizontal line as point M when the failure plane is horizontal. The Mohr circle at failure is tangent to AM, and its center B is given by line MB perpendicular to AM.

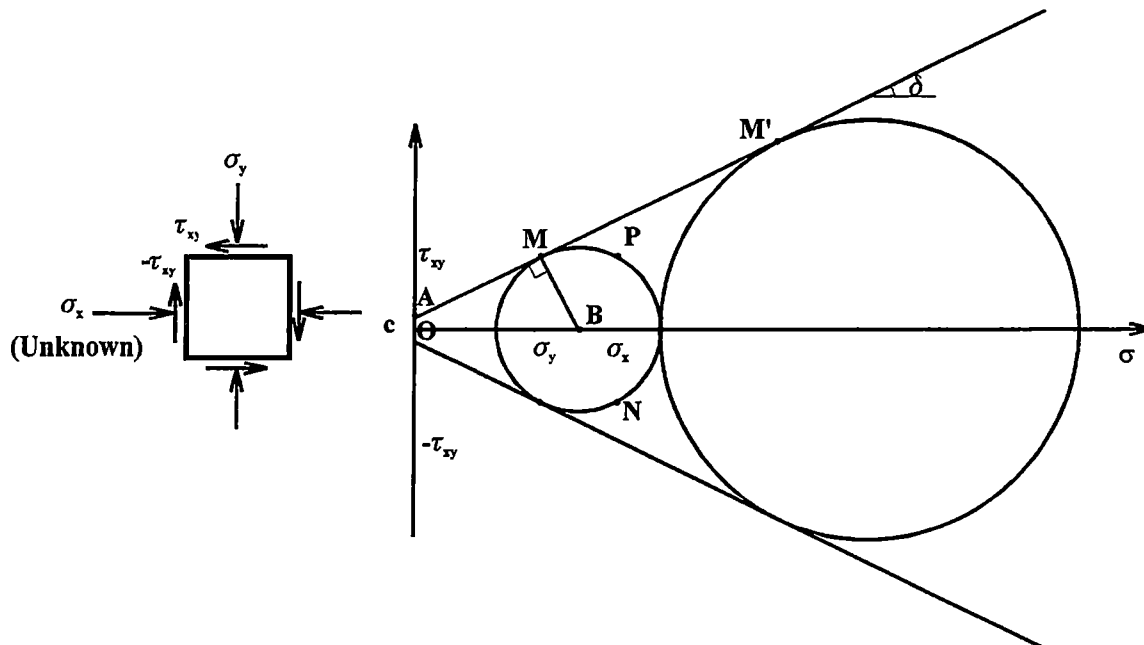


Figure 3.10 Stress state at failure and its Mohr representation (Bardet, 1996).

The test results suggested that the contact between the Zorbax silica sample and the stainless steel plate followed a Mohr-Coulomb failure law with a cohesion, $c = 0$ kPa, and a friction angle, $\delta = 21^\circ$, corresponding to coefficient of friction, $\tan \delta = 0.39$, as shown in Figure 3.11.

3.3.2 Effects of Solvents

To evaluate the effects of different solvents on the wall friction in HPLC columns, an additional series of direct shear tests were conducted. The same methods mentioned in Section 3.3.1.1.1 were used, except acetone (density of 0.79 g/cm^3) was used as the solvent in the tests rather than methanol. The tests were performed at normal stresses of 250 kPa, 500 kPa, 1000 kPa, and 3000 kPa, and several replications were obtained at most normal stresses. Figure 3.12 illustrates the measured shear stress deformation response, and the resulting Mohr-Coulomb failure envelopes are shown in Figure 3.13. The test results

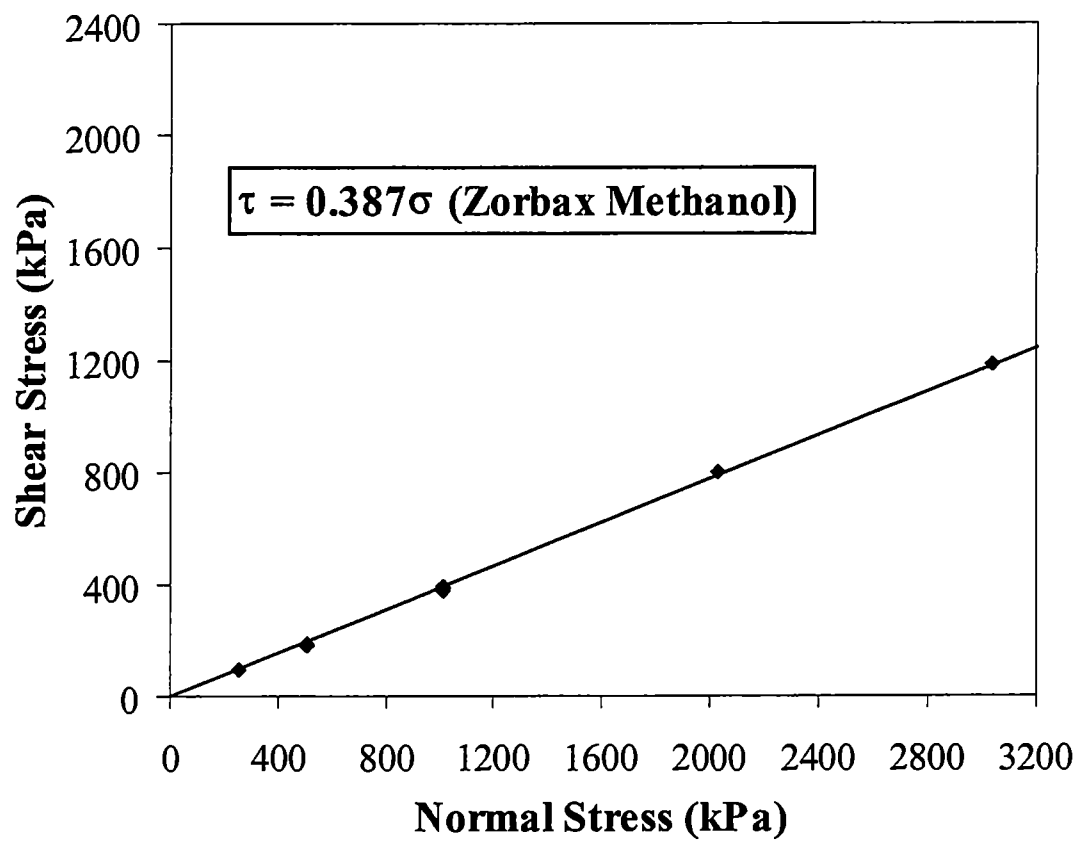


Figure 3.11 Mohr-Coulomb failure envelope for direct shear tests on Zorbax-steel contact.

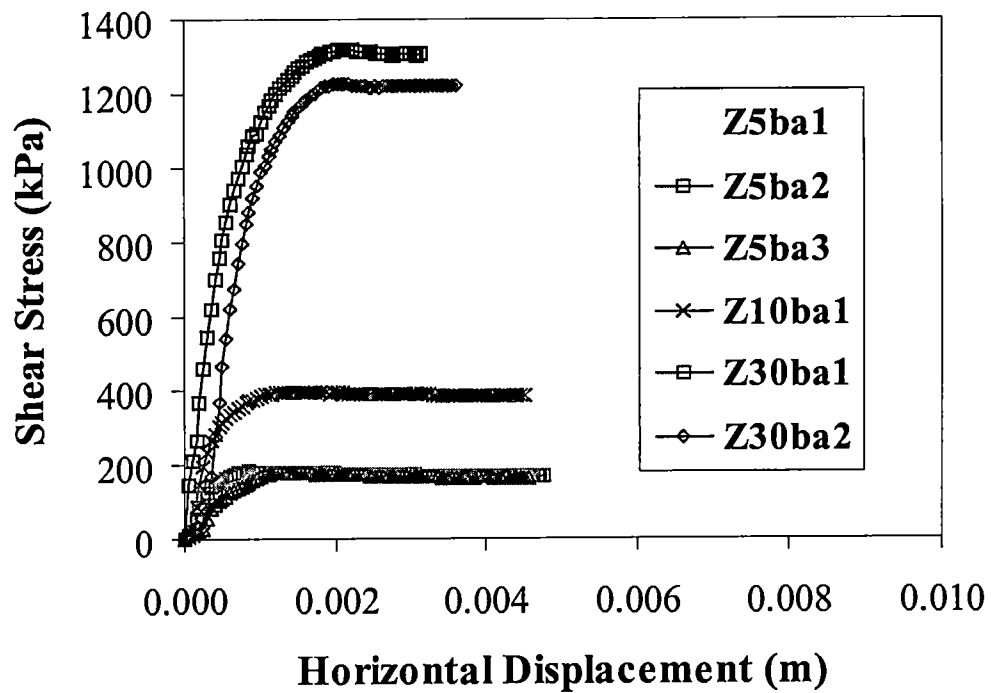


Figure 3.12 A typical shear stress vs. horizontal response for Zorbax with acetone.

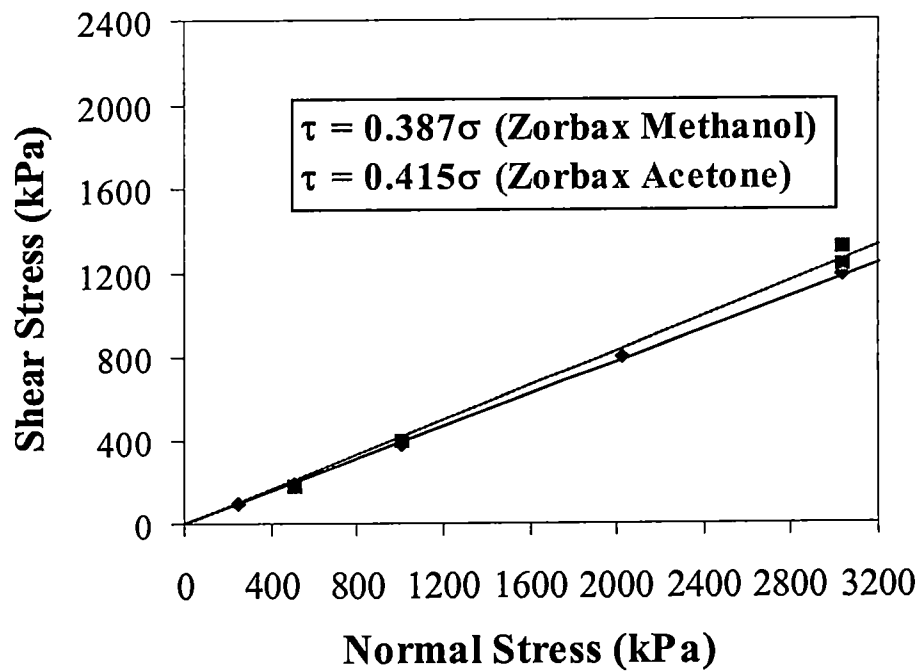


Figure 3.13 Mohr-Coulomb failure envelope.

suggested that the contact between the silica sample and the stainless steel plate followed a Mohr-Coulomb failure law with a cohesion, $c = 0$ kPa, and a friction angle, $\delta = 22.5^\circ$ ($\tan \delta = 0.415$). For comparison, the strength envelope for the Zorbax with methanol is also shown in Figure 3.13. Zorbax with acetone tends to have a slightly higher friction angle (difference of $\delta = 1.36^\circ$) than the Zorbax with methanol. This difference between the coefficient of friction with methanol and acetone can be considered to be insignificant, which is consistent with accepted theories of contact friction. This suggests that the wall friction in the HPLC columns is independent of the nature of the solvent since the difference in the measured friction angles is small. The small difference might be due to the fact that the particles in the bed interact strongly with each other and this interaction depends on the surface tensions between the liquid and the solid, which may be different for the two solvents.

However, these direct shear results contradict friction measurements in chromatography columns with methanol and acetone (Guiochon *et al.*, 1999) where significant differences in the frictional resistance were measured. This suggests that the solvent may affect the particle density, which in turn affects the coefficient of friction. This aspect of the problem warrants further investigation.

3.3.3 Effects of Packing Materials

To further understand the wall friction effects inside HPLC columns, additional direct shear tests were conducted with different silica packing material. The test procedures were the same as those mentioned in Section 3.3.1.1.1, except Kromasil C8 spherical silica particles (average particle size of $10\ \mu\text{m}$, solids density of $2.65\ \text{g/cm}^3$) with methanol solvent

were used as the packing material. The tests were conducted at the normal stresses of 1000 kPa, 2000 kPa, and 3000 kPa, and several replications were obtained at most normal stresses. Figure 3.14 shows the shear stress-deformation measurements for Kromasil with methanol, and the resulting Mohr-Coulomb failure envelopes are shown in Figure 3.15. For comparison, the strength envelope for the Zorbax with methanol is shown in Figure 3.15. The test results suggested that the contact between the silica sample and the stainless steel plate followed a Mohr-Coulomb failure law with a cohesion, $c = 0$ kPa, and a friction angle, $\delta = 11.64^\circ$ ($\tan \delta = 0.206$).

Kromasil with methanol tends to have a lower friction angle (difference of 9.52°) than the Zorbax with methanol. In other words, the measured coefficient of friction for Kromasil with methanol is about half of the measured coefficient of friction for Zorbax with methanol. This suggests that the wall friction in HPLC columns is dependent of the nature of the packing material since the difference in the measured friction angles is significant. The difference might be due to the fact that the particles in the bed interact strongly with each other and this interaction depends on the surface tensions between the liquid and the solid, which may be different for the two packing materials.

These direct shear results contradict friction measurements in chromatography columns with Kromasil and Zorbax (Guiochon, 1999), in which significant differences in the frictional resistance of the two material was measured. This aspect of the problem warrants further investigation.

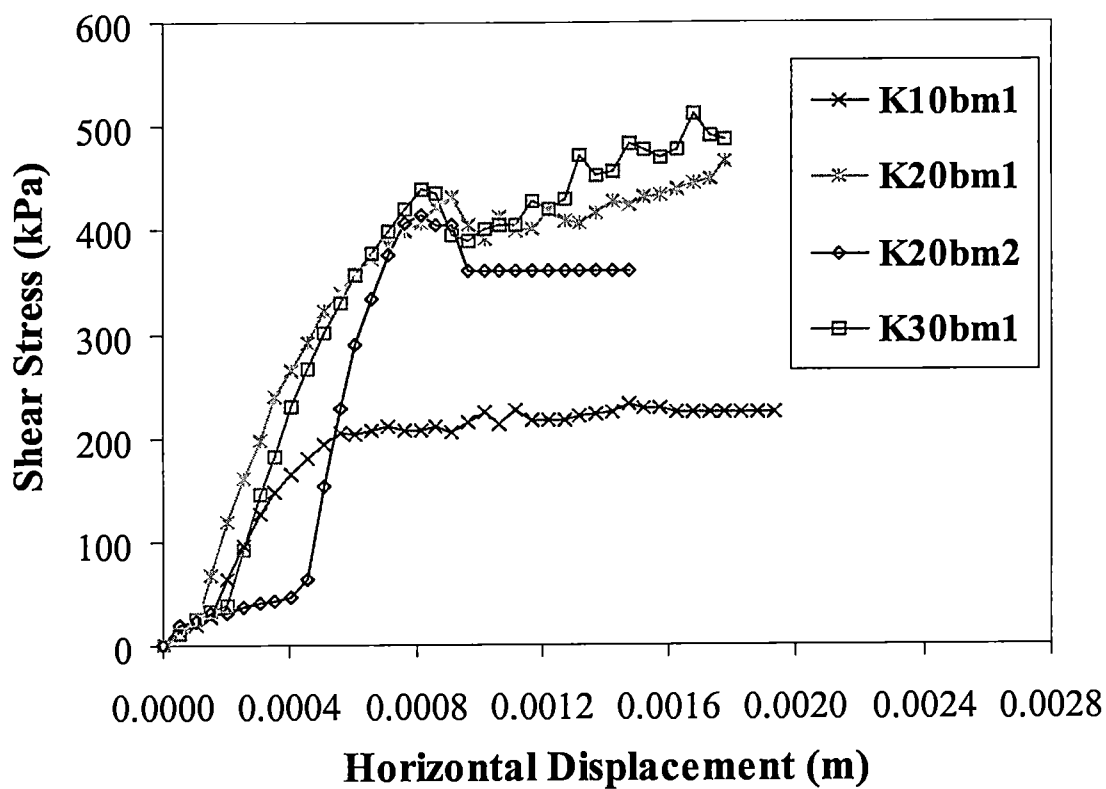


Figure 3.14 Shear stress vs. horizontal response for Kromasil with methanol.

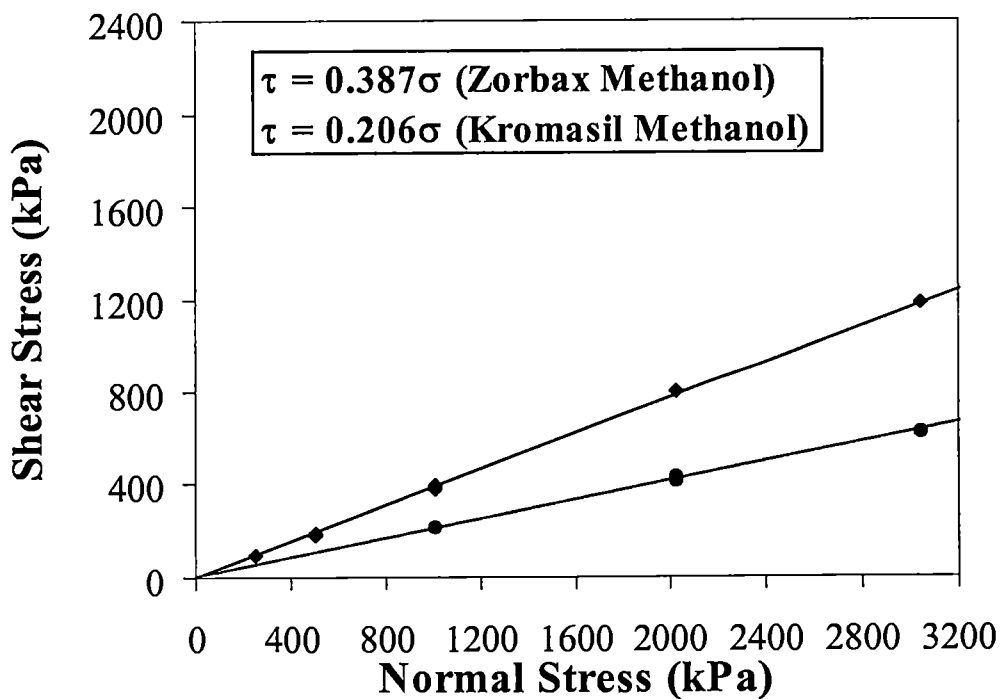


Figure 3.15 Mohr-Coulomb failure envelope.

3.3.4 Effect of Lubricant

Wall friction is thought to contribute to the non-homogeneity of the packing material, and will be investigated by numerical analysis (discussed in Chapter 4). An experimental investigation of several potential wall lubricants was conducted. Prior to conducting direct shear tests with the lubricants, the relative difference between several potential lubricants was investigated using tilt tests. The tilt tests were done on interfaces between a steel plate and block of phenolic material with the various lubricants. The lubricant with the best potential for improving the column packing procedure would be used in direct shear tests between the lubricated stainless steel plate and the Zorbax spherical C18-bonded silica packing material.

3.3.4.1 Tilt Tests

Since the interface coefficient of friction between the packing material and the stainless steel column decreases the efficiency of the chromatography columns, several wall lubricants were investigated. These lubricants included flake graphite powder, Sprayon graphite spray, Teflon spray and Boron Nitride (ceramic) spray. To evaluate the performance of the lubricants, tilt tests were conducted on the lubricated stainless steel plate and a block of phenolic. Tilt tests were chosen because they are an easy, cheap and quick method to compare the various lubricants.

3.3.4.1.1 Experimental Setup

The tilt tests were conducted by using a block of phenolic and a steel plate. A schematic of the apparatus used in the tilt tests is shown in Figure 3.16. The plate was attached to a machinist's sine plate (shown in Figure 3.16) where one end of the plate was

raised by cranking the handle of the sine plate at a constant rate of about 90 mm/minute, while the other end was held constant. Consider the block of weight, W , resting on a plane surface which is inclined at an angle, α , to the horizontal surface. The block is acted upon by gravity only and hence the weight, W , acts vertically downwards as illustrated in Figure 3.16.

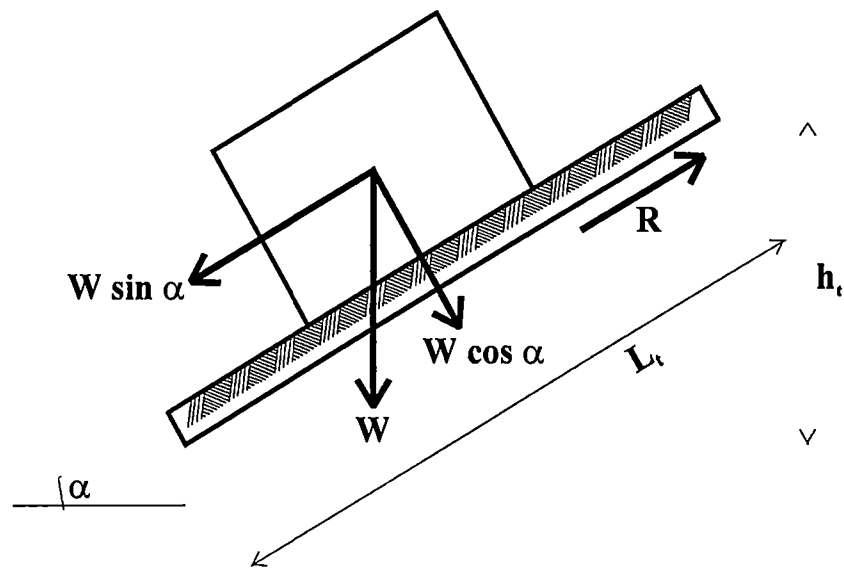


Figure 3.16 Schematic view of the tilt test.

The resolved component of W which acts down the plane and which tends to cause the block to slide is $W \sin \alpha$. The component of W which acts across the plane and which tends to stabilize the slope is $W \cos \alpha$. The normal stress, σ which acts across the potential sliding surface is given by:

$$\sigma = \frac{W \cos \alpha}{A} \quad (3.15)$$

where A is the base area of the block.

The relationship between shear strength of the sliding surface and the normal stresses can be expressed as:

$$\tau = \sigma \tan \delta + c \quad (3.16)$$

where τ is the shear stress, σ is the normal stress, δ is the interface friction angle, and c is the cohesive strength of the material contact.

Assuming that the shear strength of the surface is defined by equation (3.16) and substituting for the normal stress from equation (3.15):

$$\tau = \left[\frac{W \cos \alpha}{A} \right] \tan \delta + c \quad (3.17)$$

and the resisting force, τA that resists the block from sliding is given by:

$$\tau A = (W \cos \alpha) \tan \delta + cA \quad (3.18)$$

The block will be just on the point of sliding or in a condition of limiting equilibrium when the disturbing force acting down the plane is exactly equal to the resisting force:

$$W \sin \alpha = (W \cos \alpha) \tan \delta + cA \quad (3.19)$$

If the cohesion $c = 0$, which was the case in the packing material-steel contacts investigated in the direct shear tests, the condition of limiting equilibrium defined by equation (3.19) reduces to:

$$\alpha = \delta \quad (3.20)$$

Thus, the angle at which the block began to slide is the interface angle of friction, δ ,

between these two materials. By measuring the height of the plate, h , when the block started to slide and knowing the length of the plate, L , the interface friction angle can be determined:

$$\delta = \sin^{-1}\left(\frac{h}{L}\right) \quad (3.21)$$

3.3.4.1.2 Discussion of Results

Tilt tests were performed for a range of lubricants, and the coefficient of friction ($\tan\delta$) is compared in Figure 3.17. Also shown is the coefficient of friction for the phenolic block without lubricant. This unlubricated value of 0.24 compares favorably with that of Zorbax ($\tan\delta = 0.387$) and Kromasil ($\tan\delta = 0.212$) with methanol measured in direct shear tests. Sprayon graphite spray (density of 0.66 g/cm^3) was identified as the lubricant with the

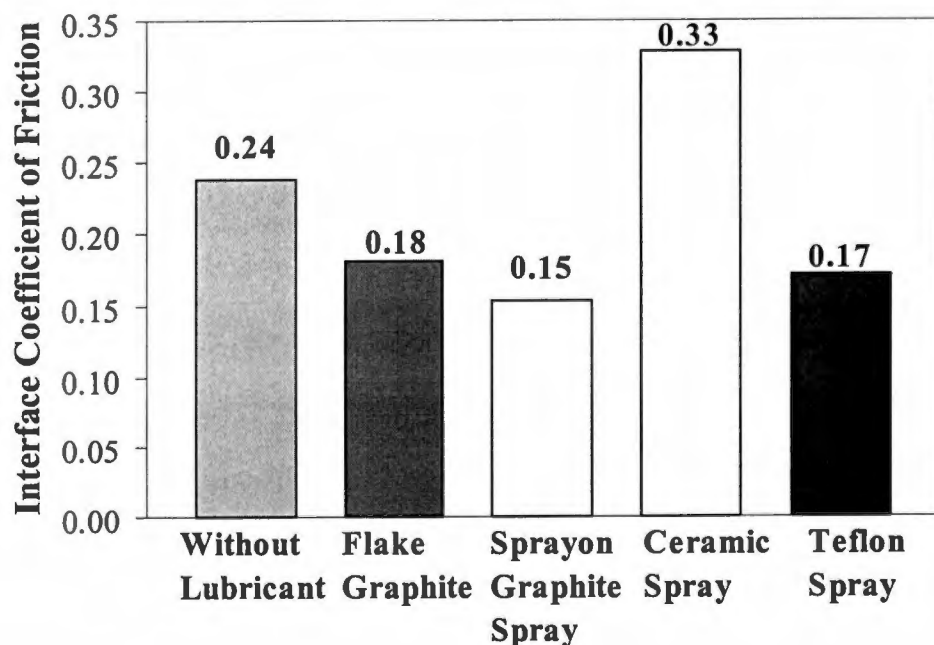


Figure 3.17 Interface coefficient of friction between phenolic and various lubricants.

best potential for improving the column packing procedure (shown in Figure 3.17). A series of direct shear tests were then conducted between the stainless steel plate lubricated with Sprayon graphite spray and the Zorbax silica packing material to observe the effects of lubricant on the interface friction between the plate and the packing materials.

3.3.4.2 Direct Shear Tests with Lubricant

The same methods mentioned in Section 3.3.1.1.1 were used in the tests, except Sprayon graphite spray was used as a coating material on the stainless steel plate. The graphite was sprayed slowly and carefully so that a uniform layer of graphite was applied to the plate. The thickness of the graphite was approximately $3.5 \mu\text{m}$, as estimated by measuring the mass difference before and after spraying the graphite onto the test slide, and knowing the density of the graphite and the area of the sprayed slide.

The tests were performed at normal stresses of 2000 kPa and 3000 kPa respectively. The shear stress displacement response is shown in Figure 3.18, and the resulting Mohr-Coulomb failure envelope (Figure 3.19) was obtained based on the peak failure shear stresses. The test results suggested that the contact between the silica sample and the lubricated stainless steel plate followed a Mohr-Coulomb failure law with a cohesion, $c = 0$ kPa, and a friction angle, $\delta = 18.3^\circ$ ($\tan \delta = 0.33$). In other words, the graphite spray reduced the coefficient of friction to about 85.2 percent the non-lubricated value. Comparing the reduction in coefficient of friction in direct shear tests (14.8%) with the reduction in coefficient of friction from tilt tests (37.5%), the reduction is not as significant as with the phenolic. This might be expected due to the difficulty of achieving a uniform coating under the packing material particles.

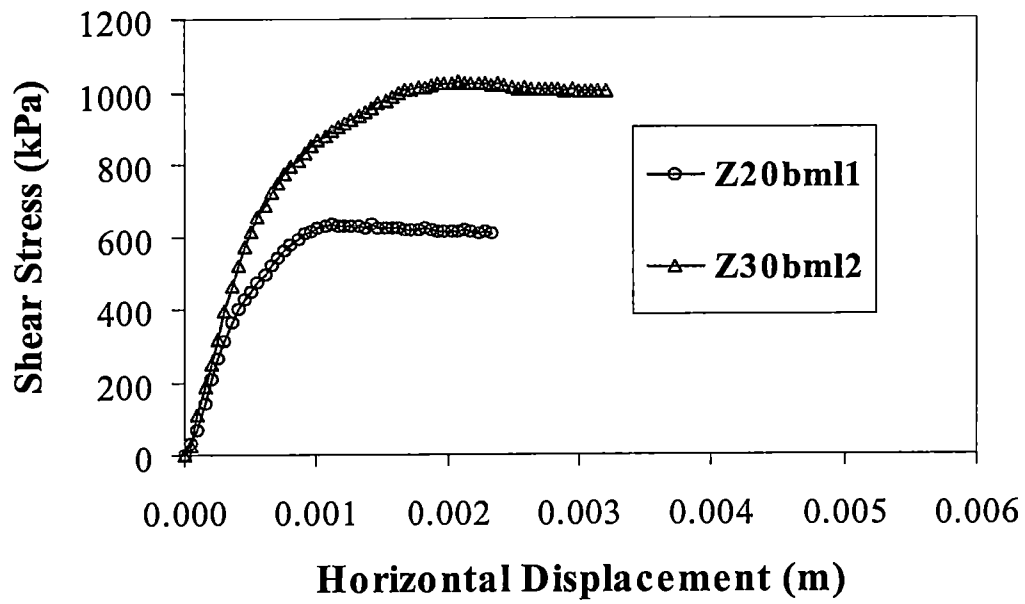


Figure 3.18 A typical shear stress vs horizontal displacement response for Zorbax with methanol (lubricated steel plate).

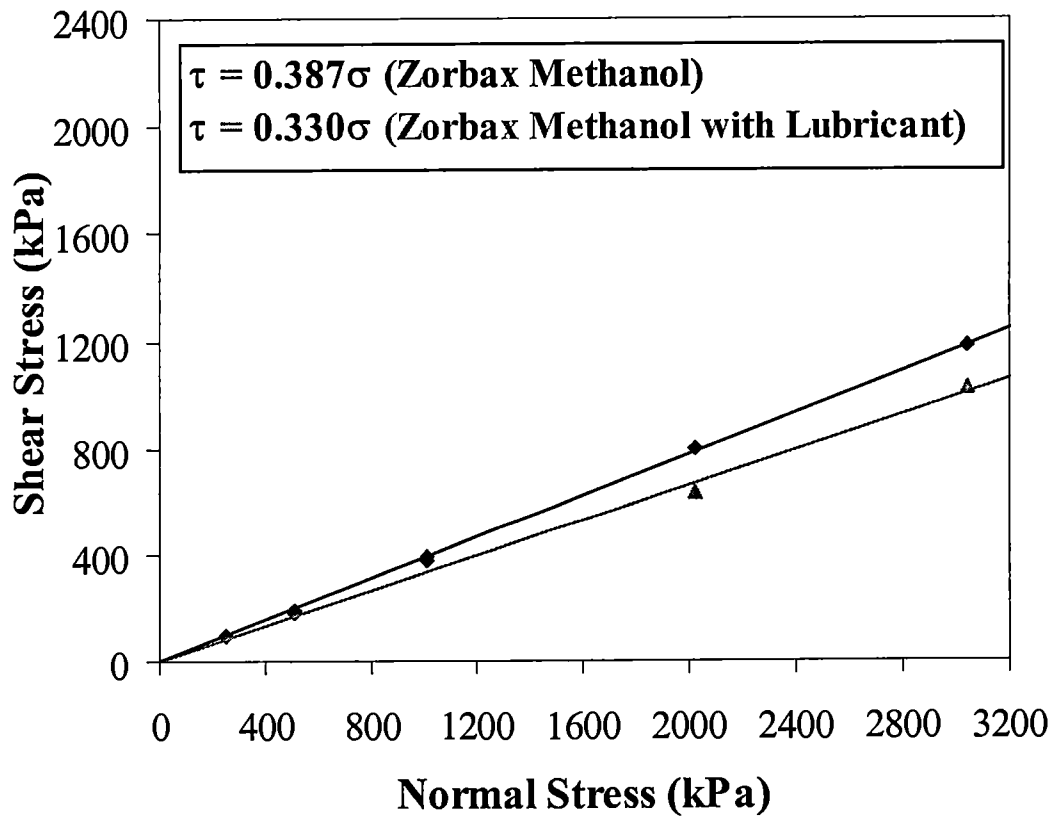


Figure 3.19 Mohr-Coulomb failure envelope for Zorbax with methanol (lubricated steel plate).

3.3.5 Discussion of Results

Figure 3.20 compares the shear stress vs. horizontal displacement response for the two packing materials (Zorbax and Kromasil) used in HPLC columns with the two different solvents (methanol and acetone). The Mohr-Coulomb failure envelopes are compared in Figure 3.21

As illustrated in Figure 3.21, the lowest interface coefficient of friction between the silica sample and the stainless steel plate is found in Kromasil C8 with methanol solvent ($\tan \delta = 0.21$). This suggests that Kromasil C8 could be used in HPLC columns, such that a more homogeneous column can be prepared. The test results also suggest that the contact between the Zorbax with methanol and the stainless steel plate had the greatest coefficient of friction ($\tan \delta = 0.39$). This value of the interface friction angle is close to the two thirds of the internal friction angle ($\phi = 36^\circ$) measured Muhlbachler *et al.* (1998) on a similar packing material Pro 10 Sil, which is consistent with the results reported by Potyondy (1961) for interface between soils and various construction materials.

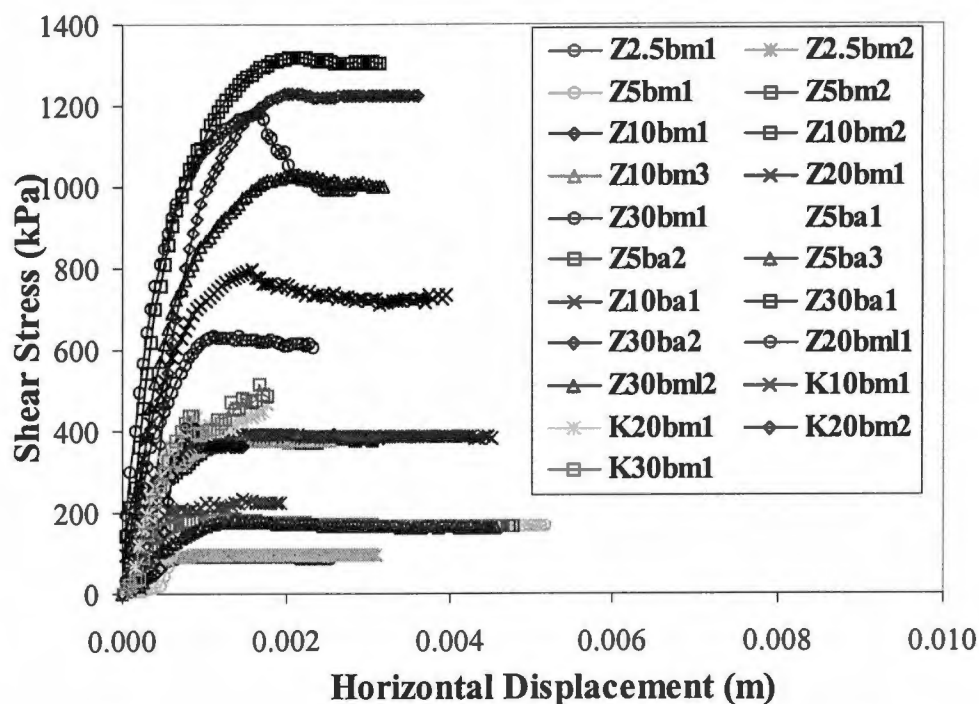


Figure 3.20 A typical shear stress vs. horizontal displacement response for packing materials used in HPLC columns with various solvents.

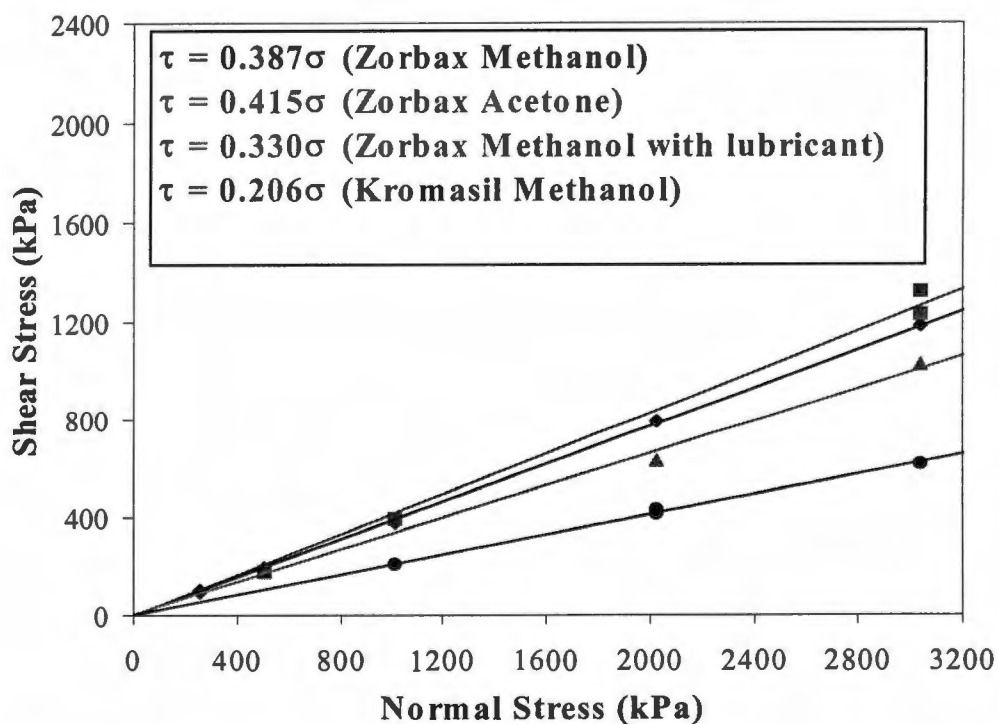


Figure 3.21 Mohr-Coulomb failure envelope for the packing materials used in HPLC columns.

Chapter 4

Numerical Modeling

Numerical modeling techniques such as the Finite Element Method (FEM) can be used to simulate the stress-state inside HPLC columns during the packing process. The FEM is a collection of theory-rich techniques, which can produce near-optimal approximate solutions to the initial-boundary value partial differential equations common to engineering and mathematical physics (Baker and Pepper, 1991). In general, a finite element analysis requires the idealization of an actual physical problem into a mathematical model and then the finite element solution of that model. The stress distribution in a typical preparative HPLC column was investigated using the commercial general-purpose finite element code ABAQUS, version 5.8 (1998). The material parameters used in the analysis were obtained from the laboratory testing. The numerical results from ABAQUS were evaluated via the post processing package, ABAQUS/Post (1998), which generated the graphical results.

4.1 Mechanical Response due to Piston Loading

As described in Section 2.1, a piston is used to consolidate the HPLC column in a few seconds. The effects of this mechanical loading was studied using a nonlinear elastic-plastic model. The laboratory results from the direct shear tests and fixed ring consolidation tests incorporating falling head permeability tests were used in a numerical analysis of a chromatography column

4.1.1 Idealization of HPLC Columns

The typical HPLC column used in this research is 16.0 cm long with a diameter of 5.0 cm, as shown in Figure 4.1. Since the FEM is an approximate numerical procedure for solving engineering problems, it is valuable to recognize that a mathematical model is actually implied in the finite element representation of the physical problem.

4.1.1.1 Idealization and Boundary Conditions of the Model

To model HPLC column, a three-dimensional model could be used. However, due to the axisymmetric nature of the column and packing process, the column can be simplified to a two-dimensional model by taking advantage of the axial symmetry as illustrated in Figure 4.2. 4-node linear axisymmetric continuum elements (2 x 2 integration points) were used. These elements are torsionless axisymmetric elements, which only allow axially symmetric loading conditions. The body of revolution is generated by revolving a plane cross-section about an axis (the symmetry axis) and is readily described in cylindrical polar coordinates: r , z , and θ . The radial and axial coordinates of a point on this cross-section are denoted by r and z , respectively. At $\theta = 0$, the radial and axial coordinates coincide with the global Cartesian X- and Y-coordinates (ABAQUS, 1998). If the loading consists of an axial component that is independent of θ , as in this problem, the displacement at any point will only have radial, u_r and axial, u_z components and the only non-zero stress components are σ_{rr} , σ_{zz} , $\sigma_{\theta\theta}$, and σ_{rz} .

The frictional surface between the bed and the steel wall was represented using contact pairs, with a coefficient of friction $= \tan \delta = 0.39$. As illustrated in Figure 4.3, a vertical constraint was imposed on top of the column while a displacement of 3.40 mm

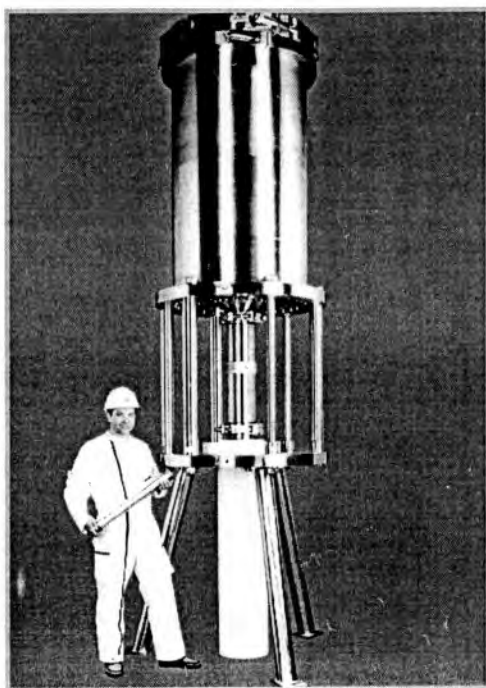


Figure 4.1 Typical HPLC column used in the research (in the hand of the man) compared with a large preparative column.

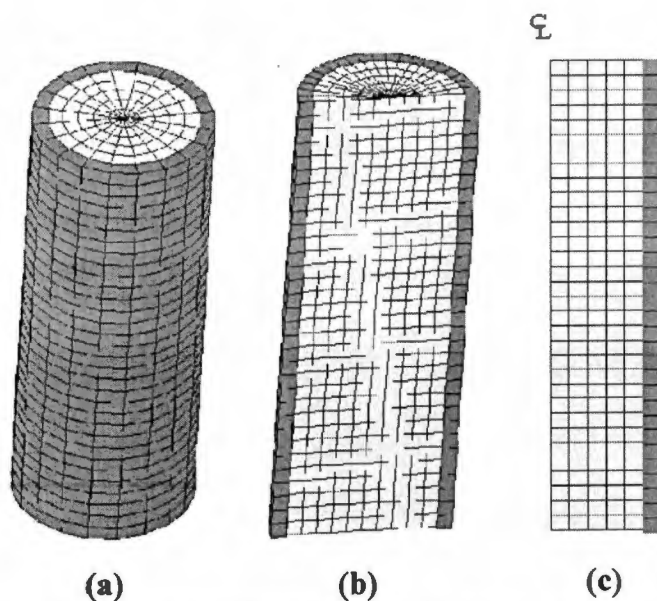


Figure 4.2 Idealization of HPLC column (a) Tilted column, (b) Cross section of the column, (c) Idealized column.

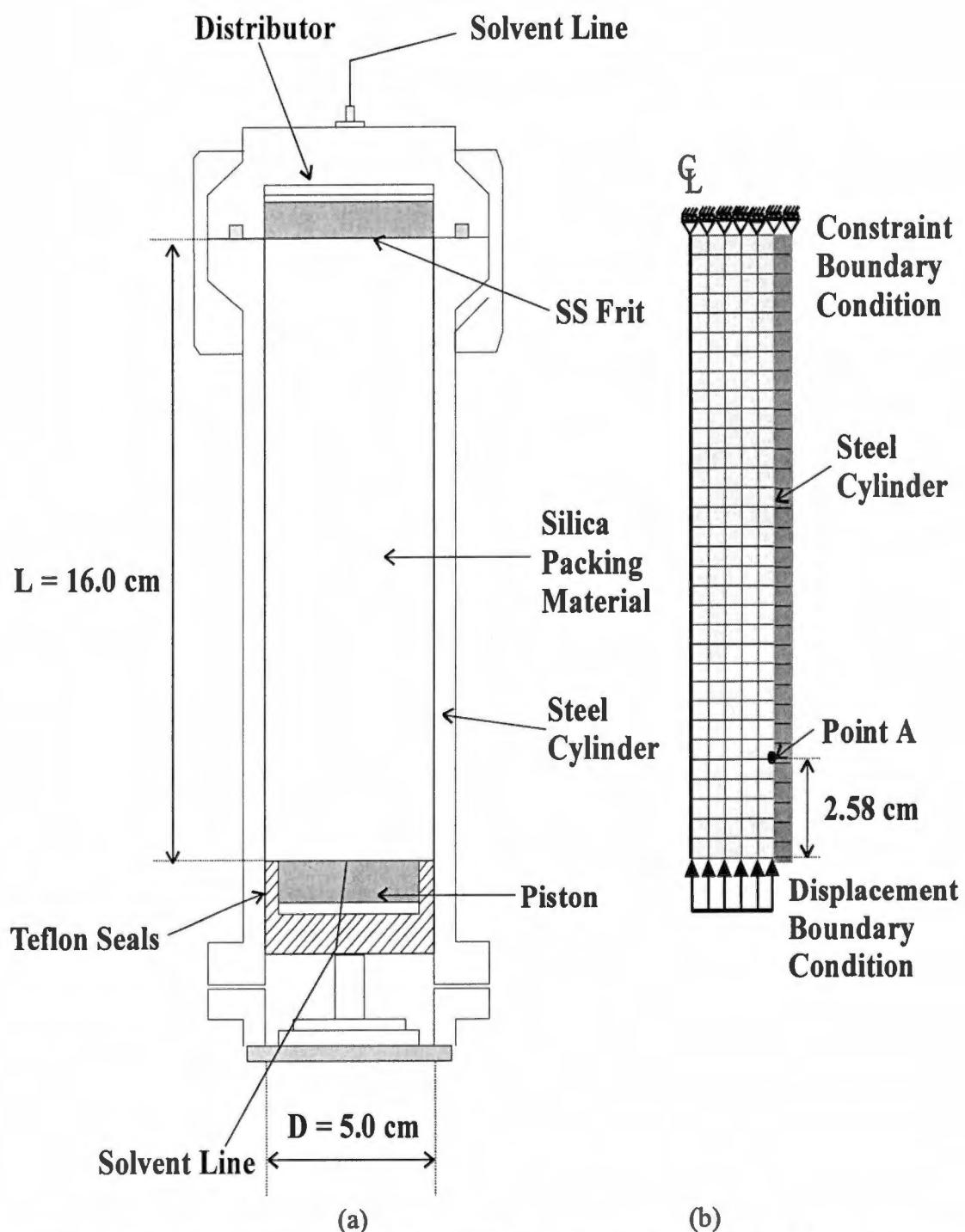


Figure 4.3 Typical Preparative HPLC column (a) Schematic of column, (b) Axisymmetric finite element idealized.

(corresponding to mean compression pressure of 130 bar) was then applied at the bottom of the bed corresponding to the piston displacement. This value is consistent with results of chromatographic experiments (Guiochon *et al.*, 1999a).

4.1.1.2 Investigation of the Mesh Size

The finite element method is an approximate numerical procedure for solving engineering problems, it is valuable to recognize that a mathematical model is actually implied in the finite element representation of the physical problem. In other words, as the number of elements is increased, a proper finite element solution should converge to the analytical or exact solution of the differential equations that govern the response of the mathematical model. If the differential equations of motion are not known, as in preparative HPLC columns analysis, and/or analytical solutions cannot be obtained, the convergence of the finite element solutions can be evaluated only on the assumption that all basic kinematic, static, and constitutive conditions contained in the mathematical model must ultimately be satisfied at the convergence. Thus, in all discussions of the convergence of the finite element solutions, we imply that the convergence to the exact solution of a mathematical model is meant.

For monotonic convergence, the elements must be complete and the elements and mesh must be compatible. If these conditions are fulfilled, the accuracy of the solution results will increase continuously as we continue to refine the finite element mesh. At some stage of refinement, there should be little change in the results. This mesh refinement should be performed by subdividing a previously used element into two or more elements. Thus, the old mesh will be embedded in the new mesh. This also means mathematically that the new space of finite element interpolation functions will contain the previously used space, and

as the mesh is refined, the dimension of the finite element solution space will be continuously increased to contain ultimately the exact solution.

To investigate the convergence issue in the model used for preparative HPLC columns, a series of analyses with 2, 5, and 10 elements across the half-width of the column was conducted. By comparing the axial displacements at point A (Figure 4.2), it can be seen that there is very little difference in the displacement compared with 5 and 10 elements, yet the displacement with 2 elements produce much greater displacement (Figure 4.4). Thus, it can be concluded that the 5-element provides satisfactory results.

4.1.2 Nonlinear Elastic-Plastic Model

The packing material was represented by a frictional material model (Drucker-Prager nonlinear elastic-plastic model), in which yielding was permitted. Laboratory results obtained from direct shear tests and consolidation tests were input into the model.

4.1.2.1 Material Modeling

The stainless steel column surrounding the bed was represented as a linear elastic material with an assumed modulus of elasticity = 2×10^{11} kPa and a Poisson ratio = 0.3. A Drucker-Prager elastic-plastic model was used to simulate the response of the packing material. In the elastic range, the porous elastic material model implemented in ABAQUS was used, in which the change in volume of the material is proportional to the logarithm of the mean stress, $p = -\frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33})$

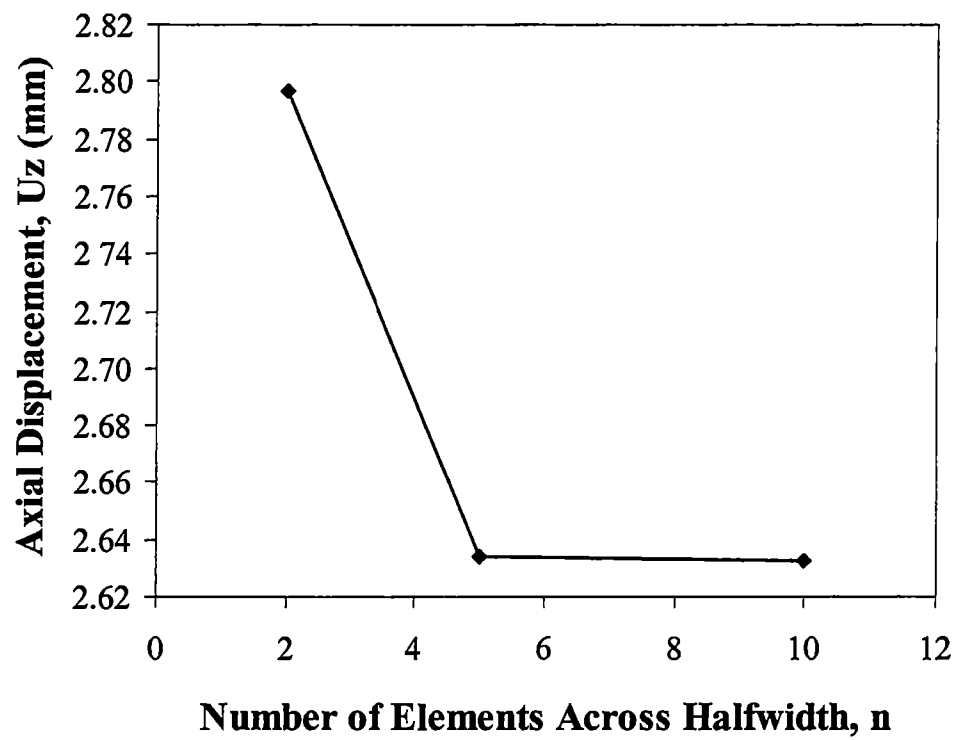


Figure 4.4 Monotonic convergence study on meshes used in HPLC columns.

The volumetric strain ϵ_v of the porous materials is defined by $\ln(J^{el})$ where J^{el} is the logarithmic measure of the elastic volume change (ABAQUS, 1998):

$$J^{el} = \frac{\kappa}{(1 + e_o)} \ln \left(\frac{p_o + p_t^{el}}{p + p_t^{el}} \right) + 1 \quad (4.1)$$

and κ is the logarithmic bulk modulus, e_o is the initial void ratio, p_o is the initial value of the equivalent pressure or stress, and p_t^{el} is the elastic tensile strength of the material. As shown in Figure 4.5, Equation (4.1) provides a good approximation of the observed volumetric response during the application of the normal stress in the direct shear test. Poisson's ratio was assumed to be 0.3, and values of $\kappa = 0.010$, $p_o = 0.0$ kPa, and $p_t^{el} = 100.0$ kPa were used to produce this response

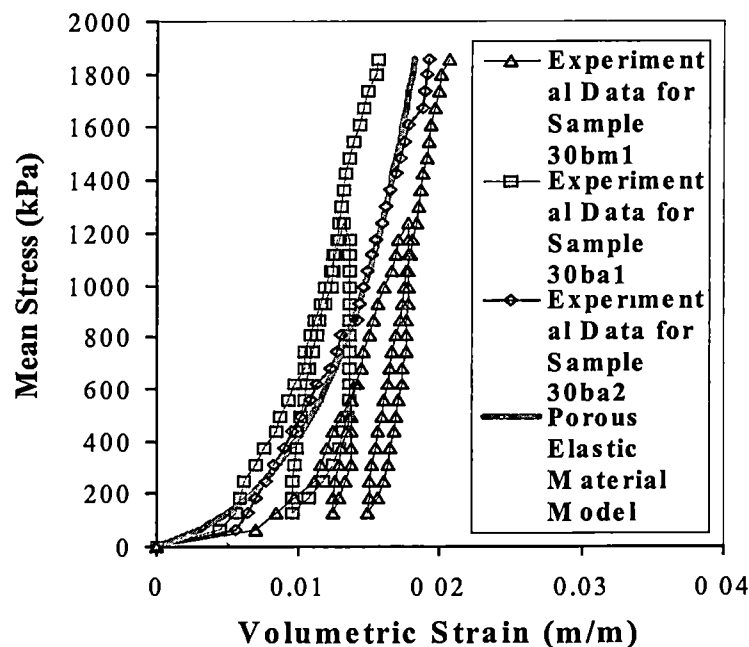


Figure 4.5 Typical interface results: Mean stress vs. volumetric strain from direct shear tests.

A linear Drucker-Prager yield surface function, F , was used (ABAQUS, 1998)

$$F = q - p \tan \beta - d = 0 \quad (4.2)$$

where β is the slope of the yield function in the p - q stress space, q is the Mises equivalent stress, and d is the yield function intercept on the q axis as illustrated in Figure 4.6. As indicated in Figure 4.6, β is related to ϕ and d is related to c . A non-associative flow rule was used such that non-dilatant response could be represented. This was accomplished by assuming that the dilation angle, $\psi = 0$. Based on the friction angle measured for a similar silica packing material (Mihlbachler *et al.*, 1998), values of $\beta = 46^\circ$, and $d = 0.73$ kPa were used.

4.1.3 Results for Zorbax with Methanol

Typical numerical results of Zorbax spherical C18 bonded silica particles with Methanol solvent are shown in Figures 4.7 and 4.8. As illustrated in Figure 4.7(a), the displacement of the packed bed is maximum at the bottom of the bed, where the prescribed displacement condition is imposed due to a 3.40 mm displacement of the piston. The displacement decreases along the column, and is nearly zero at the top of the column. There is both axial and radial heterogeneity predicted along the packed bed. The model displacements agree well with experimental observations from a packed bed made up of alternating colors of packing materials (Yun and Guiochon, 1999), as indicated in Figure 4.7(b).

The mean pressure distribution of the packed bed is shown in Figure 4.8(a). The results suggest that there is a concentration of high stress near the edges at the bottom and

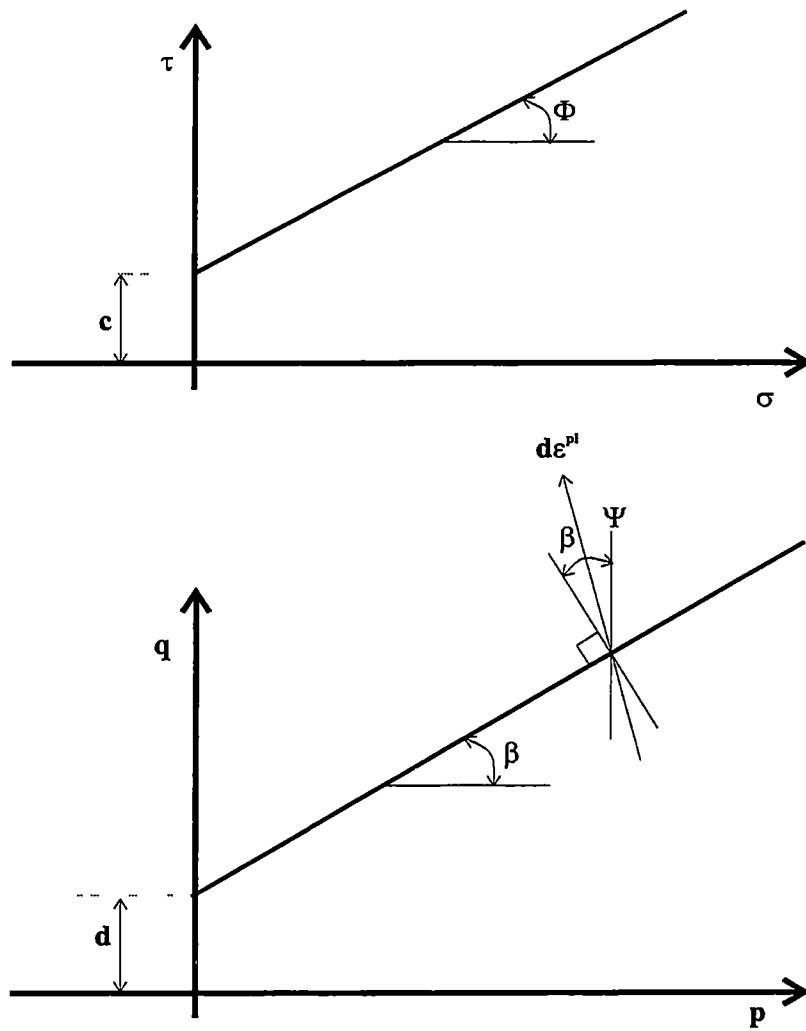


Figure 4.6 Linear Drucker-Prager model.

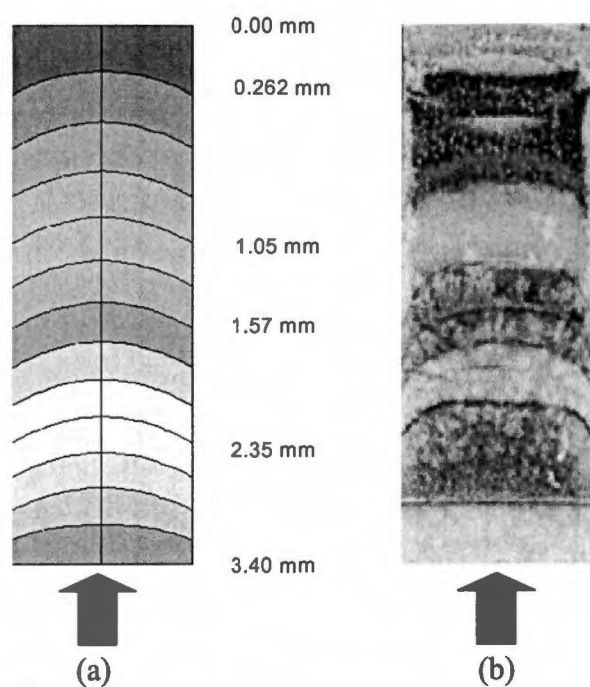


Figure 4.7 Zorbax with Methanol ($\tan \delta=0.39$): (a) Displacement distribution; (b) Cross-section of the packed bed (Yun and Guiochon, 1999).

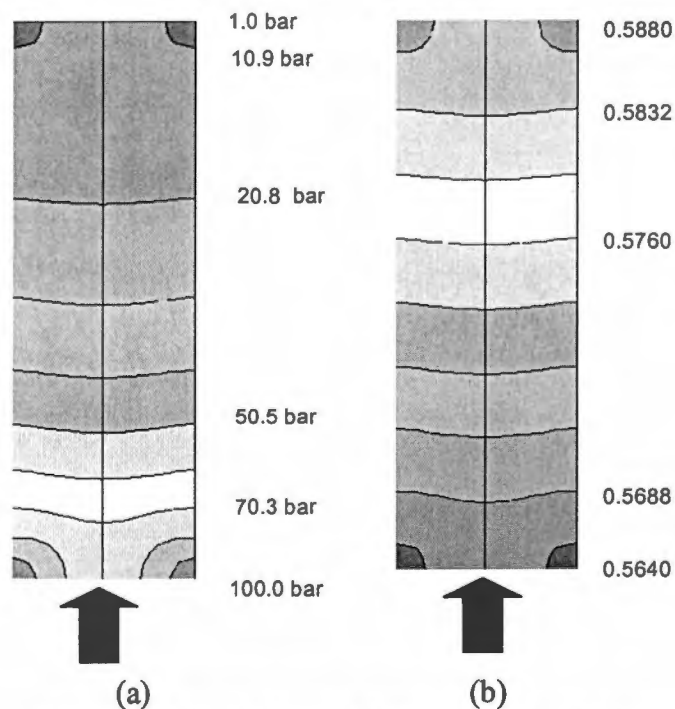


Figure 4.8 Zorbax with Methanol ($\tan \delta=0.39$): (a) Mean pressure distribution; (b) Void ratio variation.

a zone of low stress on top of the bed. Also, there is some axial and radial heterogeneity along the bed, corresponding to the variation of void ratio shown on Figure 4.8(b).

4.1.4 Parametric Study

To further understand the effects of the wall friction and the piston shape in the preparative HPLC columns, parametric studies were conducted by varying the interface coefficient of friction of the columns and the shape of the bottom piston.

4.1.4.1 Effects of Wall Friction

The results of two numerical analyses are shown in Figures 4.9 to illustrate the effects of wall friction on the radial heterogeneity of the packed bed. The results in Figure 4.9(a) are based on the measured coefficient of friction ($\tan \delta = 0.387$) of Zorbax spherical C18 particles (with methanol solvent), while the results in Figure 4.9(b) were obtained with about one half the measured wall friction, which is the interface friction obtained using Kromasil spherical C18 particles (with methanol). The results suggest that the axial heterogeneity, and more importantly the radial heterogeneity that lowers column efficiency, could be significantly reduced if the friction is decreased

Figure 4.10 illustrates the yielded zones in the packing material for the full and one half wall friction cases, respectively. As expected, the analysis suggested that under the applied loading there was little yielding of the packing material with the measured wall friction value, but the yielded zones were observed to nearly vanish when the friction was reduced.

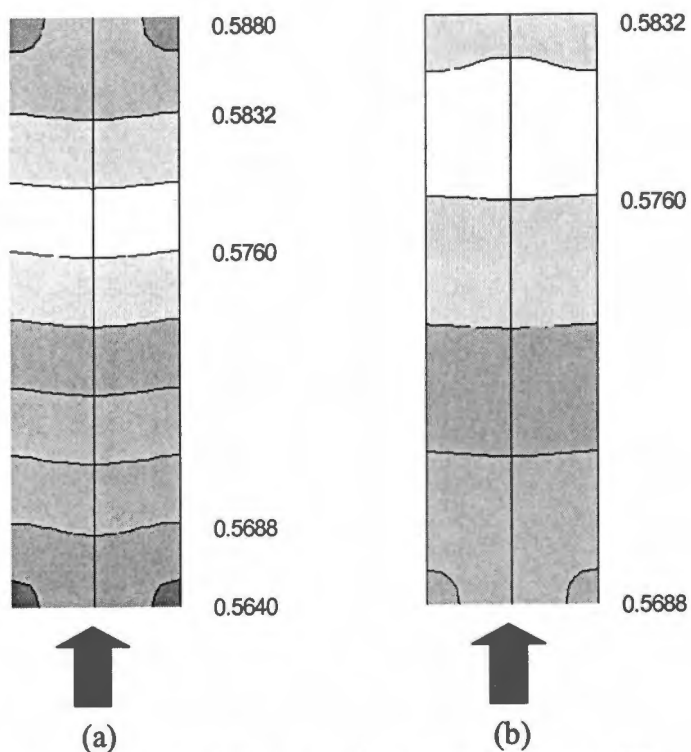


Figure 4.9 Void Ratio inside the packing material:
 (a) Zorbax: $\tan \delta = 0.39$; (b) Kromasil: $\tan \delta = 0.21$.

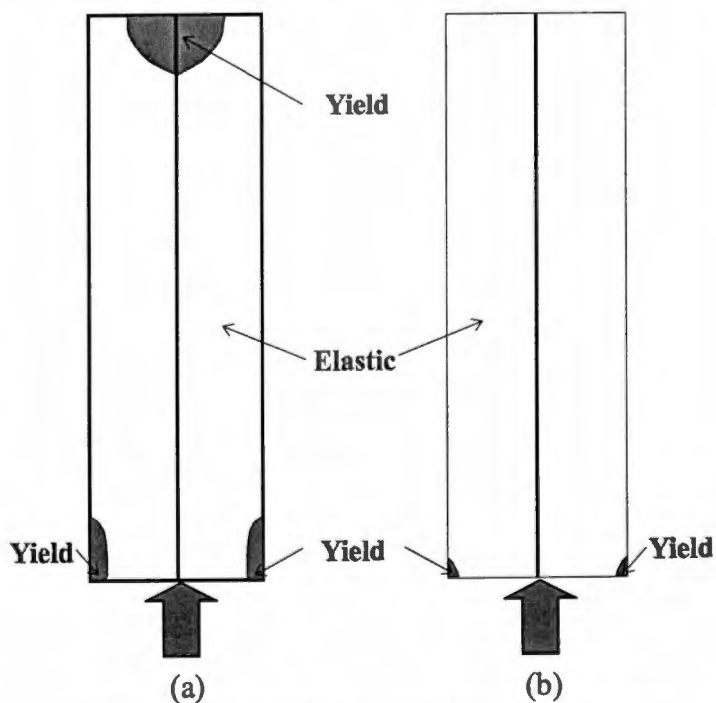


Figure 4.10 Elastic and plastic regions inside the
 packing material: (a) Zorbax: $\tan \delta = 0.39$;
 (b) Kromasil: $\tan \delta = 0.21$.

4.1.4.2 Effects of Piston Shape

The effect of the piston shape on the resulting particle density was investigated by a series of numerical simulations on the same packing procedures, except with different piston geometries. Three types of piston shape were considered: (1) flat piston, (2) concave piston, and (3) convex piston as illustrated in Figure 4.11. With a slightly concave piston (Figure 4.11(b)) relative to the flat piston (Figure 4.11(a)) (with an edge to center difference of 3mm), radial heterogeneity of the bed is improved especially at the bottom. However, if the degree of convexity of the piston is increased (Figure 4.11(c)) (with an edge to center difference of 6mm), there is not much improvement in the radial heterogeneity of the bed. On the other hand, for a concave piston (Figure 4.11(d)) (with an edge to center difference of 6mm), the radial heterogeneity of the bed is worse. In short, a convex piston may improve the radial heterogeneity of the column

4.1.5 Discussion of Results

Axial and radial heterogeneity of the column is significantly reduced if the interface friction is reduced, as illustrated in Section 4.1.4.1. The yielded zones nearly vanished when the wall friction is reduced. A slightly concave piston may improve the radial homogeneity of the column, especially at the bottom of the column.

4.2 Coupled Mechanical – Seepage Response

A chromatographic bed is submitted to a compression stress of two origins (Knox, *et al*, 1976 and Guiochon and Sarker, 1995). First, the piston causes a mechanical compression of the entire bed. This mechanical compression was modeled numerically as

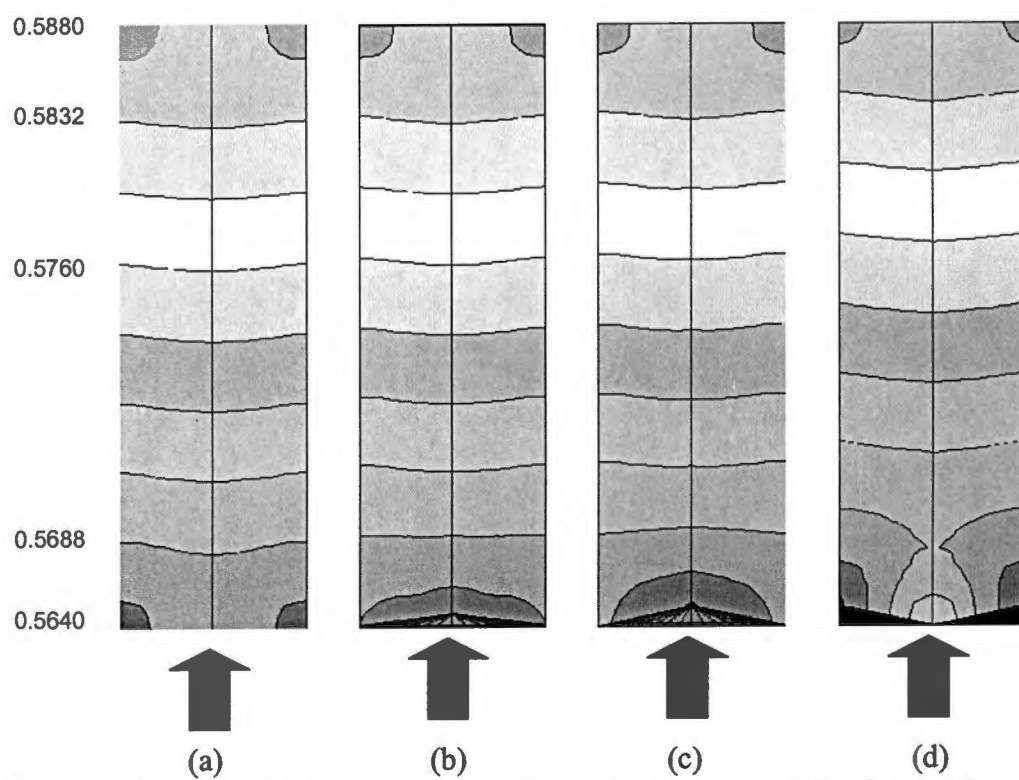


Figure 4.11 Effects of piston geometries to void ratio variation ($\tan \delta = 0.39$):
 (a) flat piston; (b) slightly convex piston; (c) greatly convex piston; (d) concave piston.

described in Section 4.1, and because of the side wall friction, this mechanical stress is the greatest at the piston (bottom) and decreases along the length of the column. In addition to this mechanical compression, the piston displacement causes a pressure increase in the fluid (solvent). Since the end away from the piston (top) is at atmospheric pressure, the column is subjected to a hydraulic gradient. The dissipation of this pore pressure is analogous to the classical consolidation problem in soil mechanics. The consolidation of the bed is governed by the permeability, which is related to the void ratio of the packing material, which in turn varies with mean stress. Thus, the consolidation and fluid flow are coupled to the mechanical compression.

4.2.1 Idealization of Consolidation in HPLC Columns

The idealization of the chromatography columns during consolidation is similar to that described in Section 4.1.1.1. The HPLC column is 16.0 cm long with a diameter of 5.0 cm, as shown in Figure 4.1. Due to the axisymmetric nature of the column and packing process, the column can be simplified to a two-dimensional model by taking advantage of the axial symmetry as illustrated in Figure 4.2. 4-node linear axisymmetric continuum elements with pore pressure were used for the packing material and contact elements with a coefficient of friction $= \tan \delta = 0.21$ were used to represent the frictional surface between the Kromasil bed and the steel wall. These elements are similar to those described in Section 4.1.1.1, except an additional degree of freedom for pore pressure is added. As in the mechanical analysis, a vertical constraint was imposed on top of the column while a displacement of 3.40 mm (corresponding to mean compression pressure of about 130 bars) was applied at the bottom of the bed corresponding to the piston displacement, as shown in

Figure 4.3. The pore pressures were free to dissipate on top of the column, corresponding to a flange which is connected to atmosphere. This boundary condition was established by setting the pore pressure equal to zero at each of the nodes across the top of the column.

4.2.2 Types of Coupled Numerical Analysis

Two types of analysis were performed: (1) Steady-state analysis, and (2) Transient analysis. The steady-state analysis enforces flow conditions such that for every increment of time, the magnitude and direction of the flow velocity are constant at any point. On the other hand, the transient analysis allows the magnitude or direction of the flow velocity to change with time at any point in the flow field during the process. This transient consolidation analysis can be terminated either when the specified consolidation time has been reached or when the steady-state conditions (magnitude and direction of flow are constant) have been reached

4.2.3 Material Modeling

A coupled flow and deformation model was developed to further simulate the effects of a single phase fully saturated flow on the radial heterogeneity of the packed chromatography beds. This coupled analysis is important because the permeability of the packing material is influenced by the void ratio of the particles, which is in turn influenced by the stress state. Since the stress state is influenced by the fluid potential, a coupled analysis may be required. The relations between permeability and void ratio were measured in the laboratory as reported in Section 3.2. For the numerical analysis, the experimental relationship, $k = 0.0076e_v^{8.28}$ was used, where e_v = void ratio of the packing material, and k = the permeability coefficient in cm/s

As illustrated in Section 4.1.2.1, the packing material was represented by a frictional material model (Drucker-Prager nonlinear elastic-plastic model), in which yielding was permitted. Laboratory results obtained from direct shear tests and consolidation tests with falling head permeability tests were used to determine parameters for the model. The stainless steel column surrounding the bed was represented as a linear elastic material with an assumed modulus of elasticity = 2×10^5 kPa and a Poisson ratio = 0.3. In the elastic range, the porous elastic material model implemented in ABAQUS was used, in which the change in volume of the material is proportional to the logarithm of the mean stress. Details of this model are provided in Section 4.1.1.1. Poisson's ratio was assumed to be 0.3, and values of $\kappa = 0.010$, $p_0 = 0.0$ kPa, and $p_t^{el} = 100.0$ kPa were used to reproduce the laboratory response, as discussed in Section 4.1.2.1. A linear Drucker-Prager yield surface function, F , was used to describe the yielding of the packing material (ABAQUS, 1998). A non-associative flow rule was used with the dilatation angle $\psi = 0$ such that non-dilatant response could be represented. Based on the friction angle measured for a similar silica packing material (Mihlbachler *et al.*, 1998), values of $\beta = 46^\circ$, and $d = 0.73$ kPa were used to represent the linear yield surface function. These material parameters are identical to those used to model the packing process in the absence of pore pressure effects.

Since Reynolds number is about 0.01 during the packing process in the HPLC columns, Darcy's law is valid, as verified by Farkas, *et al* (1999). The solid grains of the packing material and the permeating fluid (solvent) through the packing material were assumed to be fully incompressible.

4.2.4 Steady-state Analysis

Consider a unit volume of porous media such as that shown in Figure 4.12. Such an element is usually called an elemental control volume. The law of conservation of mass for steady-state flow through a saturated porous medium requires that the rate of fluid mass flow into any elemental control volume be equal to the rate of fluid mass flow out of any elemental control volume. The equation of continuity that translates this law into the mathematical form that can be written as (Freeze and Cherry, 1979):

$$\frac{\partial(\rho v_x)}{\partial x} + \frac{\partial(\rho v_y)}{\partial y} + \frac{\partial(\rho v_z)}{\partial z} = 0 \quad (4.3)$$

where ρ is the density of the permeating fluid, v_x , v_y , and v_z are the specific discharge (volume flow rate of permeating liquid per unit area) in the x, y, and z direction, respectively. Since the compressibility of the permeating fluid is small, the density of the fluid, ρ can be

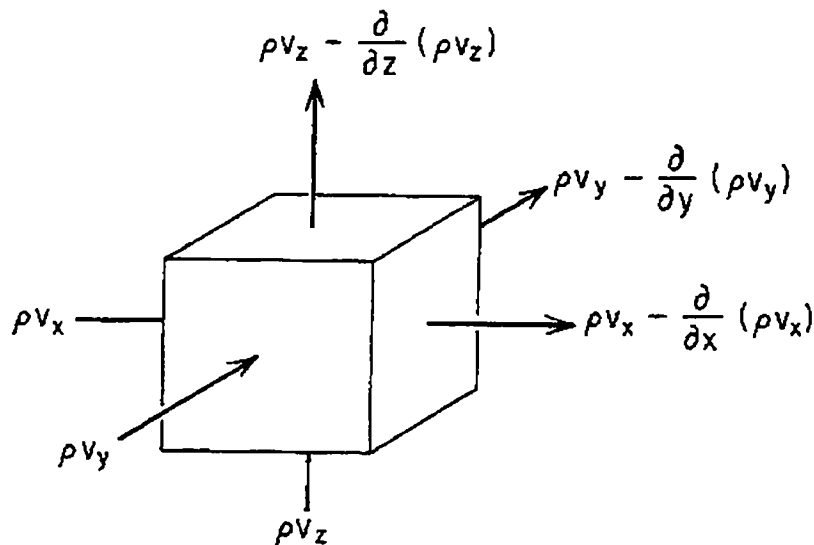


Figure 4.12 Elemental control volume for flow through porous media (Freeze and Cherry, 1979).

assumed to be a constant and thus it can be removed from equation (4.3).

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} = 0 \quad (4.4)$$

Substitution of Darcy's Law for $v_i = K_i \frac{\partial h}{\partial x_i}$ in equation (4.4) yields the equation

of flow for steady state flow through an anisotropic saturated porous medium (Freeze and Cherry, 1979):

$$\frac{\partial}{\partial x} \left(K_x \frac{\partial h}{\partial x} \right) + \frac{\partial}{\partial y} \left(K_y \frac{\partial h}{\partial y} \right) + \frac{\partial}{\partial z} \left(K_z \frac{\partial h}{\partial z} \right) = 0 \quad (4.5)$$

where K_i is the permeability of the porous medium in the i direction, where $i = x, y, z$, and h is the hydraulic head.

For an isotropic and homogeneous porous medium, $K_x = K_y = K_z$, and equation (4.5) can be simplified (Freeze and Cherry, 1979):

$$\frac{\partial^2 h}{\partial x^2} + \frac{\partial^2 h}{\partial y^2} + \frac{\partial^2 h}{\partial z^2} = 0 \quad (4.6)$$

Equation (4.6), known as Laplace's equation, describes the value of hydraulic head, h at any point in a three-dimensional homogeneous, isotropic saturated steady-state flow field. Laplace's equation is also used to describe heat transfer, electric potential, and

diffusion.

Steady-state saturated flow assumes that the rate of flow was “constant” in time inside the HPLC column during the packing process. It was controlled by Darcy’s Law where the storage effects due to compressibility of solid grains and the permeating fluid (solvent) through the packing material were neglected.

4.2.4.1 Parameters and Convergence Criteria

To simulate steady-state flow through the packing material during the packing process, the packing material was assumed to be isotropic, homogeneous, and fully saturated. Automatic incrementation was used because in a typical consolidation analysis, the increments can increase by several orders of magnitude during the simulation (ABAQUS, 1998). To activate automatic incrementation in the steady-state analysis, the UTOL parameter on the *SOILS option was set to a nonzero value. Several points along the axis of the column were identified to follow the displacement and pore pressure during the loading process, as shown in Figure 4.13.

4.2.4.2 Typical Results

Figure 4.14 shows the computed displacements and pore pressures versus time at various locations (Figure 4.13) along the length of the HPLC column during the packing process. As illustrated in Figure 4.14(a), the displacements increased linearly over time as the piston pushed from the bottom of the column. As expected, the computed displacement was found to be maximum at the bottom of the column (Point R where the piston displacement was applied), and it approached 0.00 mm near the top of the column (Point P).

The pore pressures were found to be zero over time at all positions inside the column during the packing process, as illustrated in Figure 4.14(b). This is consistent with the

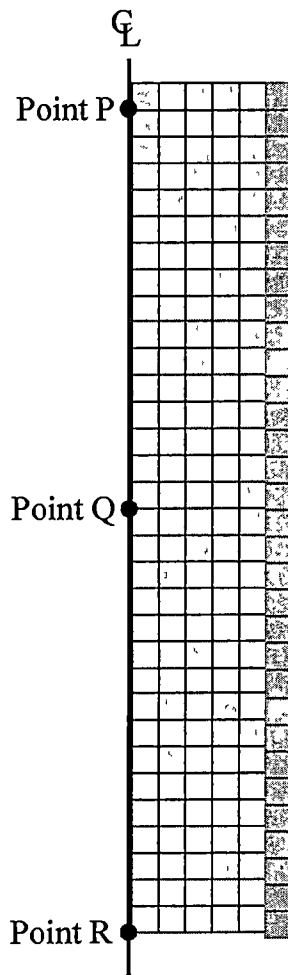


Figure 4.13 Locations inside the center of HPLC column at which nodal displacements and pore pressures were investigated.

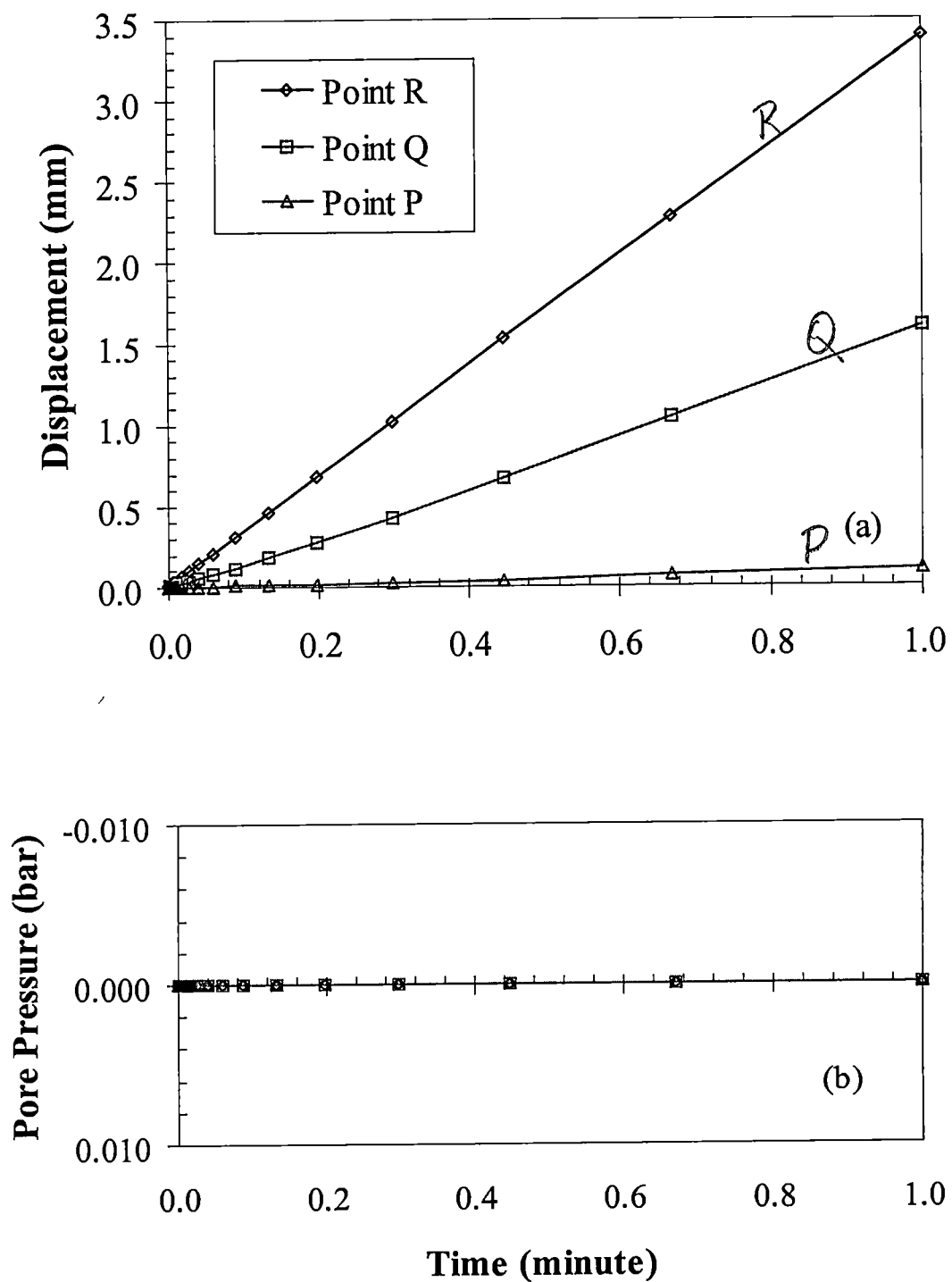


Figure 4.14 Steady-state analysis (a) Displacement vs. time response, (b) Pore pressure vs time response at various positions inside the center of HPLC column (1 bar = 100 kPa)

imposed conditions in the steady-state analysis where in every increment of time, the magnitude and direction of the flow velocity are constant at any point, and thus zero.

4.2.4.3 Comparison of Results

A comparison of numerical results from the coupled mechanical-seepage steady-state and the uncoupled mechanical analysis for Kromasil spherical C8 bonded silica particles with Methanol solvent at the end of the packing process is shown in Figures 4.15 and 4.16. As illustrated in Figure 4.15, the displacement of the packed bed was found to be maximum at the bottom of the bed, decreased along the column, and was nearly zero on top of the column. The displacement distribution for the coupled-mechanical is the same as the displacement distribution for the uncoupled mechanical response because the pore pressure inside the column is small and insignificant. Likewise, the void ratio variation for coupled mechanical-seepage is the same as the void ratio variation for the uncoupled mechanical numerical response.

Since the magnitude of the flow velocity inside HPLC columns actually changes with time at any point in a flow field during the packing process, the steady-state analysis might not be appropriate to simulate the displacement and void ratio variations inside the columns, unless the displacement is applied very slowly. Thus, a transient analysis may be a better model for the flow conditions, and useful to investigate the effect of loading rate on the column. The steady-state analysis and the uncoupled mechanical analysis represent loading conditions such that pore pressures cannot be developed in the column.

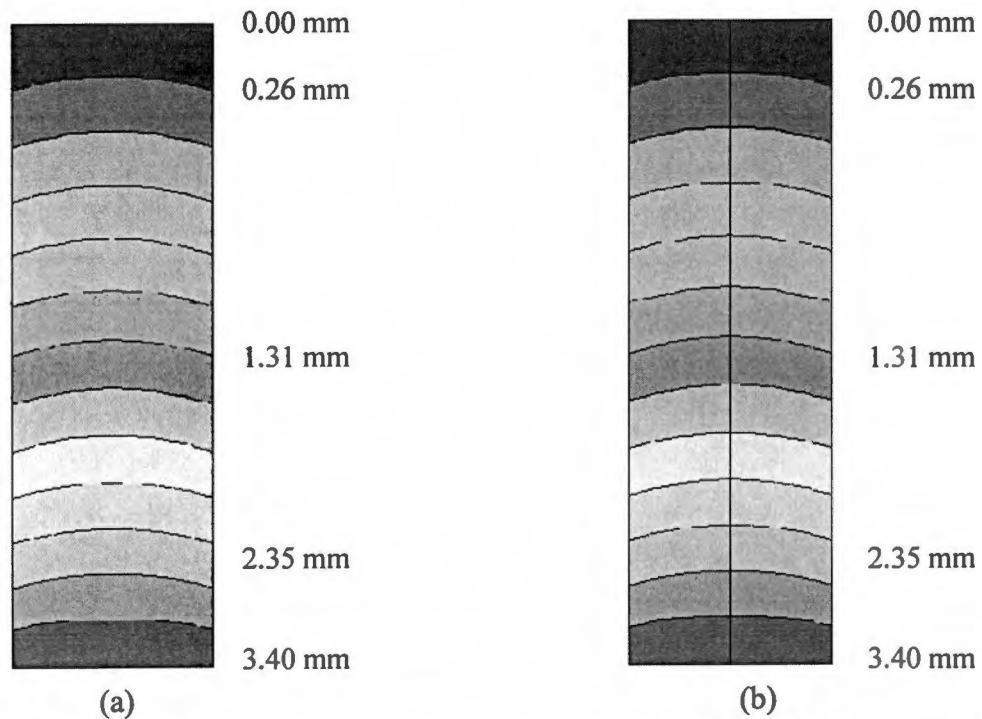


Figure 4.15 Displacement distribution for Kromasil with Methanol ($\tan \delta = 0.21$): (a) Uncoupled mechanical response, (b) Coupled mechanical-seepage steady-state response.

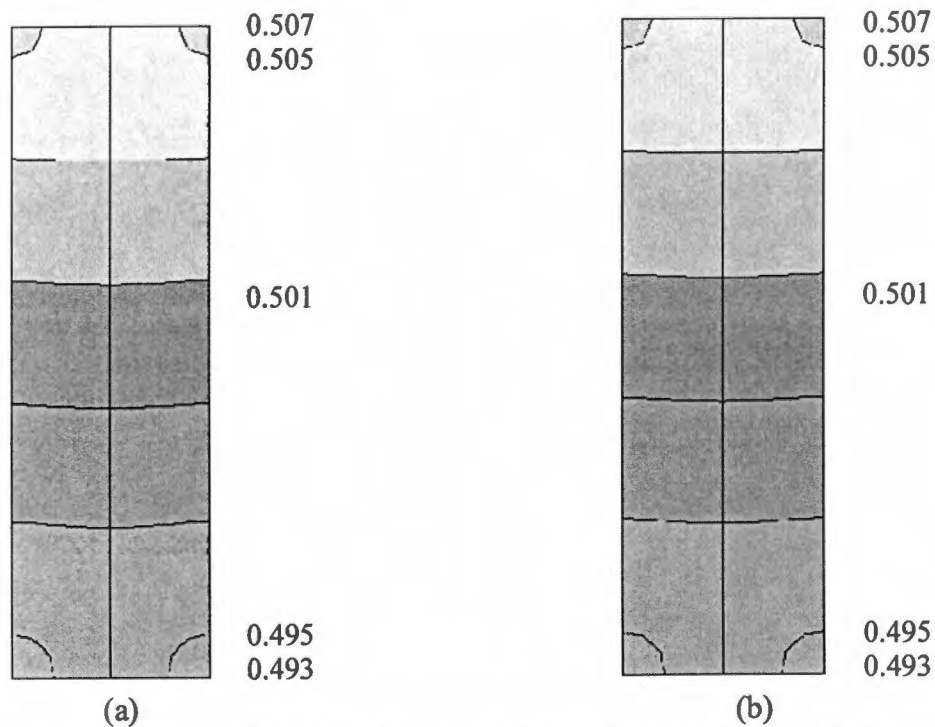


Figure 4.16 Variation of void ratio for Kromasil with Methanol ($\tan \delta = 0.21$): (a) Uncoupled mechanical response, (b) Coupled mechanical-seepage steady-state response.

4.2.5 Transient Analysis

The law of conservation of mass for transient flow in a saturated porous medium requires that the net rate of fluid mass flow into any elemental control volume be equal to the time rate of change of fluid mass storage within the element. This fluid mass storage within the element can be characterized by the specified storage, S_s , which is the volume of fluid released from a unit volume of saturated porous medium for a unit decline in hydraulic head, h :

$$S_s = \rho g (\alpha_{pm} + n\beta_w) \quad (4.7)$$

where ρ is the density of the permeating fluid, g is gravitational acceleration, α_{pm} is the compressibility of the porous medium, n is the porosity of the porous medium, and β_w is the compressibility of the permeating fluid.

With reference to Figure 4.3, the equation of continuity that describes the transient flow through a saturated porous medium takes the form (Freeze and Cherry, 1979):

$$\frac{\partial(\rho v_x)}{\partial x} + \frac{\partial(\rho v_y)}{\partial y} + \frac{\partial(\rho v_z)}{\partial z} = \frac{\partial(\rho n)}{\partial t} \quad (4.8)$$

The right-hand side of equation (4.8) can be expanded and simplified by substituting the time rate of change of fluid mass storage, $\rho S_s \partial h / \partial t$:

$$\frac{\partial(\rho v_x)}{\partial x} + \frac{\partial(\rho v_y)}{\partial y} + \frac{\partial(\rho v_z)}{\partial z} = \rho S_s \frac{\partial h}{\partial t} \quad (4.9)$$

Expanding the terms on the left-hand side by the chain rule and recognizing that terms of the form $v_x \partial \rho / \partial x$ are insignificant compared to terms of the form $\rho \partial v_x / \partial x$, the $v_x \partial \rho / \partial x$ terms can be removed from the equation. Equation (4.9) can be further simplified by eliminating ρ from both sides and substituting Darcy's Law to yield the equation for transient flow through a fully saturated anisotropic porous medium (Freeze and Cherry, 1979):

$$\frac{\partial}{\partial x} \left(K_x \frac{\partial h}{\partial x} \right) + \frac{\partial}{\partial y} \left(K_y \frac{\partial h}{\partial y} \right) + \frac{\partial}{\partial z} \left(K_z \frac{\partial h}{\partial z} \right) = S_s \frac{\partial h}{\partial t} \quad (4.10)$$

If the medium is homogeneous and isotropic, which is an appropriate assumption for the HPLC columns prior to the packing process, equation (4.10) can be simplified (Freeze and Cherry, 1979):

$$\frac{\partial^2 h}{\partial x^2} + \frac{\partial^2 h}{\partial y^2} + \frac{\partial^2 h}{\partial z^2} = \frac{S_s}{K} \frac{\partial h}{\partial t} \quad (4.11)$$

In summary, transient saturated flow assumes that the rate of flow changes with time inside HPLC columns during the packing process. It is controlled by Darcy's Law and the storage effects due to the compressibility of the packing material.

4.2.5.1 Parameters and Convergence Criteria

In ABAQUS, a transient coupled mechanical-seepage analysis is performed when the CONSOLIDATION parameter is included on the *SOILS option. In the transient case, the backward difference operator is used to integrate the continuity equation. This operator

provides unconditional stability so that the only concern with respect to time integration is accuracy (ABAQUS, 1998). The integration procedure used in ABAQUS for consolidation analysis introduces a relationship between the minimum usable time increment and the element size, as shown below for fully saturated flows. If time increments smaller than these values are used, spurious oscillations may appear in the solution. These oscillations are nonphysical and may cause problems if pressure-sensitive plasticity is used to model the porous medium (ABAQUS, 1998). If the problem requires analysis with smaller time increments than the relationships given below allow, a finer mesh is required. Generally, there is no upper limit on the time step except accuracy, since the integration procedure is unconditionally stable unless nonlinearities cause convergence problems (ABAQUS, 1998).

A simple guideline that can be used for the minimum usable time increment in the case of fully saturated flow is (ABAQUS, 1998).

$$\Delta t > \frac{\gamma_w(1 + \beta_F v_w)}{6Ek} \left(1 - \frac{E}{K_g} \right)^2 (\Delta l)^2 \quad (4.12)$$

where Δt is the time increment, γ_w is the specific weight of the wetting liquid, E is the Young's modulus of the porous material, k is the permeability of the porous material, v_w is the magnitude of the velocity of the pore fluid, β_F is the velocity coefficient in Forchheimer's flow law, K_g is the bulk modulus of the solid grains, and Δl is a typical element dimension.

For Darcy flow, the velocity coefficient in Forchheimer's flow law, β_F , is assumed to be zero. In addition, the bulk modulus of the solid grains, K_g , is assumed to be infinite because the packing material is assumed to be fully incompressible. Thus, equation (4.12)

can be simplified (ABAQUS, 1998):

$$\Delta t > \frac{\gamma_w}{6 E k} (\Delta l)^2 \quad (4.13)$$

For the HPLC column finite element mesh shown in Figure 4.13, $\Delta l = 0.005$ m, $\gamma_w = 7.75$ kN/m³, $k = 3.53 \times 10^{-2}$ m/day, and $E = p/\kappa = 1,300,000$ kPa. This results in Δt of 7.0×10^{-8} day. The maximum pore pressure that was allowed to dissipate in each time increment, UTOL = 1,300 kPa (13.0 bar) was assumed, which is about 10% of the initial pore pressure.

In addition to the convergence criteria above, the maximum rate of pore pressure dissipation over time in each time step is required for the transient reaching steady-state analysis to describe the maximum rate of pore pressure dissipation used to define the steady-state condition. However, due to the relatively high permeability of the packing material, this type of numerical solution would stop when the flows reached the steady-state conditions, usually before the intended piston displacement was reached. Thus, this type of analysis was not fully investigated.

4.2.5.2 Typical Results

Figure 4.17 shows the computed displacements and pore pressures versus time at the same locations investigated previously (Figure 4.13) in the HPLC column during the packing process. The load was applied to the bottom of the column through a piston within two minutes, and then the piston was held at its final displacement for two minutes to allow the pore pressures inside the column to dissipate. This loading is typical of the actual packing process (Guiochon, *et al.*, 1999b). As illustrated in Figure 4.17(a), the displacements increased linearly for 2 minutes and then remained constant over time as the piston pushed

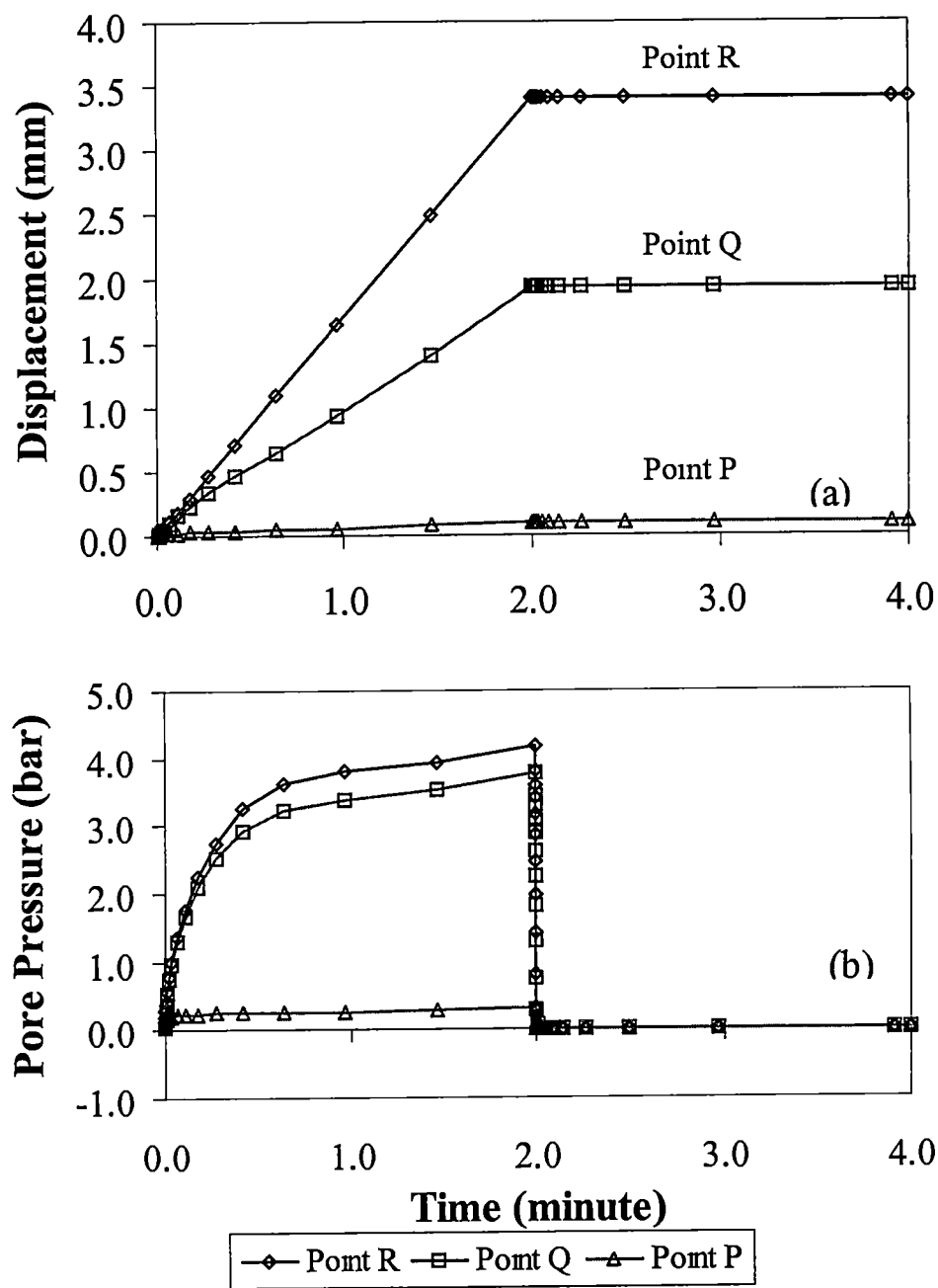


Figure 4 17 Transient analysis (a) Displacement vs. time response, (b) Pore pressure vs. time response at various positions inside the center of HPLC column (1 bar = 100 kPa).

from the bottom of the column. Similar to the uncoupled mechanical analysis, the displacement was found to be maximum at the bottom of the column (Point R where displacement was applied) and reduced along the column (away from the piston), and it approached zero on top of the column (Point P), as shown in Figure 4.17(a).

As expected, the computed pore pressure increased as the piston pushed from the bottom during the packing process, as shown in Figure 4.17(b). Once the piston stopped pushing from the bottom of the column, the pore pressures at the bottom of the column dissipated rapidly through the top of the column (flange), as illustrated in Figure 4.17(b). Since the drainage distances of Points R and Q are larger than at Point P, the pore pressure build up at these points is greater.

Figure 4.18 shows the void ratio variation and mean pressure distribution computed at the end of the packing process. As illustrated in Figure 4.18(a), there was some axial and radial heterogeneity along the column. The void ratio was found to be lower near the edges at the bottom of the column, increased along the column, and was maximum near the edges on top of the column. This indicates that the density is higher near the edges than the center of the column at the bottom and on top of the column. Figure 4.18(b) shows the mean stress distribution corresponding to the void ratio distribution, illustrated in Figure 4.18(a). The mean pressure was found to be maximum near the edges at the bottom of the column and decreasing along the column.

4.2.5.3 Comparison of Results

The variation of void ratio and distribution of mean pressure at the end of the packing process for the uncoupled mechanical analysis and the coupled transient analysis are shown in Figures 4.19 and 4.20. As illustrated in Figure 4.19(b), the void ratio was found to be

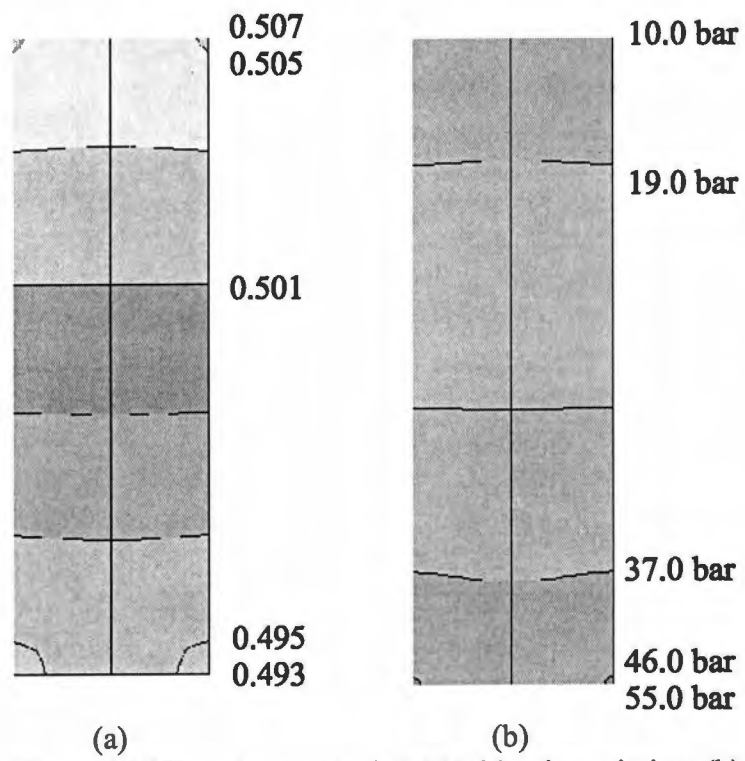


Figure 4.18 Transient analysis (a) Void ratio variation, (b) Mean pressure distribution inside the HPLC column (1 bar = 100 kPa).

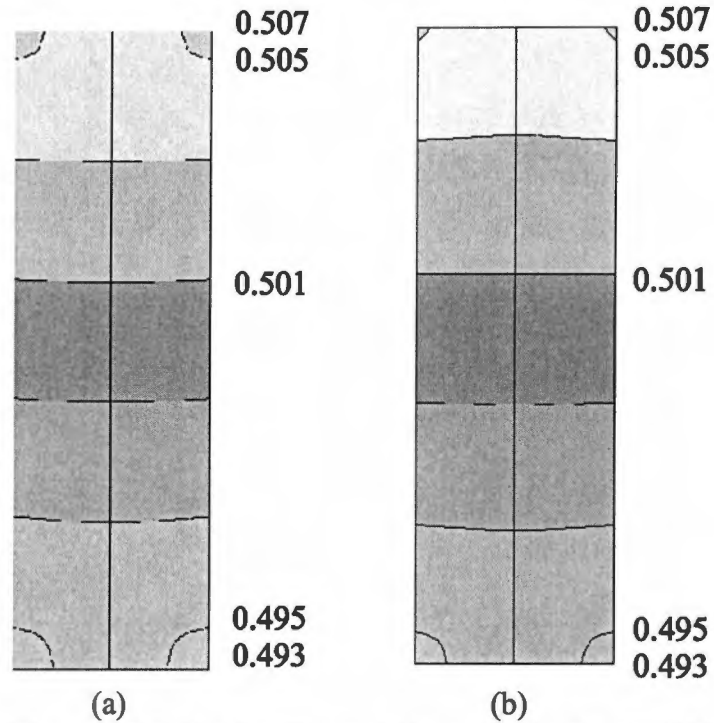


Figure 4.19 Void ratio variations inside the HPLC columns (a) Uncoupled Mechanical response, (b) Coupled Mechanical-Seepage response under 2 minutes loading.

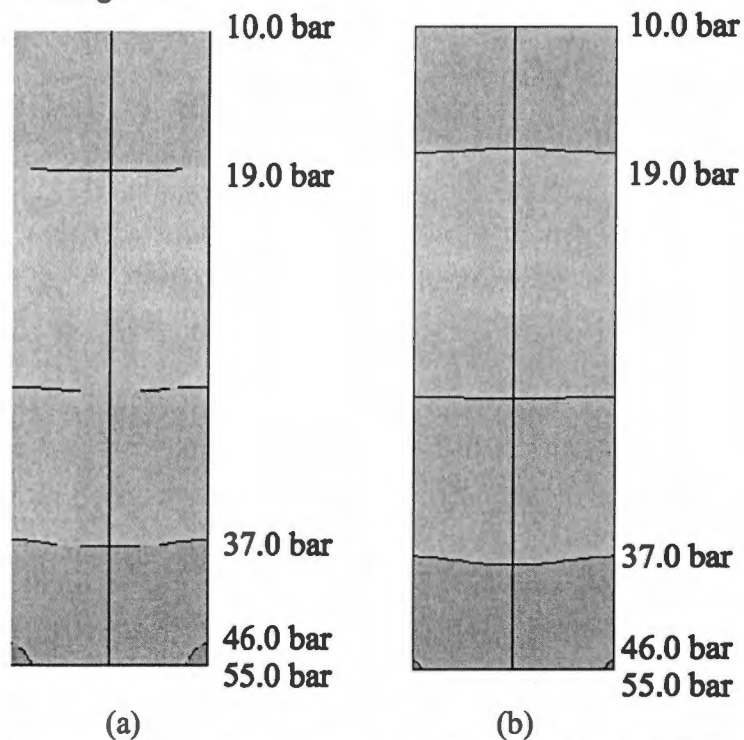


Figure 4.20 Mean pressure distributions inside the HPLC columns (a) Uncoupled Mechanical response, (b) Coupled Mechanical-Seepage response under 2 minutes loading.

lower near the edges at the bottom of the column, increased along the column, and largest near the edges on top of the column. This void ratio distribution computed from the transient analysis is similar to the uncoupled mechanical and the coupled mechanical-seepage steady-state response, as shown in Figure 4.19(a), indicating that the pore pressures developed inside the HPLC columns during the 2 minutes loading process do not have significant effects on the void ratio or density of the columns.

Figure 4.20(b) shows the mean stress distribution corresponding to the void ratio distribution, illustrated in Figure 4.19(b). The results suggest that the mean pressure distribution is similar to the uncoupled mechanical and the coupled mechanical-seepage steady-state response, shown in Figure 4.20(a).

4.2.6 Parametric Study

To further understand the coupled mechanical-seepage analysis, especially the effects of the rate of loading in the preparation of HPLC columns, a parametric study was conducted by varying the loading rate of the bottom piston.

4.2.6.1 Effects of the Rate of Consolidation

To illustrate the effects of the piston loading rate on the computed displacements and pore pressures over time at various locations inside the center of HPLC column during the packing process, the analysis was repeated with a faster loading rate. The load was applied to the bottom of the column through a piston within one minute and the piston was held at its final displacement for two minutes. The computed displacements and pore pressures over time at various locations inside the center of HPLC column for the 1-minute loading are shown in Figure 4.21. For comparison, the results from the 2-minute loading are also shown in Figure 4.21. As illustrated in Figure 4.21(a), the displacement increased linearly for a

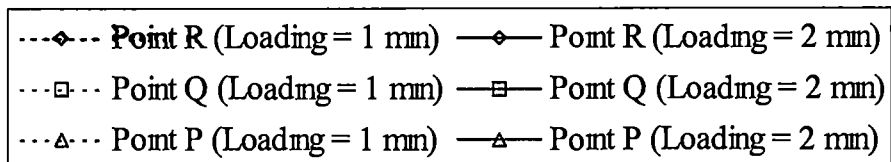
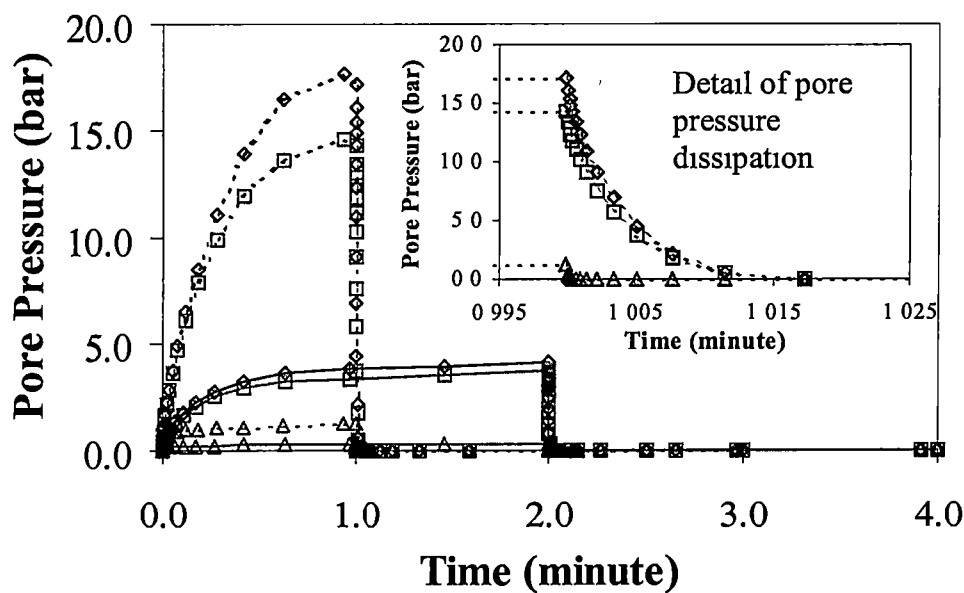
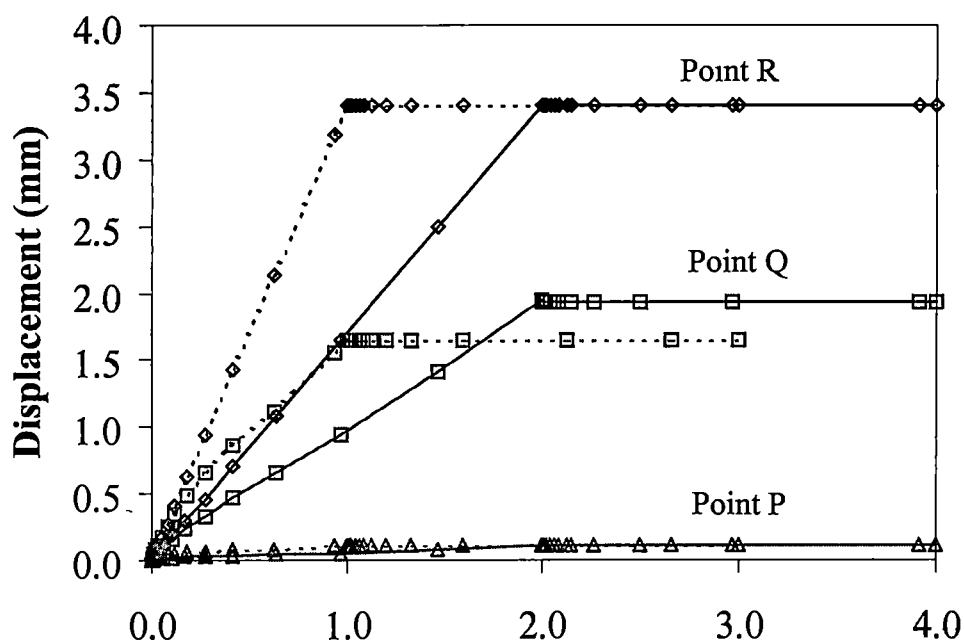


Figure 4.21 Transient analysis (a) Displacement vs. time response, (b) Pore pressure vs. time response at various positions inside the center of HPLC column (1 bar = 100 kPa).

period of 1 or 2 minutes, after which it remained constant over time.

The computed pore pressures increased as the piston pushed from the bottom during the packing process, and the pore pressure increase at Point R during the 1 minute loading was about 3.6 times greater than during the 2-minute loading. Once the piston stopped pushing from the bottom, the pore pressures at the bottom of the column dissipated rapidly, as illustrated in Figure 4.21(b). The inset figure in Figure 4.21(b) shows detail of the pore pressure dissipation with an expanded time scale.

Figures 4.22 and 4.23 show the computed void ratio variation and mean pressure distribution at the end of the packing process. For comparison, the results for the uncoupled mechanical and coupled mechanical-seepage response (loaded for both 2-minute and 1-minute) are included. In this comparison, the uncoupled mechanical analysis can be considered to represent a column in which the piston is displaced very slowly, such that no pore pressure is built up. The coupled mechanical-seepage analysis with a 2 minutes period of loading represents an intermediate loading rate, while the 1 minute loading can be considered a fast loading rate. As illustrated in Figure 4.22(c), when the piston displacement was applied over a 1 minute period, there was less axial and radial heterogeneity in the column. The void ratio distribution was much more uniform, especially at the bottom of the column compared with the uncoupled mechanical and coupled mechanical-seepage response, as shown in Figures 4.22 (a) and (b).

Figure 4.23 shows the mean stress distribution corresponding to the void ratio distribution, illustrated in Figure 4.22. Irrespective of loading rate, the coupled mean pressure was found to be maximum near the edges at the bottom of the column and decreased

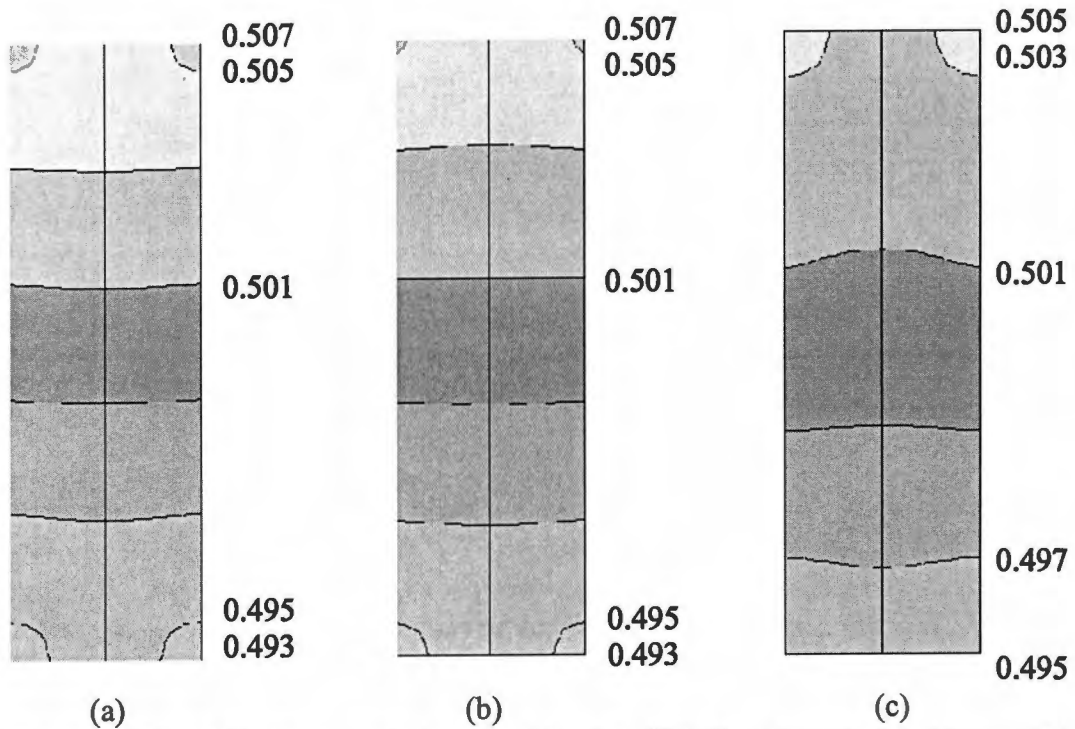


Figure 4.22 Void ratio variations inside the HPLC columns (a) Uncoupled Mechanical response, (b) Coupled Mechanical-Seepage response under 2 minutes loading, and (c) Coupled Mechanical-Seepage response under 1 minute loading.

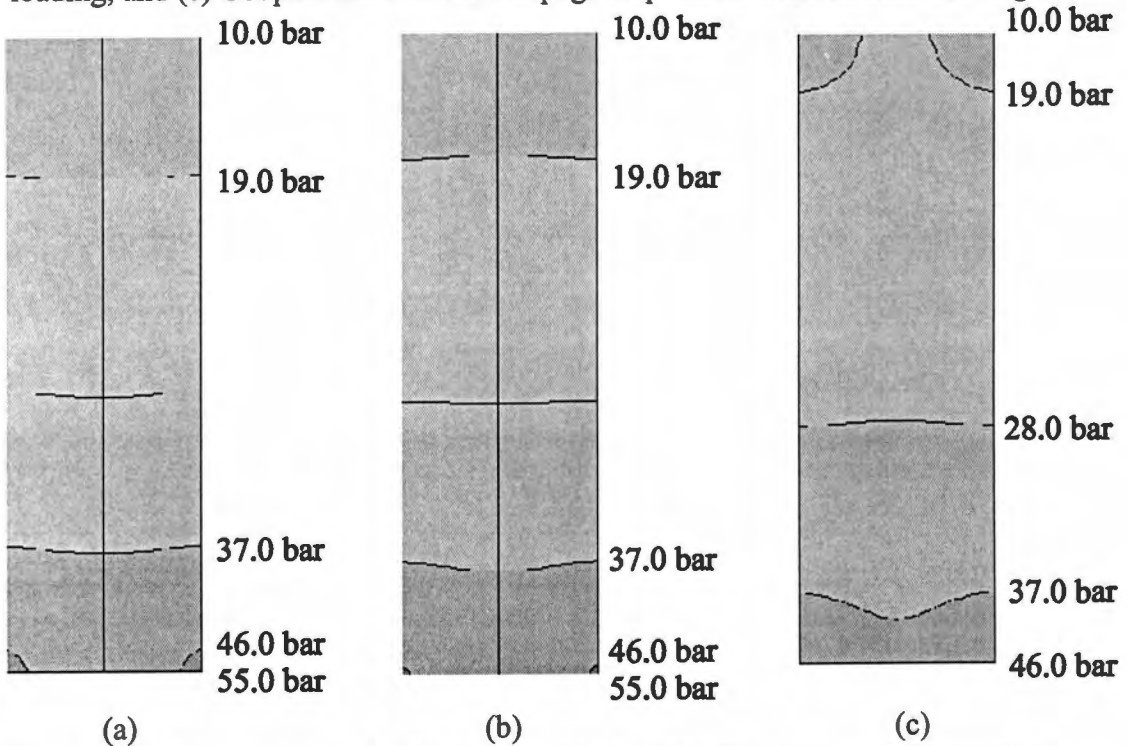


Figure 4.23 Mean pressure distributions inside the HPLC columns (a) Uncoupled Mechanical response, (b) Coupled Mechanical-Seepage response under 2 minutes loading, and (c) Coupled Mechanical-Seepage response under 1 minute loading.

along the column. However, the mean pressure is more uniform when the load is applied over 1 minute than when applied over 2 minutes or very slowly.

4.2.7 Discussion of Results

The numerical results suggest that the rate of loading is important when packing the HPLC columns because if the piston is pushed relatively fast (with respect to the permeability of the packing material), the pore pressure does not have enough time to dissipate through the flange on top of the column, and a more uniform column is produced. However, if the piston is pushed slowly with respect to the permeability of the packing material, the pore pressures would dissipate quickly and a less uniform column would be obtained. This is consistent with the laboratory observations in which a more uniform column was produced if the bottom piston was pushed quickly with respect to the permeability of the packing material (Guiochon, 1999b). However, in practice, the piston cannot be pushed too quickly due to the difficulty in controlling the piston pressure that is applied to the column.

Chapter 5

Conclusions and Recommendations

The efficiency of the separation process conducted in High Performance Liquid Chromatography (HPLC) columns is strongly dependent upon techniques used to prepare or pack the column. During the preparation of the column, friction between the packing material and the wall of the column results in a nonuniform density or void ratio across the radius of the column, which significantly reduces the efficiency of the separation process. Concepts from soil mechanics and numerical approximations using the commercial finite element code, ABAQUS (5.8) were utilized to investigate the mechanics of the chromatography column preparation process.

To obtain parameters for the numerical analysis, several series of laboratory tests were conducted. These tests included interface direct shear tests on both Zorbax spherical C18 and Kromasil spherical C8 packing materials, and fixed ring consolidation tests incorporating falling head permeability tests on the Kromasil C8 packing materials. The lowest interface coefficient of friction between the silica sample and the stainless steel plate was found in Kromasil C8 with methanol solvent ($\tan \delta = 0.21$). The test results found that the contact between the Zorbax with methanol and the stainless steel plate had the greatest coefficient of friction ($\tan \delta = 0.39$). This value of the interface friction angle is close to the two thirds of the internal friction angle ($\phi = 36^\circ$) measured Muhlbachler *et al* (1998) on a similar packing material Pro 10 Sil, which is consistent with the results reported by Potyondy (1961) for interface between soils and various construction materials.

In the numerical analysis, the packing material was represented by the Drucker-Prager elastic-plastic model, which is often used to represent the frictional behavior of soil. A linear Drucker-Prager yield surface function, F , was used to describe the yielding of the packing material. A non-associative flow rule was used such that non-dilatant response could be represented. In the elastic range, a nonlinear porous elastic material model was used, in which the change in volume of the material is proportional to the logarithm of the mean stress. The stainless steel column surrounding the bed was represented as a linear elastic material.

The numerical results suggest that if the interface friction is reduced, the axial and radial heterogeneity of the column is significantly reduced. The yielded zones nearly vanished when the wall friction is reduced. A slightly concave piston may improve the radial homogeneity of the column, especially at the bottom of the column.

To investigate the seepage effects inside the HPLC columns during the packing process, a coupled mechanical-seepage model was used. The results suggested that the rate of loading was important when packing the HPLC columns. If the piston was pushed quickly with respect to its permeability, the pore pressures do not have enough time to dissipate through the flange on top of the column, and a more uniform column, especially at the bottom, could be produced. However, if the piston was pushed slowly with respect to its permeability, the pore pressures would dissipate rapidly and a more non-uniform column would be produced.

Further laboratory testing such as triaxial tests should be performed to improve the characterization of the packing material. Additional numerical analyses may also be useful to evaluate the packing process of the column and the effect of loading rate. These analyses

include adding a low permeable layer on top of the column such that the pore pressure dissipation at the top of the column could be controlled, to investigate the effects on the column void ratio.

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Appendices

Appendix A

Interface Direct Shear Test Data:

Shear Stress vs. Displacement Response

Sample ID:	Z10bm1					
Description of the Sample:	Zorbax C18 Dry Silica	Solvent:	Methanol			
Diameter of the Sample:	2.5	in	=	6.35	cm	
Area of the Sample:	4.9087	in ²	=	31.67	cm	
Normal Pressure:	10	bar				
Mass of the Sample (wet):	40.3	g				
Initial Height of the Sample:	1.5400	cm				
Initial Volume of the Sample:	48.7706	cm ³				
Initial Density of the Sample:	0.8263	g/cm ³				
Horizontal Displacement	Horizontal Dial	Shear	Shear	Normalized Shear	Vertical	Change of Vertical
(inch)	Reading (m)	Force (lb)	Stress (kPa)	Force (kPa)	Displacement (in)	Displacement (m)
0	0.000000	0	0.00	0.00	0.00E+00	0.0000000
0.002	0.000051	19	26.69	18.40	0.00E+00	0.0000000
0.004	0.000102	41	57.59	39.71	0.00E+00	0.0000000
0.006	0.000152	65	91.30	62.95	0.00E+00	0.0000000
0.008	0.000203	99	139.05	95.87	0.00E+00	0.0000000
0.01	0.000254	126	176.98	122.02	0.00E+00	0.0000000
0.012	0.000305	148	207.88	143.33	0.00E+00	0.0000000
0.014	0.000356	167	234.57	161.73	0.00E+00	0.0000000
0.016	0.000406	182	255.64	176.25	0.00E+00	0.0000000
0.018	0.000457	196	275.30	189.81	0.00E+00	0.0000000
0.02	0.000508	220	309.01	213.05	0.00E+00	0.0000000
0.022	0.000559	227	318.84	219.83	0.00E+00	0.0000000
0.024	0.000610	234	328.67	226.61	0.00E+00	0.0000000
0.026	0.000660	243	341.32	235.33	0.00E+00	0.0000000
0.028	0.000711	255	358.17	246.95	0.00E+00	0.0000000
0.03	0.000762	260	365.19	251.79	0.00E+00	0.0000000
0.032	0.000813	263	369.41	254.70	1.00E-05	0.0000003
0.034	0.000864	267	375.03	258.57	2.00E-05	0.0000005
0.036	0.000914	270	379.24	261.48	4.00E-05	0.0000010
0.038	0.000965	272	382.05	263.41	8.00E-05	0.0000020
0.04	0.001016	276	387.67	267.29	9.00E-05	0.0000023
0.042	0.001067	276	387.67	267.29	1.00E-04	0.0000025
0.044	0.001118	276	387.67	267.29	1.20E-04	0.0000030
0.046	0.001168	276	387.67	267.29	1.40E-04	0.0000036
0.048	0.001219	276	387.67	267.29	1.50E-04	0.0000038
0.05	0.001270	277	389.07	268.26	1.60E-04	0.0000041
0.052	0.001321	278	390.48	269.22	1.80E-04	0.0000046
0.054	0.001372	278	390.48	269.22	1.90E-04	0.0000048
0.056	0.001422	278	390.48	269.22	2.10E-04	0.0000053
0.058	0.001473	278	390.48	269.22	2.20E-04	0.0000056
0.06	0.001524	278	390.48	269.22	2.20E-04	0.0000056
0.062	0.001575	278	390.48	269.22	2.30E-04	0.0000058
0.064	0.001626	277	389.07	268.26	2.35E-04	0.0000060
0.066	0.001676	277	389.07	268.26	2.40E-04	0.0000061
0.068	0.001727	277	389.07	268.26	2.50E-04	0.0000063
0.07	0.001778	278	390.48	269.22	2.50E-04	0.0000063
0.072	0.001829	279	391.88	270.19	2.50E-04	0.0000063
0.074	0.001880	278	390.48	269.22	2.60E-04	0.0000066
0.076	0.001930	279	391.88	270.19	2.60E-04	0.0000066
0.078	0.001981	276	387.67	267.29	2.60E-04	0.0000066
0.08	0.002032	276	387.67	267.29	2.60E-04	0.0000066
0.082	0.002083	278	390.48	269.22	2.60E-04	0.0000066
0.084	0.002134	276	387.67	267.29	2.70E-04	0.0000069
0.086	0.002184	276	387.67	267.29	2.70E-04	0.0000069
0.088	0.002235	274	384.86	265.35	2.70E-04	0.0000069
0.09	0.002286	273	383.45	264.38	2.80E-04	0.0000071
0.092	0.002337	273	383.45	264.38	2.80E-04	0.0000071
0.094	0.002388	275	386.26	266.32	2.85E-04	0.0000072
0.096	0.002438	273	383.45	264.38	2.85E-04	0.0000072
0.098	0.002489	274	384.86	265.35	2.90E-04	0.0000074
0.1	0.002540	276	387.67	267.29	2.90E-04	0.0000074
0.102	0.002591	277	389.07	268.26	2.90E-04	0.0000074
0.104	0.002642	276	387.67	267.29	2.90E-04	0.0000074
0.106	0.002692	276	387.67	267.29	3.00E-04	0.0000076
0.108	0.002743	273	383.45	264.38	3.00E-04	0.0000076
0.11	0.002794	274	384.86	265.35	3.10E-04	0.0000079
0.112	0.002845	273	383.45	264.38	3.10E-04	0.0000079
0.114	0.002896	273	383.45	264.38	3.10E-04	0.0000079
0.116	0.002946	272	382.05	263.41	3.10E-04	0.0000079
0.118	0.002997	272	382.05	263.41	3.10E-04	0.0000079
0.12	0.003048	270	379.24	261.48	3.10E-04	0.0000079
0.122	0.003099	272	382.05	263.41	3.15E-04	0.0000080
0.124	0.003150	275	386.26	266.32	3.20E-04	0.0000081
0.126	0.003200	272	382.05	263.41	3.20E-04	0.0000081

Note: There were no methanol around and on top of the sample.

Sample ID:	Z10bm2					
Description of the Sample:	Zorbax C18 Dry Silica	Solvent:	Methanol			
Diameter of the Sample:	2.5	in	=	6.35	cm	
Area of the Sample:	4.9087	in ²	=	31.67	cm	
Normal Pressure:	10	bar				
Mass of the Sample (wet):	39.0	g				
Initial Height of the Sample:	1.1400	cm				
Initial Volume of the Sample:	36.1029	cm ³				
Initial Density of the Sample:	1.0802	g/cm ³				
Horizontal Displacement	Horizontal Dial Reading	Shear	Shear Stress	Normalized Shear	Vertical	Change of Vertical
(inch)	(m)	Force (lb)	(kPa)	Force (kPa)	Displacement (in)	Displacement (m)
0	0.000000	0	0.00	0.00	0.00E+00	0.0000000
0.002	0.000051	6	8.43	5.81	0.00E+00	0.0000000
0.004	0.000102	33	46.35	31.96	0.00E+00	0.0000000
0.006	0.000152	60	84.28	58.11	0.00E+00	0.0000000
0.008	0.000203	91	127.82	88.13	0.00E+00	0.0000000
0.01	0.000254	112	157.31	108.46	0.00E+00	0.0000000
0.012	0.000305	137	192.43	132.67	1.00E-05	0.0000003
0.014	0.000356	155	217.71	150.11	3.00E-05	0.0000008
0.016	0.000406	169	237.38	163.66	4.00E-05	0.0000010
0.018	0.000457	181	254.23	175.29	6.00E-05	0.0000015
0.02	0.000508	191	268.28	184.97	9.00E-05	0.0000023
0.022	0.000559	202	283.73	195.62	1.30E-04	0.0000033
0.024	0.000610	206	289.35	199.50	1.40E-04	0.0000036
0.026	0.000660	213	299.18	206.28	1.40E-04	0.0000036
0.028	0.000711	219	307.60	212.09	1.40E-04	0.0000036
0.03	0.000762	225	316.03	217.90	1.50E-04	0.0000038
0.032	0.000813	232	325.86	224.68	2.10E-04	0.0000053
0.034	0.000864	236	331.48	228.55	2.80E-04	0.0000071
0.036	0.000914	245	344.12	237.27	2.90E-04	0.0000074
0.038	0.000965	249	349.74	241.14	3.00E-04	0.0000076
0.04	0.001016	253	355.36	245.01	4.00E-04	0.0000102
0.042	0.001067	257	360.98	248.89	5.00E-04	0.0000127
0.044	0.001118	264	370.81	255.67	6.00E-04	0.0000152
0.046	0.001168	266	373.62	257.60	6.60E-04	0.0000168
0.048	0.001219	267	375.03	258.57	7.30E-04	0.0000185
0.05	0.001270	268	376.43	259.54	7.80E-04	0.0000198
0.052	0.001321	269	377.83	260.51	8.20E-04	0.0000208
0.054	0.001372	270	379.24	261.48	8.50E-04	0.0000216
0.056	0.001422	270	379.24	261.48	8.50E-04	0.0000216
0.058	0.001473	270	379.24	261.48	9.00E-04	0.0000229
0.06	0.001524	270	379.24	261.48	9.00E-04	0.0000229
0.062	0.001575	271	380.64	262.44	9.30E-04	0.0000236
0.064	0.001626	271	380.64	262.44	9.50E-04	0.0000241
0.066	0.001676	272	382.05	263.41	9.80E-04	0.0000249
0.068	0.001727	272	382.05	263.41	1.00E-03	0.0000254
0.07	0.001778	274	384.86	265.35	1.03E-03	0.0000262
0.072	0.001829	274	384.86	265.35	1.05E-03	0.0000267
0.074	0.001880	275	386.26	266.32	1.05E-03	0.0000267
0.076	0.001930	276	387.67	267.29	1.05E-03	0.0000267
0.078	0.001981	276	387.67	267.29	1.09E-03	0.0000277
0.08	0.002032	276	387.67	267.29	1.10E-03	0.0000279
0.082	0.002083	276	387.67	267.29	1.13E-03	0.0000287
0.084	0.002134	275	386.26	266.32	1.13E-03	0.0000287
0.086	0.002184	266	373.62	257.60	1.13E-03	0.0000287
0.088	0.002235	267	375.03	258.57	1.13E-03	0.0000287
0.09	0.002286	266	373.62	257.60	1.14E-03	0.0000290
0.092	0.002337	266	373.62	257.60	1.15E-03	0.0000292
0.094	0.002388	264	370.81	255.67	1.17E-03	0.0000297
0.096	0.002438	273	383.45	264.38	1.19E-03	0.0000302
0.098	0.002489	275	386.26	266.32	1.19E-03	0.0000302
0.1	0.002540	276	387.67	267.29	1.20E-03	0.0000305
0.102	0.002591	274	384.86	265.35	1.20E-03	0.0000305
0.104	0.002642	276	387.67	267.29	1.21E-03	0.0000307
0.106	0.002692	272	382.05	263.41	1.22E-03	0.0000310
0.108	0.002743	273	383.45	264.38	1.23E-03	0.0000312
0.11	0.002794	270	379.24	261.48	1.24E-03	0.0000315
0.112	0.002845	268	376.43	259.54	1.25E-03	0.0000317
0.114	0.002896	270	379.24	261.48	1.26E-03	0.0000320
0.116	0.002946	270	379.24	261.48	1.26E-03	0.0000320
0.118	0.002997	270	379.24	261.48	1.27E-03	0.0000323
0.12	0.003048	269	377.83	260.51	1.31E-03	0.0000333

Sample ID: Z10bm3 Description of the Sample: Zorbax C18 Dry Silica Solvent: Methanol Diameter of the Sample: 2.5 in = 6.35 cm Area of the Sample: 4.9087 in ² = 31.67 cm ² Normal Pressure: 10 bar Mass of the Sample (wet): 46.4 g Initial Height of the Sample: 1.1400 cm Initial Volume of the Sample: 36.1029 cm ³ Initial Density of the Sample: 1.2852 g/cm ³						
Horizontal Displacement	Horizontal Dial Reading	Shear	Shear Stress	Normalized	Vertical	Change of Vertical
(inch)	(m)	Force (lb)	(kPa)	Shear Force (kPa)	Displacement (in)	Displacement (m)
0	0.000000	0	0.00	0.00	0.00E+00	0.0000000
0.002	0.000051	35	49.16	33.90	0.00E+00	0.0000000
0.004	0.000102	60	84.28	58.11	0.00E+00	0.0000000
0.006	0.000152	92	129.22	89.10	0.00E+00	0.0000000
0.008	0.000203	118	165.74	114.27	0.00E+00	0.0000000
0.01	0.000254	140	196.64	135.58	0.00E+00	0.0000000
0.012	0.000305	159	223.33	153.98	0.00E+00	0.0000000
0.014	0.000356	179	251.42	173.35	0.00E+00	0.0000000
0.016	0.000406	185	259.85	179.16	0.00E+00	0.0000000
0.018	0.000457	196	275.30	189.81	0.00E+00	0.0000000
0.02	0.000508	204	286.54	197.56	0.00E+00	0.0000000
0.022	0.000559	212	297.77	205.31	0.00E+00	0.0000000
0.024	0.000610	220	309.01	213.05	0.00E+00	0.0000000
0.026	0.000660	226	317.44	218.87	0.00E+00	0.0000000
0.028	0.000711	231	324.46	223.71	0.00E+00	0.0000000
0.03	0.000762	238	334.29	230.49	0.00E+00	0.0000000
0.032	0.000813	243	341.32	235.33	0.00E+00	0.0000000
0.034	0.000864	246	345.53	238.23	0.00E+00	0.0000000
0.036	0.000914	251	352.55	243.08	0.00E+00	0.0000000
0.038	0.000965	254	356.77	245.98	0.00E+00	0.0000000
0.04	0.001016	257	360.98	248.89	3.00E-05	0.0000008
0.042	0.001067	260	365.19	251.79	7.00E-05	0.0000018
0.044	0.001118	262	368.00	253.73	1.00E-04	0.0000025
0.046	0.001168	265	372.22	256.63	1.50E-04	0.0000038
0.048	0.001219	265	372.22	256.63	1.70E-04	0.0000043
0.05	0.001270	265	372.22	256.63	1.80E-04	0.0000046
0.052	0.001321	267	375.03	258.57	2.00E-04	0.0000051
0.054	0.001372	267	375.03	258.57	2.00E-04	0.0000051
0.056	0.001422	267	375.03	258.57	2.00E-04	0.0000051
0.058	0.001473	267	375.03	258.57	2.00E-04	0.0000051
0.06	0.001524	268	376.43	259.54	2.20E-04	0.0000056
0.062	0.001575	267	375.03	258.57	2.30E-04	0.0000058
0.064	0.001626	267	375.03	258.57	2.30E-04	0.0000058
0.066	0.001676	268	376.43	259.54	2.40E-04	0.0000061
0.068	0.001727	269	377.83	260.51	2.60E-04	0.0000066
0.07	0.001778	268	376.43	259.54	2.70E-04	0.0000069
0.072	0.001829	268	376.43	259.54	2.80E-04	0.0000071
0.074	0.001880	268	376.43	259.54	2.80E-04	0.0000071
0.076	0.001930	270	379.24	261.48	2.85E-04	0.0000072
0.078	0.001981	267	375.03	258.57	2.90E-04	0.0000074
0.08	0.002032	266	373.62	257.60	2.90E-04	0.0000074
0.082	0.002083	268	376.43	259.54	2.95E-04	0.0000075
0.084	0.002134	268	376.43	259.54	2.95E-04	0.0000075
0.086	0.002184	268	376.43	259.54	3.00E-04	0.0000076
0.088	0.002235	268	376.43	259.54	3.00E-04	0.0000076
0.09	0.002286	268	376.43	259.54	3.00E-04	0.0000076
0.092	0.002337	268	376.43	259.54	3.00E-04	0.0000076
0.094	0.002388	268	376.43	259.54	3.00E-04	0.0000076
0.096	0.002438	268	376.43	259.54	3.00E-04	0.0000076
0.098	0.002489	268	376.43	259.54	3.00E-04	0.0000076
0.1	0.002540	268	376.43	259.54	3.00E-04	0.0000076

Sample ID: **Z2.5bm1**

Description of the Sample: **Zorbax C18 Dry Silica**

Diameter of the Sample: **2.5**

Area of the Sample: **4.9087**

Normal Pressure: **2.5**

Mass of the Sample (wet): **44.0**

Initial Height of the Sample: **1.3400**

Initial Volume of the Sample: **42.4368**

Initial Density of the Sample: **1.0368**

Solvent:

Methanol

in

=

6.35

cm

in²

=

31.67

cm

bar

g

cm

cm³

g/cm³

Horizontal Displacement	Horizontal Dial Reading	Shear Force	Shear Stress	Normalized Shear	Vertical	Change of Vertical
(inch)	(m)	(lb)	(kPa)	Force (kPa)	Displacement (in)	Displacement (m)
0	0.000000	0	0.00	0.00	0.00E+00	0.0000000
0.002	0.000051	5	7.02	19.37	0.00E+00	0.0000000
0.004	0.000102	9	12.64	34.86	0.00E+00	0.0000000
0.006	0.000152	22	30.90	85.22	0.00E+00	0.0000000
0.008	0.000203	32	44.95	123.96	0.00E+00	0.0000000
0.01	0.000254	40	56.18	154.95	0.00E+00	0.0000000
0.012	0.000305	47	66.02	182.06	0.00E+00	0.0000000
0.014	0.000356	51	71.63	197.56	0.00E+00	0.0000000
0.016	0.000406	53	74.44	205.31	0.00E+00	0.0000000
0.018	0.000457	56	78.66	216.93	0.00E+00	0.0000000
0.02	0.000508	57	80.06	220.80	0.00E+00	0.0000000
0.022	0.000559	59	82.87	228.55	0.00E+00	0.0000000
0.024	0.000610	60	84.28	232.42	0.00E+00	0.0000000
0.026	0.000660	62	87.08	240.17	0.00E+00	0.0000000
0.028	0.000711	63	88.49	244.04	0.00E+00	0.0000000
0.03	0.000762	63	88.49	244.04	0.00E+00	0.0000000
0.032	0.000813	64	89.89	247.92	0.00E+00	0.0000000
0.034	0.000864	64	89.89	247.92	0.00E+00	0.0000000
0.036	0.000914	65	91.30	251.79	0.00E+00	0.0000000
0.038	0.000965	65	91.30	251.79	0.00E+00	0.0000000
0.04	0.001016	65	91.30	251.79	3.00E-05	0.0000008
0.042	0.001067	65	91.30	251.79	7.00E-05	0.0000018
0.044	0.001118	65	91.30	251.79	1.00E-04	0.0000025
0.046	0.001168	65	91.30	251.79	1.50E-04	0.0000038
0.048	0.001219	65	91.30	251.79	1.70E-04	0.0000043
0.05	0.001270	66	92.70	255.67	1.80E-04	0.0000046
0.052	0.001321	64	89.89	247.92	2.00E-04	0.0000051
0.054	0.001372	64	89.89	247.92	2.00E-04	0.0000051
0.056	0.001422	64	89.89	247.92	2.00E-04	0.0000051
0.058	0.001473	64	89.89	247.92	2.00E-04	0.0000051
0.06	0.001524	64	89.89	247.92	2.20E-04	0.0000056
0.062	0.001575	63	88.49	244.04	2.30E-04	0.0000058
0.064	0.001626	63	88.49	244.04	2.30E-04	0.0000058
0.066	0.001676	63	88.49	244.04	2.40E-04	0.0000061
0.068	0.001727	63	88.49	244.04	2.60E-04	0.0000066
0.07	0.001778	63	88.49	244.04	2.70E-04	0.0000069
0.072	0.001829	63	88.49	244.04	2.80E-04	0.0000071
0.074	0.001880	63	88.49	244.04	2.80E-04	0.0000071
0.076	0.001930	63	88.49	244.04	2.85E-04	0.0000072
0.078	0.001981	63	88.49	244.04	2.90E-04	0.0000074
0.08	0.002032	63	88.49	244.04	2.90E-04	0.0000074
0.082	0.002083	63	88.49	244.04	2.95E-04	0.0000075
0.084	0.002134	62	87.08	240.17	2.95E-04	0.0000075
0.086	0.002184	62	87.08	240.17	3.00E-04	0.0000076
0.088	0.002235	62	87.08	240.17	3.00E-04	0.0000076
0.09	0.002286	62	87.08	240.17	3.00E-04	0.0000076
0.092	0.002337	62	87.08	240.17	3.00E-04	0.0000076
0.094	0.002388	61	85.68	236.30	3.00E-04	0.0000076
0.096	0.002438	61	85.68	236.30	3.00E-04	0.0000076
0.098	0.002489	61	85.68	236.30	3.00E-04	0.0000076
0.1	0.002540	61	85.68	236.30	3.00E-04	0.0000076

Sample ID:	Z2.5bm2					
Description of the Sample:	Zorbax C18 Dry Silica	Solvent:	Methanol			
Diameter of the Sample:	2.5	in	=	6.35	cm	
Area of the Sample:	4.9087	in ²	=	31.67	cm	
Normal Pressure:	2.5	bar				
Mass of the Sample (wet):	33.9	g				
Initial Height of the Sample:	0.9400	cm				
Initial Volume of the Sample:	29.7691	cm ³				
Initial Density of the Sample:	1.1388	g/cm ³				
Horizontal Displacement	Horizontal Dial Reading	Shear	Shear Stress	Normalized Shear	Vertical Displacement	Change of Vertical
(inch)	(m)	Force (lb)	(kPa)	Force (kPa)	(in)	Displacement (m)
0	0.000000	0	0.00	0.00	0.00E+00	0.000000
0.002	0.000051	6	8.43	23.24	0.00E+00	0.000000
0.004	0.000102	10	14.05	38.74	0.00E+00	0.000000
0.006	0.000152	19	26.69	73.60	0.00E+00	0.000000
0.008	0.000203	33	46.35	127.83	0.00E+00	0.000000
0.01	0.000254	40	56.18	154.95	0.00E+00	0.000000
0.012	0.000305	45	63.21	174.32	0.00E+00	0.000000
0.014	0.000356	50	70.23	193.69	0.00E+00	0.000000
0.016	0.000406	54	75.85	209.18	0.00E+00	0.000000
0.018	0.000457	58	81.47	224.68	0.00E+00	0.000000
0.02	0.000508	60	84.28	232.42	0.00E+00	0.000000
0.022	0.000559	62	87.08	240.17	0.00E+00	0.000000
0.024	0.000610	64	89.89	247.92	0.00E+00	0.000000
0.026	0.000660	64	89.89	247.92	0.00E+00	0.000000
0.028	0.000711	65	91.30	251.79	5.00E-06	0.000001
0.03	0.000762	65	91.30	251.79	1.00E-05	0.000003
0.032	0.000813	66	92.70	255.67	1.00E-05	0.000003
0.034	0.000864	67	94.11	259.54	2.00E-05	0.000005
0.036	0.000914	67	94.11	259.54	3.00E-05	0.000008
0.038	0.000965	67	94.11	259.54	3.50E-05	0.000009
0.04	0.001016	67	94.11	259.54	3.50E-05	0.000009
0.042	0.001067	67	94.11	259.54	4.00E-05	0.000010
0.044	0.001118	67	94.11	259.54	4.00E-05	0.000010
0.046	0.001168	67	94.11	259.54	4.00E-05	0.000010
0.048	0.001219	67	94.11	259.54	6.00E-05	0.000015
0.05	0.001270	67	94.11	259.54	7.00E-05	0.000018
0.052	0.001321	67	94.11	259.54	7.50E-05	0.000019
0.054	0.001372	67	94.11	259.54	8.00E-05	0.000020
0.056	0.001422	68	95.51	263.41	8.50E-05	0.000022
0.058	0.001473	68	95.51	263.41	9.00E-05	0.000023
0.06	0.001524	69	96.92	267.29	9.50E-05	0.000024
0.062	0.001575	69	96.92	267.29	9.50E-05	0.000024
0.064	0.001626	69	96.92	267.29	1.00E-04	0.000025
0.066	0.001676	69	96.92	267.29	1.10E-04	0.000028
0.068	0.001727	69	96.92	267.29	1.20E-04	0.000030
0.07	0.001778	68	95.51	263.41	1.20E-04	0.000030
0.072	0.001829	68	95.51	263.41	1.20E-04	0.000030
0.074	0.001880	69	96.92	267.29	1.20E-04	0.000030
0.076	0.001930	69	96.92	267.29	1.20E-04	0.000030
0.078	0.001981	68	95.51	263.41	1.20E-04	0.000030
0.08	0.002032	69	96.92	267.29	1.25E-04	0.000032
0.082	0.002083	69	96.92	267.29	1.25E-04	0.000032
0.084	0.002134	69	96.92	267.29	1.30E-04	0.000033
0.086	0.002184	69	96.92	267.29	1.35E-04	0.000034
0.088	0.002235	69	96.92	267.29	1.40E-04	0.000036
0.09	0.002286	69	96.92	267.29	1.45E-04	0.000037
0.092	0.002337	68	95.51	263.41	1.50E-04	0.000038
0.094	0.002388	68	95.51	263.41	1.60E-04	0.000041
0.096	0.002438	68	95.51	263.41	1.60E-04	0.000041
0.098	0.002489	68	95.51	263.41	1.65E-04	0.000042
0.1	0.002540	69	96.92	267.29	1.70E-04	0.000043
0.102	0.002591	69	96.92	267.29	1.70E-04	0.000043
0.104	0.002642	68	95.51	263.41	1.75E-04	0.000044
0.106	0.002692	68	95.51	263.41	1.75E-04	0.000044
0.108	0.002743	68	95.51	263.41	1.75E-04	0.000044
0.11	0.002794	68	95.51	263.41	1.75E-04	0.000044
0.112	0.002845	67	94.11	259.54	1.75E-04	0.000044
0.114	0.002896	68	95.51	263.41	1.80E-04	0.000046
0.116	0.002946	68	95.51	263.41	1.85E-04	0.000047
0.118	0.002997	68	95.51	263.41	1.85E-04	0.000047
0.12	0.003048	68	95.51	263.41	1.90E-04	0.000048
0.122	0.003099	68	95.51	263.41	1.90E-04	0.000048

Sample ID:	Z5bm1						
Description of the Sample:	Zorbax C18 Dry Silica	Solvent:	Methanol				
Diameter of the Sample:	2.5	in	=	6.35	cm		
Area of the Sample:	4.9087	in ²	=	31.67	cm		
Normal Pressure:	5	bar					
Mass of the Sample (wet):	42.4	g					
Initial Height of the Sample:	1.3400	cm					
Initial Volume of the Sample:	42.4368	cm ³					
Initial Density of the Sample:	0.9991	g/cm ³					
Horizontal Displacement (inch)	Horizontal Dial Reading (mm)	Shear Force (lb)	Shear Stress (kPa)	Normalized Shear Force (kPa)	Vertical Displacement (in)	Change of Vertical Displacement (mm)	
0	0.000000	0	0.00	0.00	0.00E+00	0.000000	
0.002	0.000051	2	2.81	3.87	0.00E+00	0.000000	
0.004	0.000102	2	2.81	3.87	0.00E+00	0.000000	
0.006	0.000152	3	4.21	5.81	0.00E+00	0.000000	
0.008	0.000203	4	5.62	7.75	0.00E+00	0.000000	
0.01	0.000254	5	7.02	9.68	0.00E+00	0.000000	
0.012	0.000305	6	8.43	11.62	0.00E+00	0.000000	
0.014	0.000356	9	12.64	17.43	0.00E+00	0.000000	
0.016	0.000406	11	15.45	21.31	0.00E+00	0.000000	
0.018	0.000457	15	21.07	29.05	0.00E+00	0.000000	
0.02	0.000508	29	40.73	56.17	0.00E+00	0.000000	
0.022	0.000559	46	64.61	89.10	0.00E+00	0.000000	
0.024	0.000610	67	94.11	129.77	0.00E+00	0.000000	
0.026	0.000660	80	112.37	154.95	0.00E+00	0.000000	
0.028	0.000711	93	130.63	180.13	0.00E+00	0.000000	
0.03	0.000762	103	144.67	199.50	0.00E+00	0.000000	
0.032	0.000813	109	153.10	211.12	0.00E+00	0.000000	
0.034	0.000864	114	160.12	220.80	0.00E+00	0.000000	
0.036	0.000914	117	164.34	226.61	0.00E+00	0.000000	
0.038	0.000965	120	168.55	232.42	0.00E+00	0.000000	
0.04	0.001016	122	171.36	236.30	0.00E+00	0.000000	
0.042	0.001067	124	174.17	240.17	0.00E+00	0.000000	
0.044	0.001118	127	178.38	245.98	0.00E+00	0.000000	
0.046	0.001168	127	178.38	245.98	0.00E+00	0.000000	
0.048	0.001219	128	179.79	247.92	0.00E+00	0.000000	
0.05	0.001270	128	179.79	247.92	0.00E+00	0.000000	
0.052	0.001321	128	179.79	247.92	0.00E+00	0.000000	
0.054	0.001372	128	179.79	247.92	0.00E+00	0.000000	
0.056	0.001422	128	179.79	247.92	0.00E+00	0.000000	
0.058	0.001473	128	179.79	247.92	0.00E+00	0.000000	
0.06	0.001524	127	178.38	245.98	0.00E+00	0.000000	
0.062	0.001575	127	178.38	245.98	0.00E+00	0.000000	
0.064	0.001626	126	176.98	244.04	0.00E+00	0.000000	
0.066	0.001676	126	176.98	244.04	0.00E+00	0.000000	
0.068	0.001727	126	176.98	244.04	0.00E+00	0.000000	
0.07	0.001778	125	175.57	242.11	0.00E+00	0.000000	
0.072	0.001829	125	175.57	242.11	0.00E+00	0.000000	
0.074	0.001880	125	175.57	242.11	0.00E+00	0.000000	
0.076	0.001930	124	174.17	240.17	0.00E+00	0.000000	
0.078	0.001981	124	174.17	240.17	0.00E+00	0.000000	
0.08	0.002032	123	172.76	238.23	0.00E+00	0.000000	
0.082	0.002083	122	171.36	236.30	0.00E+00	0.000000	
0.084	0.002134	122	171.36	236.30	0.00E+00	0.000000	
0.086	0.002184	122	171.36	236.30	0.00E+00	0.000000	
0.088	0.002235	122	171.36	236.30	0.00E+00	0.000000	
0.09	0.002286	122	171.36	236.30	0.00E+00	0.000000	
0.092	0.002337	122	171.36	236.30	0.00E+00	0.000000	
0.094	0.002388	122	171.36	236.30	0.00E+00	0.000000	
0.096	0.002438	121	169.96	234.36	0.00E+00	0.000000	
0.098	0.002489	121	169.96	234.36	0.00E+00	0.000000	
0.1	0.002540	121	169.96	234.36	0.00E+00	0.000000	
0.102	0.002591	121	169.96	234.36	0.00E+00	0.000000	
0.104	0.002642	121	169.96	234.36	0.00E+00	0.000000	
0.106	0.002692	122	171.36	236.30	0.00E+00	0.000000	
0.108	0.002743	121	169.96	234.36	0.00E+00	0.000000	
0.11	0.002794	121	169.96	234.36	0.00E+00	0.000000	
0.112	0.002845	121	169.96	234.36	0.00E+00	0.000000	
0.114	0.002896	121	169.96	234.36	0.00E+00	0.000000	
0.116	0.002946	121	169.96	234.36	0.00E+00	0.000000	
0.118	0.002997	121	169.96	234.36	0.00E+00	0.000000	
0.12	0.003048	120	168.55	232.42	0.00E+00	0.000000	
0.122	0.003099	120	168.55	232.42	0.00E+00	0.000000	
0.124	0.003150	120	168.55	232.42	0.00E+00	0.000000	
0.126	0.003200	120	168.55	232.42	0.00E+00	0.000000	
0.128	0.003251	120	168.55	232.42	0.00E+00	0.000000	
0.13	0.003302	120	168.55	232.42	0.00E+00	0.000000	
0.132	0.003353	120	168.55	232.42	0.00E+00	0.000000	
0.134	0.003404	120	168.55	232.42	0.00E+00	0.000000	
0.136	0.003454	120	168.55	232.42	0.00E+00	0.000000	
0.138	0.003505	120	168.55	232.42	0.00E+00	0.000000	
0.14	0.003556	119	167.15	230.49	0.00E+00	0.000000	
0.142	0.003607	119	167.15	230.49	0.00E+00	0.000000	
0.144	0.003658	119	167.15	230.49	0.00E+00	0.000000	
0.146	0.003708	119	167.15	230.49	0.00E+00	0.000000	
0.148	0.003759	119	167.15	230.49	0.00E+00	0.000000	
0.15	0.003810	119	167.15	230.49	0.00E+00	0.000000	
0.152	0.003861	118	165.74	228.55	0.00E+00	0.000000	
0.154	0.003912	118	165.74	228.55	0.00E+00	0.000000	
0.156	0.003962	119	167.15	230.49	0.00E+00	0.000000	
0.158	0.004013	119	167.15	230.49	0.00E+00	0.000000	
0.16	0.004064	118	165.74	228.55	0.00E+00	0.000000	
0.162	0.004115	118	165.74	228.55	0.00E+00	0.000000	
0.164	0.004166	118	165.74	228.55	0.00E+00	0.000000	
0.166	0.004216	118	165.74	228.55	0.00E+00	0.000000	
0.168	0.004267	118	165.74	228.55	0.00E+00	0.000000	
0.17	0.004318	119	167.15	230.49	0.00E+00	0.000000	
0.172	0.004369	119	167.15	230.49	0.00E+00	0.000000	
0.174	0.004420	118	165.74	228.55	0.00E+00	0.000000	
0.176	0.004470	118	165.74	228.55	0.00E+00	0.000000	
0.178	0.004521	118	165.74	228.55	0.00E+00	0.000000	
0.18	0.004572	118	165.74	228.55	0.00E+00	0.000000	
0.182	0.004623	118	165.74	228.55	0.00E+00	0.000000	
0.184	0.004674	118	165.74	228.55	0.00E+00	0.000000	
0.186	0.004724	118	165.74	228.55	0.00E+00	0.000000	
0.188	0.004775	118	165.74	228.55	0.00E+00	0.000000	
0.19	0.004826	118	165.74	228.55	0.00E+00	0.000000	
0.192	0.004877	118	165.74	228.55	0.00E+00	0.000000	
0.194	0.004928	118	165.74	228.55	0.00E+00	0.000000	
0.196	0.004978	118	165.74	228.55	0.00E+00	0.000000	
0.198	0.005029	117	164.34	226.61	0.00E+00	0.000000	
0.2	0.005080	118	165.74	228.55	0.00E+00	0.000000	
0.202	0.005131	118	165.74	228.55	0.00E+00	0.000000	
0.204	0.005182	117	164.34	226.61	0.00E+00	0.000000	

Sample ID:	Z5bm2	Solvent:	Methanol			
Description of the Sample:	Zorbax C18 Dry Silica					
Diameter of the Sample:	2.5	in	=	6.35	cm	
Area of the Sample:	4.9087	in ²	=	31.67	cm	
Normal Pressure:	5	bar				
Mass of the Sample (wet):	40.0	g				
Initial Height of the Sample:	0.9900	cm				
Initial Volume of the Sample:	31.3525	cm ³				
Initial Density of the Sample:	1.2758	g/cm ³				
Horizontal Displacement (inch)	Horizontal Dial Reading (m)	Shear Force (lb)	Shear Stress (kPa)	Normalized Shear Force (kPa)	Vertical Displacement (in)	Change of Vertical Displacement (m)
0	0.000000	0	0.00	0.00	0.00E+00	0.0000000
0.002	0.000051	12	16.86	23.24	0.00E+00	0.0000000
0.004	0.000102	19	26.69	36.80	0.00E+00	0.0000000
0.006	0.000152	36	50.57	69.73	0.00E+00	0.0000000
0.008	0.000203	50	70.23	96.84	0.00E+00	0.0000000
0.01	0.000254	64	89.89	123.96	0.00E+00	0.0000000
0.012	0.000305	76	106.75	147.20	0.00E+00	0.0000000
0.014	0.000356	86	120.79	166.57	0.00E+00	0.0000000
0.016	0.000406	97	136.25	187.88	0.00E+00	0.0000000
0.018	0.000457	105	147.48	203.37	0.00E+00	0.0000000
0.02	0.000508	110	154.50	213.05	0.00E+00	0.0000000
0.022	0.000559	114	160.12	220.80	0.00E+00	0.0000000
0.024	0.000610	118	165.74	228.55	0.00E+00	0.0000000
0.026	0.000660	122	171.36	236.30	0.00E+00	0.0000000
0.028	0.000711	126	176.98	244.04	0.00E+00	0.0000000
0.03	0.000762	128	179.79	247.92	0.00E+00	0.0000000
0.032	0.000813	130	182.60	251.79	0.00E+00	0.0000000
0.034	0.000864	132	185.41	255.67	0.00E+00	0.0000000
0.036	0.000914	133	186.81	257.60	0.00E+00	0.0000000
0.038	0.000965	134	188.21	259.54	0.00E+00	0.0000000
0.04	0.001016	135	189.62	261.48	0.00E+00	0.0000000
0.042	0.001067	136	191.02	263.41	0.00E+00	0.0000000
0.044	0.001118	136	191.02	263.41	0.00E+00	0.0000000
0.046	0.001168	136	191.02	263.41	0.00E+00	0.0000000
0.048	0.001219	135	189.62	261.48	0.00E+00	0.0000000
0.05	0.001270	133	186.81	257.60	0.00E+00	0.0000000
0.052	0.001321	132	185.41	255.67	0.00E+00	0.0000000
0.054	0.001372	131	184.00	253.73	0.00E+00	0.0000000
0.056	0.001422	130	182.60	251.79	0.00E+00	0.0000000
0.058	0.001473	130	182.60	251.79	0.00E+00	0.0000000
0.06	0.001524	129	181.19	249.86	0.00E+00	0.0000000
0.062	0.001575	129	181.19	249.86	0.00E+00	0.0000000
0.064	0.001626	128	179.79	247.92	0.00E+00	0.0000000
0.066	0.001676	126	176.98	244.04	0.00E+00	0.0000000
0.068	0.001727	126	176.98	244.04	5.00E-05	0.0000013
0.07	0.001778	126	176.98	244.04	5.00E-05	0.0000013
0.072	0.001829	126	176.98	244.04	1.00E-04	0.0000025
0.074	0.001880	126	176.98	244.04	1.00E-04	0.0000025
0.076	0.001930	126	176.98	244.04	1.00E-04	0.0000025
0.078	0.001981	124	174.17	240.17	1.50E-04	0.0000038
0.08	0.002032	124	174.17	240.17	1.50E-04	0.0000038
0.082	0.002083	124	174.17	240.17	2.00E-04	0.0000051
0.084	0.002134	122	171.36	236.30	2.00E-04	0.0000051
0.086	0.002184	122	171.36	236.30	2.00E-04	0.0000051
0.088	0.002235	123	172.76	238.23	2.50E-04	0.0000063
0.09	0.002286	122	171.36	236.30	2.50E-04	0.0000063
0.092	0.002337	121	169.96	234.36	2.50E-04	0.0000063
0.094	0.002388	123	172.76	238.23	2.50E-04	0.0000063
0.096	0.002439	121	169.96	234.36	2.50E-04	0.0000063
0.098	0.002489	120	168.55	232.42	2.50E-04	0.0000063
0.1	0.002540	122	171.36	236.30	2.50E-04	0.0000063
0.102	0.002591	119	167.15	230.49	2.50E-04	0.0000063
0.104	0.002642	120	168.55	232.42	2.50E-04	0.0000063
0.106	0.002692	119	167.15	230.49	2.50E-04	0.0000063
0.108	0.002743	120	168.55	232.42	2.50E-04	0.0000063
0.11	0.002794	119	167.15	230.49	2.50E-04	0.0000063
0.112	0.002845	119	167.15	230.49	2.50E-04	0.0000063
0.114	0.002896	120	168.55	232.42	2.50E-04	0.0000063
0.116	0.002946	118	165.74	228.55	2.50E-04	0.0000063
0.118	0.002997	118	165.74	228.55	2.50E-04	0.0000063
0.12	0.003048	117	164.34	226.61	2.50E-04	0.0000063
0.122	0.003099	119	167.15	230.49	2.50E-04	0.0000063
0.124	0.003150	119	167.15	230.49	2.50E-04	0.0000063
0.126	0.003200	117	164.34	226.61	2.50E-04	0.0000063
0.128	0.003251	117	164.34	226.61	2.50E-04	0.0000063
0.13	0.003302	117	164.34	226.61	2.50E-04	0.0000063
0.132	0.003353	117	164.34	226.61	2.50E-04	0.0000063
0.134	0.003404	117	164.34	226.61	2.50E-04	0.0000063
0.136	0.003454	117	164.34	226.61	2.50E-04	0.0000063
0.138	0.003505	117	164.34	226.61	2.50E-04	0.0000063
0.14	0.003556	117	164.34	226.61	2.50E-04	0.0000063
0.142	0.003607	117	164.34	226.61	2.50E-04	0.0000063
0.144	0.003658	117	164.34	226.61	2.50E-04	0.0000063
0.146	0.003708	117	164.34	226.61	2.50E-04	0.0000063
0.148	0.003759	116	162.93	224.68	2.50E-04	0.0000063
0.15	0.003810	116	162.93	224.68	2.50E-04	0.0000063
0.152	0.003861	116	162.93	224.68	3.00E-04	0.0000076
0.154	0.003912	116	162.93	224.68	3.00E-04	0.0000076
0.156	0.003962	116	162.93	224.68	3.00E-04	0.0000076
0.158	0.004013	116	162.93	224.68	3.00E-04	0.0000076
0.16	0.004064	116	162.93	224.68	3.50E-04	0.0000089
0.162	0.004115	116	162.93	224.68	4.00E-04	0.0000102
0.164	0.004166	116	162.93	224.68	5.00E-04	0.0000127

Sample ID:	Z10bml	Solvent:	Methanol			
Description of the Sample:	Zorbax C18 Dry Silica					
Diameter of the Sample:	2.5	in	=	6.35	cm	
Area of the Sample:	4.9087	in ²	=	31.67	cm ²	
Normal Pressure:	20	bar				
Mass of the Sample (wet):	34.0	g				
Initial Height of the Sample:	1.0400	cm				
Initial Volume of the Sample:	32.9360	cm ³				
Initial Density of the Sample:	1.0323	g/cm ³				
Horizontal Displacement (inch)	Horizontal Dial Reading (m)	Shear Force (lb)	Shear Stress (kPa)	Normalized Shear Force (kPa)	Vertical Displacement (in)	Change of Vertical Displacement (m)
0	0.000000	0	0.00	0.00	0.00E+00	0.0000000
0.002	0.000051	67	94.11	32.44	0.00E+00	0.0000000
0.004	0.000102	106	148.89	51.33	0.00E+00	0.0000000
0.006	0.000152	159	223.33	76.99	0.00E+00	0.0000000
0.008	0.000203	197	276.70	95.39	0.00E+00	0.0000000
0.01	0.000254	237	332.89	114.76	-6.00E-05	-0.0000015
0.012	0.000305	270	379.24	130.74	-6.50E-05	-0.0000017
0.014	0.000356	297	417.16	143.81	-6.50E-05	-0.0000017
0.016	0.000406	327	459.30	158.34	-6.50E-05	-0.0000017
0.018	0.000457	348	488.80	168.51	-1.00E-04	-0.0000025
0.02	0.000508	374	525.32	181.10	-1.50E-04	-0.0000038
0.022	0.000559	396	556.22	191.75	-1.50E-04	-0.0000038
0.024	0.000610	413	580.10	199.98	-1.55E-04	-0.0000039
0.026	0.000660	430	603.97	208.21	-1.60E-04	-0.0000041
0.028	0.000711	447	627.85	216.44	-1.70E-04	-0.0000043
0.03	0.000762	461	647.52	223.22	-1.80E-04	-0.0000046
0.032	0.000813	476	668.58	230.49	-1.90E-04	-0.0000048
0.034	0.000864	487	684.03	235.81	-2.00E-04	-0.0000051
0.036	0.000914	497	698.08	240.65	-2.20E-04	-0.0000056
0.038	0.000965	505	709.32	244.53	-2.40E-04	-0.0000061
0.04	0.001016	513	720.55	248.40	-2.45E-04	-0.0000062
0.042	0.001067	519	728.98	251.31	-2.45E-04	-0.0000062
0.044	0.001118	525	737.41	254.21	-2.45E-04	-0.0000062
0.046	0.001168	532	747.24	257.60	-2.45E-04	-0.0000062
0.048	0.001219	538	755.67	260.51	-2.45E-04	-0.0000062
0.05	0.001270	545	765.50	263.90	-2.45E-04	-0.0000062
0.052	0.001321	548	769.71	265.35	-2.45E-04	-0.0000062
0.054	0.001372	553	776.74	267.77	-2.45E-04	-0.0000062
0.056	0.001422	557	782.36	269.71	-2.45E-04	-0.0000062
0.058	0.001473	561	787.97	271.64	-2.45E-04	-0.0000062
0.06	0.001524	563	790.78	272.61	-2.45E-04	-0.0000062
0.062	0.001575	567	796.40	274.55	-2.45E-04	-0.0000062
0.064	0.001626	554	778.14	268.26	-2.45E-04	-0.0000062
0.066	0.001676	554	778.14	268.26	-2.45E-04	-0.0000062
0.068	0.001727	543	762.69	262.93	-2.45E-04	-0.0000062
0.07	0.001778	544	764.10	263.41	-2.40E-04	-0.0000061
0.072	0.001829	544	764.10	263.41	-2.40E-04	-0.0000061
0.074	0.001880	535	751.46	259.06	-2.40E-04	-0.0000061
0.076	0.001930	538	755.67	260.51	-2.40E-04	-0.0000061
0.078	0.001981	543	762.69	262.93	-2.40E-04	-0.0000061
0.08	0.002032	538	755.67	260.51	-2.40E-04	-0.0000061
0.082	0.002083	532	747.24	257.60	-2.40E-04	-0.0000061
0.084	0.002134	528	741.62	255.67	-2.40E-04	-0.0000061
0.086	0.002184	529	743.03	256.15	-2.40E-04	-0.0000061
0.088	0.002235	522	733.20	252.76	-2.40E-04	-0.0000061
0.09	0.002286	528	741.62	255.67	-2.20E-04	-0.0000056
0.092	0.002337	522	733.20	252.76	-2.00E-04	-0.0000051
0.094	0.002388	522	733.20	252.76	-1.50E-04	-0.0000038
0.096	0.002438	521	731.79	252.28	-1.20E-04	-0.0000030
0.098	0.002489	519	728.98	251.31	-1.00E-04	-0.0000025
0.1	0.002540	522	733.20	252.76	-5.00E-05	-0.0000013
0.102	0.002591	524	736.00	253.73	-1.00E-05	-0.0000003
0.104	0.002642	517	726.17	250.34	0.00E+00	0.0000000
0.106	0.002692	519	728.98	251.31	5.00E-06	0.0000001
0.108	0.002743	519	728.98	251.31	2.00E-05	0.0000005
0.11	0.002794	516	724.77	249.86	4.00E-05	0.0000010
0.112	0.002845	512	719.15	247.92	4.50E-05	0.0000011
0.114	0.002896	517	726.17	250.34	5.00E-05	0.0000013
0.116	0.002946	517	726.17	250.34	5.50E-05	0.0000014
0.118	0.002997	513	720.55	248.40	5.50E-05	0.0000014
0.12	0.003048	514	721.96	248.89	6.00E-05	0.0000015
0.122	0.003099	515	723.36	249.37	8.00E-05	0.0000020
0.124	0.003150	506	710.72	245.01	9.00E-05	0.0000023
0.126	0.003200	509	714.94	246.47	9.50E-05	0.0000024
0.128	0.003251	508	713.53	245.98	1.00E-04	0.0000025
0.13	0.003302	511	717.74	247.43	1.05E-04	0.0000027
0.132	0.003353	512	719.15	247.92	1.10E-04	0.0000028
0.134	0.003404	512	719.15	247.92	1.10E-04	0.0000028
0.136	0.003454	514	721.96	248.89	1.15E-04	0.0000029
0.138	0.003505	515	723.36	249.37	1.15E-04	0.0000029
0.14	0.003556	512	719.15	247.92	1.20E-04	0.0000030
0.142	0.003607	517	726.17	250.34	1.25E-04	0.0000032
0.144	0.003658	514	721.96	248.89	1.30E-04	0.0000033
0.146	0.003708	507	712.13	245.50	1.35E-04	0.0000034
0.148	0.003759	522	733.20	252.76	1.35E-04	0.0000034
0.15	0.003810	517	726.17	250.34	1.40E-04	0.0000036
0.152	0.003861	522	733.20	252.76	1.50E-04	0.0000038
0.154	0.003912	515	723.36	249.37	1.60E-04	0.0000041
0.156	0.003962	522	733.20	252.76	1.80E-04	0.0000046

Note: The sample was reused from the previous 2.5, 5 and 10 bars with methanol.
Stick-slip behavior was observed after the sample reached the peak shear strength (sample failed).

Sample ID: Z30bm1 Description of the Sample: Zorbax C18 Dry Silica Solvent: Methanol Diameter of the Sample: 2.5 in = 6.35 cm Area of the Sample: 4.9087 in² = 31.67 cm² Normal Pressure: 30 bar Mass of the Dry Sample: 24.3 g Initial Height of the Sample: 1.1400 cm Initial Volume of the Sample: 36.1029 cm³ Initial Density of the Sample: 0.6731 g/cm³						
Horizontal Displacement	Horizontal Dial	Shear	Shear	Normalized Shear	Vertical	Change of Vertical
(inch)	Reading (m)	Force (lb)	Stress (kPa)	Force (kPa)	Displacement (in)	Displacement (m)
0	0.000000	0	0.00	0.00	0.00E+00	0.0000000
0.002	0.000051	138	193.83	44.55	2.00E-05	0.0000005
0.004	0.000102	215	301.99	69.40	2.00E-05	0.0000005
0.006	0.000152	285	400.31	92.00	2.00E-05	0.0000005
0.008	0.000203	352	494.42	113.63	2.00E-05	0.0000005
0.01	0.000254	403	566.05	130.09	2.00E-05	0.0000005
0.012	0.000305	456	640.49	147.20	2.00E-05	0.0000005
0.014	0.000356	500	702.29	161.41	2.00E-05	0.0000005
0.016	0.000406	538	755.67	173.67	3.00E-05	0.0000008
0.018	0.000457	576	809.04	185.94	6.50E-05	0.0000017
0.02	0.000508	602	845.56	194.33	8.50E-05	0.0000022
0.022	0.000559	632	887.70	204.02	1.25E-04	0.0000032
0.024	0.000610	659	925.62	212.73	1.65E-04	0.0000042
0.026	0.000660	680	955.12	219.51	2.25E-04	0.0000057
0.028	0.000711	701	984.62	226.29	2.55E-04	0.0000065
0.03	0.000762	716	1005.69	231.13	3.05E-04	0.0000077
0.032	0.000813	732	1028.16	236.30	3.45E-04	0.0000088
0.034	0.000864	747	1049.23	241.14	4.15E-04	0.0000105
0.036	0.000914	760	1067.49	245.34	4.95E-04	0.0000126
0.038	0.000965	770	1081.53	248.56	5.55E-04	0.0000141
0.04	0.001016	779	1094.17	251.47	6.05E-04	0.0000154
0.042	0.001067	785	1102.60	253.41	6.65E-04	0.0000169
0.044	0.001118	792	1112.43	255.67	7.15E-04	0.0000182
0.046	0.001168	798	1120.86	257.60	7.45E-04	0.0000189
0.048	0.001219	806	1132.10	260.18	7.55E-04	0.0000192
0.05	0.001270	812	1140.53	262.12	7.55E-04	0.0000192
0.052	0.001321	818	1148.95	264.06	7.60E-04	0.0000193
0.054	0.001372	824	1157.38	266.00	7.60E-04	0.0000193
0.056	0.001422	829	1164.40	267.61	7.60E-04	0.0000193
0.058	0.001473	831	1167.21	268.26	7.60E-04	0.0000193
0.06	0.001524	834	1171.43	269.22	7.65E-04	0.0000194
0.062	0.001575	839	1178.45	270.84	7.80E-04	0.0000198
0.064	0.001626	842	1182.66	271.81	7.85E-04	0.0000199
0.066	0.001676	842	1182.66	271.81	7.95E-04	0.0000202
0.068	0.001727	830	1165.81	267.93	8.00E-04	0.0000203
0.07	0.001778	805	1130.69	259.86	8.10E-04	0.0000206
0.072	0.001829	797	1119.46	257.28	8.20E-04	0.0000208
0.074	0.001880	775	1088.56	250.18	8.20E-04	0.0000208
0.076	0.001930	771	1082.94	248.89	8.25E-04	0.0000210
0.078	0.001981	774	1087.15	249.86	8.25E-04	0.0000210
0.08	0.002032	750	1053.44	242.11	8.45E-04	0.0000215
0.082	0.002083	733	1029.56	236.62	8.65E-04	0.0000220
0.084	0.002134	732	1028.16	236.30	8.65E-04	0.0000220
0.086	0.002184	727	1021.14	234.68	8.90E-04	0.0000226
0.088	0.002235	723	1015.52	233.39	9.05E-04	0.0000230
0.09	0.002286	721	1012.71	232.75	9.20E-04	0.0000234
0.092	0.002337	719	1009.90	232.10	9.35E-04	0.0000237
0.094	0.002388	711	998.66	229.52	9.45E-04	0.0000240
0.096	0.002438	705	990.24	227.58	9.55E-04	0.0000243
0.098	0.002489	705	990.24	227.58	9.65E-04	0.0000245
0.1	0.002540	705	990.24	227.58	9.70E-04	0.0000246
0.102	0.002591	705	990.24	227.58	9.80E-04	0.0000249
0.104	0.002642	705	990.24	227.58	9.90E-04	0.0000251
0.106	0.002692	705	990.24	227.58	1.00E-03	0.0000254
0.108	0.002743	705	990.24	227.58	1.01E-03	0.0000255
0.11	0.002794	705	990.24	227.58	1.02E-03	0.0000258

Note: The sample was reused from the previous 5 and 10 bars with acetone. Stick-slip behavior was observed after the sample reached the peak shear strength (sample failed).

Sample ID:	Z30bml2	* Lubricant: Graphite spray was used				
Description of the Sample:	Zorbax C18 Dry Silica	Solvent:	Methanol			
Diameter of the Sample:	2.5	in	=	6.35	cm	
Area of the Sample:	4.9087	in ²	=	31.67	cm ²	
Normal Pressure:	30	bar				
Density of the graphite spray:	660.33	kg/m ³		Thickness of the graphite:	4.69E-06	m
Mass of the Sample (Dry):	21.5	g		Mass of the Sample (Wet):	33.6	g
Initial Height of the Sample:	1.3163	cm				
Initial Volume of the Sample:	41.6846	cm ³				
Initial Density of the Sample:	0.5158	g/cm ³				
Horizontal Displacement (inch)	Horizontal Dial Reading (m)	Shear Force (lb)	Shear Stress (kPa)	Normalized Shear Force (kPa)	Vertical Displacement (in)	Change of Vertical Displacement (m)
0	0.000000	0	0.00	0.00	0.00E+00	0.0000000
0.002	0.000051	19	26.69	6.13	5.00E-06	0.0000001
0.004	0.000102	79	110.96	25.50	1.00E-05	0.0000003
0.006	0.000152	133	186.81	42.93	1.50E-05	0.0000004
0.008	0.000203	179	251.42	57.78	2.00E-05	0.0000005
0.01	0.000254	225	316.03	72.63	2.50E-05	0.0000006
0.012	0.000305	280	393.28	90.39	3.00E-05	0.0000008
0.014	0.000356	329	462.11	106.20	5.00E-05	0.0000013
0.016	0.000406	370	519.70	119.44	8.00E-05	0.0000020
0.018	0.000457	408	573.07	131.71	1.00E-04	0.0000025
0.02	0.000508	437	613.81	141.07	1.10E-04	0.0000028
0.022	0.000559	465	653.13	150.11	1.40E-04	0.0000036
0.024	0.000610	490	688.25	158.18	1.60E-04	0.0000041
0.026	0.000660	514	721.96	165.92	1.80E-04	0.0000046
0.028	0.000711	533	748.65	172.06	2.00E-04	0.0000051
0.03	0.000762	550	772.52	177.55	2.10E-04	0.0000053
0.032	0.000813	565	793.59	182.39	2.30E-04	0.0000058
0.034	0.000864	578	811.85	186.58	2.50E-04	0.0000063
0.036	0.000914	593	832.92	191.43	2.60E-04	0.0000066
0.038	0.000965	606	851.18	195.62	2.70E-04	0.0000069
0.04	0.001016	616	865.23	198.85	3.00E-04	0.0000076
0.042	0.001067	625	877.87	201.76	3.10E-04	0.0000079
0.044	0.001118	635	891.91	204.98	3.30E-04	0.0000084
0.046	0.001168	644	904.56	207.89	3.45E-04	0.0000088
0.048	0.001219	652	915.79	210.47	3.75E-04	0.0000095
0.05	0.001270	659	925.62	212.73	4.10E-04	0.0000104
0.052	0.001321	667	936.86	215.31	4.60E-04	0.0000117
0.054	0.001372	674	946.69	217.57	5.20E-04	0.0000132
0.056	0.001422	680	955.12	219.51	6.00E-04	0.0000152
0.058	0.001473	690	969.17	222.74	6.30E-04	0.0000160
0.06	0.001524	696	977.59	224.68	6.70E-04	0.0000170
0.062	0.001575	704	988.83	227.26	6.90E-04	0.0000175
0.064	0.001626	710	997.26	229.20	7.25E-04	0.0000184
0.066	0.001676	716	1005.69	231.13	7.50E-04	0.0000190
0.068	0.001727	718	1008.49	231.78	7.80E-04	0.0000198
0.07	0.001778	722	1014.11	233.07	7.90E-04	0.0000201
0.072	0.001829	722	1014.11	233.07	8.10E-04	0.0000206
0.074	0.001880	725	1018.33	234.04	8.30E-04	0.0000211
0.076	0.001930	727	1021.14	234.68	8.50E-04	0.0000216
0.078	0.001981	728	1022.54	235.01	8.70E-04	0.0000221
0.08	0.002032	729	1023.95	235.33	8.80E-04	0.0000224
0.082	0.002083	731	1026.75	235.97	8.00E-04	0.0000203
0.084	0.002134	730	1025.35	235.65	8.20E-04	0.0000208
0.086	0.002184	727	1021.14	234.68	8.30E-04	0.0000211
0.088	0.002235	729	1023.95	235.33	8.50E-04	0.0000216
0.09	0.002286	729	1023.95	235.33	8.70E-04	0.0000221
0.092	0.002337	725	1018.33	234.04	9.30E-04	0.0000236
0.094	0.002388	730	1025.35	235.65	9.80E-04	0.0000249
0.096	0.002438	725	1018.33	234.04	1.01E-03	0.0000257
0.098	0.002489	720	1011.30	232.42	1.04E-03	0.0000264
0.1	0.002540	719	1009.90	232.10	1.06E-03	0.0000269
0.102	0.002591	721	1012.71	232.75	1.08E-03	0.0000274
0.104	0.002642	719	1009.90	232.10	1.10E-03	0.0000279
0.106	0.002692	716	1005.69	231.13	1.11E-03	0.0000282
0.108	0.002743	717	1007.09	231.45	1.11E-03	0.0000282
0.11	0.002794	719	1009.90	232.10	1.11E-03	0.0000282
0.112	0.002845	719	1009.90	232.10	1.12E-03	0.0000284
0.114	0.002896	715	1004.28	230.81	1.13E-03	0.0000287
0.116	0.002946	719	1009.90	232.10	1.14E-03	0.0000290
0.118	0.002997	714	1002.88	230.49	1.15E-03	0.0000291
0.12	0.003048	712	1000.07	229.84	1.16E-03	0.0000293
0.122	0.003099	712	1000.07	229.84	1.16E-03	0.0000295
0.124	0.003150	712	1000.07	229.84	1.17E-03	0.0000297
0.126	0.003200	712	1000.07	229.84	1.19E-03	0.0000301

Note: The sample was reused from the previous tests. Stick-slip behavior was observed after the sample reached the peak shear strength (sample failed).

Sample ID:	Z20bml1	Spray Graphite lubricant * Sample used for other acetone tests, but not the Z30bml test				
Description of the Sample:	Zorbax C18 Dry Silica Solvent:	Methanol				
Diameter of the Sample:	2.5	in	=	6.35	cm	
Area of the Sample:	4.9087	in ²	=	31.67	cm	
Normal Pressure:	20	bar				
Density of the graphite spray:	660.33	kg/m ³		Thickness of the graphite:	4.69E-06	m
Mass of the Sample (dry):	21.5	g				
Initial Height of the Sample:	0.8400	cm				
Initial Volume of the Sample:	26.6021	cm ³				
Initial Density of the Sample:	0.8082	g/cm ³				
Horizontal Displacement	Horizontal Dial	Shear Force	Shear Stress	Normalized Shear Force	Vertical	Change of Vertical
(inch)	Reading (m)	(lb)	(kPa)	(kPa)	Displacement (in)	Displacement (m)
0	0.000000	0	0.00	0.00	0.00E+00	0.000000
0.002	0.000051	23	32.31	11.14	0.00E+00	0.000000
0.004	0.000102	47	66.02	22.76	0.00E+00	0.000000
0.006	0.000152	100	140.46	48.42	0.00E+00	0.000000
0.008	0.000203	149	209.28	72.15	0.00E+00	0.000000
0.01	0.000254	188	264.06	91.03	0.00E+00	0.000000
0.012	0.000305	223	313.22	107.98	0.00E+00	0.000000
0.014	0.000356	258	362.38	124.93	0.00E+00	0.000000
0.016	0.000406	283	397.50	137.03	0.00E+00	0.000000
0.018	0.000457	302	424.19	146.23	0.00E+00	0.000000
0.02	0.000508	317	445.25	153.50	0.00E+00	0.000000
0.022	0.000559	336	471.94	162.70	0.00E+00	0.000000
0.024	0.000610	352	494.42	170.44	0.00E+00	0.000000
0.026	0.000660	369	518.29	178.68	5.00E-05	0.000013
0.028	0.000711	386	542.17	186.91	1.00E-04	0.000025
0.03	0.000762	399	560.43	193.20	1.50E-04	0.000038
0.032	0.000813	412	578.69	199.50	2.00E-04	0.000051
0.034	0.000864	422	592.74	204.34	2.50E-04	0.000063
0.036	0.000914	431	605.38	208.70	3.00E-04	0.000076
0.038	0.000965	438	615.21	212.09	3.50E-04	0.000089
0.04	0.001016	444	623.64	214.99	3.50E-04	0.000089
0.042	0.001067	449	630.66	217.41	3.50E-04	0.000089
0.044	0.001118	452	634.87	218.87	3.50E-04	0.000089
0.046	0.001168	449	630.66	217.41	3.50E-04	0.000089
0.048	0.001219	449	630.66	217.41	3.50E-04	0.000089
0.05	0.001270	449	630.66	217.41	3.50E-04	0.000089
0.052	0.001321	447	627.85	216.44	3.50E-04	0.000089
0.054	0.001372	445	625.04	215.48	3.50E-04	0.000089
0.056	0.001422	450	632.07	217.90	3.50E-04	0.000089
0.058	0.001473	443	622.23	214.51	3.50E-04	0.000089
0.06	0.001524	444	623.64	214.99	3.50E-04	0.000089
0.062	0.001575	444	623.64	214.99	3.50E-04	0.000089
0.064	0.001626	444	623.64	214.99	4.00E-04	0.000102
0.066	0.001676	441	619.42	213.54	4.00E-04	0.000102
0.068	0.001727	441	619.42	213.54	4.00E-04	0.000102
0.07	0.001778	441	619.42	213.54	4.00E-04	0.000102
0.072	0.001829	444	623.64	214.99	4.00E-04	0.000102
0.074	0.001880	441	619.42	213.54	4.00E-04	0.000102
0.076	0.001930	436	612.40	211.12	4.00E-04	0.000102
0.078	0.001981	435	611.00	210.63	4.00E-04	0.000102
0.08	0.002032	435	611.00	210.63	4.00E-04	0.000102
0.082	0.002083	436	612.40	211.12	4.00E-04	0.000102
0.084	0.002134	439	616.61	212.57	4.00E-04	0.000102
0.086	0.002184	437	613.81	211.60	4.00E-04	0.000102
0.088	0.002235	434	609.59	210.15	4.00E-04	0.000102
0.09	0.002286	438	615.21	212.09	4.00E-04	0.000102
0.092	0.002337	432	606.78	209.18	4.00E-04	0.000102

Sample ID:	Z5ba1	Solvent:	Acetone			
Description of the Sample:	Zorbax C18 Dry Silica	in	=	6.35	cm	
Diameter of the Sample:	2.5	in ²	=	31.67	cm	
Area of the Sample:	4.9087	bar				
Normal Pressure:	5	g				
Mass of the Sample (wet):	54.3	cm				
Initial Height of the Sample:	1.5400	cm				
Initial Volume of the Sample:	48.7706	g/cm ³				
Initial Density of the Sample:	1.1134	g/cm ³				
Horizontal Displacement (inch)	Horizontal Dial Reading (m)	Shear Force (lb)	Shear Stress (kPa)	Normalized Shear Force (kPa)	Vertical Displacement (m)	Change of Vertical Displacement (m)
0	0.000000	0	0.00	0.00	0.00E+00	0.0000000
0.002	0.000051	8	11.24	15.49	1.15E-04	0.0000029
0.004	0.000102	16	22.47	30.99	1.45E-04	0.0000037
0.006	0.000152	44	61.80	85.22	1.45E-04	0.0000037
0.008	0.000203	65	91.30	125.90	1.45E-04	0.0000037
0.01	0.000254	81	113.77	156.89	1.65E-04	0.0000042
0.012	0.000305	90	126.41	174.32	1.95E-04	0.0000050
0.014	0.000356	99	139.05	191.75	2.15E-04	0.0000055
0.016	0.000406	106	148.89	205.31	2.15E-04	0.0000055
0.018	0.000457	113	158.72	218.87	2.25E-04	0.0000057
0.02	0.000508	116	162.93	224.68	2.25E-04	0.0000057
0.022	0.000559	120	168.55	232.42	2.25E-04	0.0000057
0.024	0.000610	122	171.36	236.30	2.25E-04	0.0000057
0.026	0.000660	123	172.76	238.23	2.25E-04	0.0000057
0.028	0.000711	124	174.17	240.17	2.25E-04	0.0000057
0.03	0.000762	124	174.17	240.17	2.25E-04	0.0000057
0.032	0.000813	124	174.17	240.17	2.25E-04	0.0000057
0.034	0.000864	124	174.17	240.17	2.25E-04	0.0000057
0.036	0.000914	123	172.76	238.23	2.25E-04	0.0000057
0.038	0.000965	123	172.76	238.23	2.25E-04	0.0000057
0.04	0.001016	123	172.76	238.23	2.25E-04	0.0000057
0.042	0.001067	122	171.36	236.30	2.25E-04	0.0000057
0.044	0.001118	121	169.96	234.36	2.25E-04	0.0000057
0.046	0.001168	121	169.96	234.36	2.25E-04	0.0000057
0.048	0.001219	121	169.96	234.36	2.25E-04	0.0000057
0.05	0.001270	120	168.55	232.42	2.25E-04	0.0000057
0.052	0.001321	120	168.55	232.42	2.25E-04	0.0000057
0.054	0.001372	120	168.55	232.42	2.25E-04	0.0000057
0.056	0.001422	120	168.55	232.42	2.25E-04	0.0000057
0.058	0.001473	120	168.55	232.42	2.25E-04	0.0000057
0.06	0.001524	119	167.15	230.49	2.25E-04	0.0000057
0.062	0.001575	119	167.15	230.49	2.25E-04	0.0000057
0.064	0.001626	119	167.15	230.49	2.25E-04	0.0000057
0.066	0.001676	118	165.74	228.55	2.25E-04	0.0000057
0.068	0.001727	118	165.74	228.55	2.25E-04	0.0000057
0.07	0.001778	118	165.74	228.55	2.25E-04	0.0000057
0.072	0.001829	117	164.34	226.61	2.25E-04	0.0000057
0.074	0.001880	116	162.93	224.68	2.25E-04	0.0000057
0.076	0.001930	116	162.93	224.68	2.25E-04	0.0000057
0.078	0.001981	116	162.93	224.68	2.30E-04	0.0000058
0.08	0.002032	116	162.93	224.68	2.30E-04	0.0000058
0.082	0.002083	116	162.93	224.68	2.35E-04	0.0000060
0.084	0.002134	116	162.93	224.68	2.35E-04	0.0000060
0.086	0.002184	116	162.93	224.68	2.35E-04	0.0000060
0.088	0.002235	116	162.93	224.68	2.35E-04	0.0000060
0.09	0.002286	115	161.53	222.74	2.35E-04	0.0000060
0.092	0.002337	115	161.53	222.74	2.40E-04	0.0000061
0.094	0.002388	115	161.53	222.74	2.40E-04	0.0000061
0.096	0.002438	115	161.53	222.74	2.40E-04	0.0000061
0.098	0.002489	115	161.53	222.74	2.40E-04	0.0000061
0.1	0.002540	115	161.53	222.74	2.40E-04	0.0000061
0.102	0.002591	113	158.72	218.87	2.40E-04	0.0000061
0.104	0.002642	114	160.12	220.80	2.40E-04	0.0000061
0.106	0.002692	114	160.12	220.80	2.40E-04	0.0000061
0.108	0.002743	114	160.12	220.80	2.40E-04	0.0000061
0.11	0.002794	113	158.72	218.87	2.40E-04	0.0000061
0.112	0.002845	113	158.72	218.87	2.40E-04	0.0000061
0.114	0.002896	113	158.72	218.87	2.40E-04	0.0000061
0.116	0.002946	113	158.72	218.87	2.40E-04	0.0000061
0.118	0.002997	113	158.72	218.87	2.40E-04	0.0000061
0.12	0.003048	113	158.72	218.87	2.40E-04	0.0000061
0.122	0.003099	113	158.72	218.87	2.40E-04	0.0000061
0.124	0.003150	113	158.72	218.87	2.40E-04	0.0000061
0.126	0.003200	113	158.72	218.87	2.40E-04	0.0000061
0.128	0.003251	113	158.72	218.87	2.40E-04	0.0000061
0.13	0.003302	113	158.72	218.87	2.40E-04	0.0000061
0.132	0.003353	113	158.72	218.87	2.40E-04	0.0000061
0.134	0.003404	113	158.72	218.87	2.40E-04	0.0000061
0.136	0.003454	113	158.72	218.87	2.45E-04	0.0000062
0.138	0.003505	113	158.72	218.87	2.50E-04	0.0000063
0.14	0.003556	112	157.31	216.93	2.50E-04	0.0000063
0.142	0.003607	112	157.31	216.93	2.50E-04	0.0000063
0.144	0.003658	112	157.31	216.93	2.50E-04	0.0000063
0.146	0.003708	112	157.31	216.93	2.50E-04	0.0000063
0.148	0.003759	112	157.31	216.93	2.50E-04	0.0000063
0.15	0.003810	111	155.91	214.99	2.50E-04	0.0000063
0.152	0.003861	111	155.91	214.99	2.50E-04	0.0000063
0.154	0.003912	111	155.91	214.99	2.50E-04	0.0000063
0.156	0.003962	111	155.91	214.99	2.50E-04	0.0000063
0.158	0.004013	111	155.91	214.99	2.55E-04	0.0000065
0.16	0.004064	110	154.50	213.05	2.55E-04	0.0000065
0.162	0.004115	110	154.50	213.05	2.55E-04	0.0000065
0.164	0.004166	110	154.50	213.05	2.55E-04	0.0000065
0.166	0.004216	110	154.50	213.05	2.60E-04	0.0000066
0.168	0.004267	110	154.50	213.05	2.65E-04	0.0000067

Sample ID:	Z5ba2	Solvent:	Acetone			
Description of the Sample:	Zorbax C18 Dry Silica					
Diameter of the Sample:	2.5	in	=	6.35	cm	
Area of the Sample:	4.9087	in ²	=	31.67	cm	
Normal Pressure:	5	bar				
Mass of the Sample (wet):	46.0	g				
Initial Height of the Sample:	1.1900	cm				
Initial Volume of the Sample:	37.6864	cm ³				
Initial Density of the Sample:	1.2206	g/cm ³				
Horizontal Displacement (inch)	Horizontal Dial Reading (mm)	Shear Force (lb)	Shear Stress (kPa)	Normalized Shear Force (kPa)	Vertical Displacement (mm)	Change of Vertical Displacement (mm)
0	0.000000	0	0.00	0.00	0.00E+00	0.000000
0.002	0.000051	6	8.43	11.62	1.50E-05	0.000004
0.004	0.000102	13	18.26	25.18	1.50E-05	0.000004
0.006	0.000152	35	49.16	67.79	1.50E-05	0.000004
0.008	0.000203	61	85.68	118.15	1.50E-05	0.000004
0.01	0.000254	79	110.96	153.01	1.50E-05	0.000004
0.012	0.000305	89	125.01	172.38	2.00E-05	0.000005
0.014	0.000356	98	137.65	189.81	3.00E-05	0.000008
0.016	0.000406	103	144.67	199.50	4.50E-05	0.000011
0.018	0.000457	108	151.70	209.18	5.00E-05	0.000013
0.02	0.000508	112	157.31	216.93	5.00E-05	0.000013
0.022	0.000559	116	162.90	224.68	5.50E-05	0.000014
0.024	0.000610	119	167.15	230.49	5.50E-05	0.000014
0.026	0.000660	122	171.36	236.30	5.50E-05	0.000014
0.028	0.000711	125	175.57	242.11	5.50E-05	0.000014
0.03	0.000762	126	176.98	244.04	5.50E-05	0.000014
0.032	0.000813	128	179.79	247.92	5.50E-05	0.000014
0.034	0.000864	129	181.19	249.86	5.50E-05	0.000014
0.036	0.000914	128	179.79	247.92	5.50E-05	0.000014
0.038	0.000965	128	179.79	247.92	5.50E-05	0.000014
0.04	0.001016	128	179.79	247.92	5.50E-05	0.000014
0.042	0.001067	128	179.79	247.92	5.50E-05	0.000014
0.044	0.001118	128	179.79	247.92	5.50E-05	0.000014
0.046	0.001168	128	179.79	247.92	5.50E-05	0.000014
0.048	0.001219	128	179.79	247.92	5.50E-05	0.000014
0.05	0.001270	127	178.38	245.98	5.50E-05	0.000014
0.052	0.001321	127	178.38	245.98	5.50E-05	0.000014
0.054	0.001372	127	178.38	245.98	5.50E-05	0.000014
0.056	0.001422	127	178.38	245.98	5.50E-05	0.000014
0.058	0.001473	126	176.98	244.04	5.50E-05	0.000014
0.06	0.001524	126	176.98	244.04	5.50E-05	0.000014
0.062	0.001575	126	176.98	244.04	5.50E-05	0.000014
0.064	0.001626	126	176.98	244.04	5.50E-05	0.000014
0.066	0.001676	125	175.57	242.11	5.50E-05	0.000014
0.068	0.001727	125	175.57	242.11	5.50E-05	0.000014
0.07	0.001778	125	175.57	242.11	5.50E-05	0.000014
0.072	0.001829	125	175.57	242.11	5.50E-05	0.000014
0.074	0.001880	125	175.57	242.11	5.50E-05	0.000014
0.076	0.001930	125	175.57	242.11	5.50E-05	0.000014
0.078	0.001981	125	175.57	242.11	5.50E-05	0.000014
0.08	0.002032	124	174.17	240.17	5.50E-05	0.000014
0.082	0.002083	124	174.17	240.17	5.50E-05	0.000014
0.084	0.002134	124	174.17	240.17	5.50E-05	0.000014
0.086	0.002184	124	174.17	240.17	5.50E-05	0.000014
0.088	0.002235	124	174.17	240.17	5.50E-05	0.000014
0.09	0.002286	123	172.76	238.23	5.50E-05	0.000014
0.092	0.002337	122	171.36	236.30	5.50E-05	0.000014
0.094	0.002388	122	171.36	236.30	5.50E-05	0.000014
0.096	0.002438	122	171.36	236.30	5.50E-05	0.000014
0.098	0.002489	122	171.36	236.30	5.50E-05	0.000014
0.1	0.002540	122	171.36	236.30	5.50E-05	0.000014
0.102	0.002591	122	171.36	236.30	5.50E-05	0.000014
0.104	0.002642	122	171.36	236.30	5.50E-05	0.000014
0.106	0.002692	122	171.36	236.30	5.50E-05	0.000014
0.108	0.002743	121	169.96	234.36	5.50E-05	0.000014
0.11	0.002794	122	171.36	236.30	5.50E-05	0.000014
0.112	0.002845	122	171.36	236.30	5.50E-05	0.000014
0.114	0.002896	122	171.36	236.30	5.50E-05	0.000014
0.116	0.002946	122	171.36	236.30	5.50E-05	0.000014
0.118	0.002997	121	169.96	234.36	5.50E-05	0.000014
0.12	0.003048	121	169.96	234.36	5.50E-05	0.000014
0.122	0.003099	120	168.55	232.42	5.50E-05	0.000014
0.124	0.003150	120	168.55	232.42	6.00E-05	0.000015
0.126	0.003200	120	168.55	232.42	6.00E-05	0.000015
0.128	0.003251	120	168.55	232.42	6.00E-05	0.000015
0.13	0.003302	120	168.55	232.42	6.00E-05	0.000015
0.132	0.003353	120	168.55	232.42	6.00E-05	0.000015
0.134	0.003404	120	168.55	232.42	6.00E-05	0.000015
0.136	0.003454	120	168.55	232.42	6.00E-05	0.000015
0.138	0.003505	119	167.15	230.49	6.00E-05	0.000015
0.14	0.003556	119	167.15	230.49	6.00E-05	0.000015
0.142	0.003607	119	167.15	230.49	6.50E-05	0.000017
0.144	0.003658	119	167.15	230.49	6.50E-05	0.000017
0.146	0.003708	119	167.15	230.49	6.50E-05	0.000017
0.148	0.003759	119	167.15	230.49	7.00E-05	0.000018
0.15	0.003810	119	167.15	230.49	7.00E-05	0.000018
0.152	0.003861	119	167.15	230.49	7.00E-05	0.000018
0.154	0.003912	119	167.15	230.49	7.50E-05	0.000019
0.156	0.003962	119	167.15	230.49	7.50E-05	0.000019
0.158	0.004013	119	167.15	230.49	7.50E-05	0.000019
0.16	0.004064	119	167.15	230.49	7.50E-05	0.000019
0.162	0.004115	119	167.15	230.49	8.00E-05	0.000020
0.164	0.004166	118	165.74	228.55	8.00E-05	0.000020
0.166	0.004216	118	165.74	228.55	8.50E-05	0.000022
0.168	0.004267	118	165.74	228.55	8.50E-05	0.000022
0.17	0.004318	118	165.74	228.55	9.00E-05	0.000023
0.172	0.004369	118	165.74	228.55	9.00E-05	0.000023
0.174	0.004420	118	165.74	228.55	9.00E-05	0.000023
0.176	0.004470	118	165.74	228.55	9.00E-05	0.000023
0.178	0.004521	117	164.34	226.61	9.50E-05	0.000024
0.18	0.004572	117	164.34	226.61	9.50E-05	0.000024
0.182	0.004623	117	164.34	226.61	9.50E-05	0.000024
0.184	0.004674	117	164.34	226.61	9.50E-05	0.000024
0.186	0.004724	117	164.34	226.61	9.50E-05	0.000024
0.188	0.004775	117	164.34	226.61	1.00E-04	0.000025

Sample ID:	Z5ba3	Solvent:	Acetone	6.35	cm	
Description of the Sample:	Zorbax C18 Dry Silica					
Diameter of the Sample:	2.5	in	=	31.67	cm	
Area of the Sample:	4.9087	in ²	=		cm	
Normal Pressure:	5	bar				
Mass of the Sample (dry):	27.3	g	Mass of the sample (wet):	43.3	g	
Initial Height of the Sample:	1.2400	cm				
Initial Volume of the Sample:	39.2698	cm ³				
Initial Density of the Sample:	0.6952	g/cm ³				
Horizontal Displacement (inch)	Horizontal Dial Reading (m)	Shear Force (lb)	Shear Stress (kPa)	Normalized Shear Force (kPa)	Vertical Displacement (in)	Change of Vertical Displacement (m)
0	0.000000	0	0.00	0.00	0.00E+00	0.0000000
0.002	0.000051	10	14.05	19.37	5.00E-06	0.0000001
0.004	0.000102	11	15.45	21.31	-7.00E-05	-0.0000018
0.006	0.000152	13	18.26	25.18	-1.70E-04	-0.0000043
0.008	0.000203	14	19.66	27.12	-2.20E-04	-0.0000056
0.01	0.000254	20	28.09	38.74	-2.30E-04	-0.0000058
0.012	0.000305	39	54.78	75.54	-2.70E-04	-0.0000069
0.014	0.000356	57	80.06	110.40	-2.70E-04	-0.0000069
0.016	0.000406	66	92.70	127.83	-2.70E-04	-0.0000069
0.018	0.000457	73	102.53	141.39	-2.70E-04	-0.0000069
0.02	0.000508	77	108.15	149.14	-2.70E-04	-0.0000069
0.022	0.000559	82	115.18	158.82	-2.70E-04	-0.0000069
0.024	0.000610	89	125.01	172.38	-2.70E-04	-0.0000069
0.026	0.000660	93	130.63	180.13	-2.70E-04	-0.0000069
0.028	0.000711	97	136.25	187.88	-2.70E-04	-0.0000069
0.03	0.000762	101	141.86	195.62	-2.70E-04	-0.0000069
0.032	0.000813	105	147.48	203.37	-2.70E-04	-0.0000069
0.034	0.000864	109	153.10	211.12	-2.70E-04	-0.0000069
0.036	0.000914	112	157.31	216.93	-2.70E-04	-0.0000069
0.038	0.000965	115	161.53	222.74	-2.10E-04	-0.0000053
0.04	0.001016	119	167.15	230.49	-1.60E-04	-0.0000041
0.042	0.001067	121	169.96	234.36	-1.60E-04	-0.0000041
0.044	0.001118	123	172.76	238.23	-9.00E-05	-0.0000023
0.046	0.001168	125	175.57	242.11	-4.00E-05	-0.0000010
0.048	0.001219	127	178.38	245.98	0.00E+00	0.0000000
0.05	0.001270	127	178.38	245.98	1.00E-05	0.0000003
0.052	0.001321	127	178.38	245.98	1.00E-05	0.0000003
0.054	0.001372	128	179.79	247.92	3.00E-05	0.0000008
0.056	0.001422	127	178.38	245.98	7.00E-05	0.0000018
0.058	0.001473	127	178.38	245.98	9.00E-05	0.0000023
0.06	0.001524	126	176.98	244.04	9.00E-05	0.0000023
0.062	0.001575	125	175.57	242.11	9.50E-05	0.0000024
0.064	0.001626	125	175.57	242.11	9.50E-05	0.0000024
0.066	0.001676	125	175.57	242.11	1.05E-04	0.0000027
0.068	0.001727	124	174.17	240.17	1.15E-04	0.0000029
0.07	0.001778	124	174.17	240.17	1.15E-04	0.0000029
0.072	0.001829	124	174.17	240.17	1.35E-04	0.0000034
0.074	0.001880	123	172.76	238.23	1.45E-04	0.0000037
0.076	0.001930	123	172.76	238.23	1.45E-04	0.0000037
0.078	0.001981	122	171.36	236.30	1.60E-04	0.0000041
0.08	0.002032	122	171.36	236.30	1.60E-04	0.0000041
0.082	0.002083	122	171.36	236.30	1.80E-04	0.0000046
0.084	0.002134	122	171.36	236.30	1.90E-04	0.0000048
0.086	0.002184	122	171.36	236.30	2.00E-04	0.0000051
0.088	0.002235	122	171.36	236.30	2.05E-04	0.0000052
0.09	0.002286	122	171.36	236.30	2.10E-04	0.0000053
0.092	0.002337	121	169.96	234.36	2.35E-04	0.0000060
0.094	0.002388	121	169.96	234.36	2.45E-04	0.0000062
0.096	0.002438	120	168.55	232.42	2.45E-04	0.0000062
0.098	0.002489	120	168.55	232.42	2.70E-04	0.0000069
0.1	0.002540	120	168.55	232.42	2.80E-04	0.0000071
0.102	0.002591	120	168.55	232.42	2.90E-04	0.0000074
0.104	0.002642	120	168.55	232.42	2.95E-04	0.0000075
0.106	0.002692	120	168.55	232.42	2.95E-04	0.0000075
0.108	0.002743	120	168.55	232.42	3.00E-04	0.0000076
0.11	0.002794	119	167.15	230.49	3.05E-04	0.0000077
0.112	0.002845	119	167.15	230.49	3.05E-04	0.0000077
0.114	0.002896	119	167.15	230.49	3.05E-04	0.0000077
0.116	0.002946	119	167.15	230.49	3.05E-04	0.0000077
0.118	0.002997	119	167.15	230.49	3.05E-04	0.0000077
0.12	0.003048	119	167.15	230.49	3.05E-04	0.0000077
0.122	0.003099	118	165.74	228.55	3.10E-04	0.0000079
0.124	0.003150	118	165.74	228.55	3.15E-04	0.0000080
0.126	0.003200	117	164.34	226.61	3.20E-04	0.0000081
0.128	0.003251	117	164.34	226.61	3.20E-04	0.0000081
0.13	0.003302	117	164.34	226.61	3.25E-04	0.0000083
0.132	0.003353	117	164.34	226.61	3.25E-04	0.0000083
0.134	0.003404	116	162.93	224.68	3.30E-04	0.0000084
0.136	0.003454	116	162.93	224.68	3.30E-04	0.0000084
0.138	0.003505	116	162.93	224.68	3.30E-04	0.0000084
0.14	0.003556	116	162.93	224.68	3.30E-04	0.0000084
0.142	0.003607	116	162.93	224.68	3.30E-04	0.0000084
0.144	0.003658	116	162.93	224.68	3.30E-04	0.0000084
0.146	0.003708	117	164.34	226.61	3.35E-04	0.0000085
0.148	0.003759	117	164.34	226.61	3.40E-04	0.0000086
0.15	0.003810	117	164.34	226.61	3.40E-04	0.0000086
0.152	0.003861	116	162.93	224.68	3.40E-04	0.0000086
0.154	0.003912	117	164.34	226.61	3.45E-04	0.0000088
0.156	0.003962	117	164.34	226.61	3.45E-04	0.0000088
0.158	0.004013	117	164.34	226.61	3.50E-04	0.0000089
0.16	0.004064	117	164.34	226.61	3.50E-04	0.0000089
0.162	0.004115	116	162.93	224.68	3.55E-04	0.0000090
0.164	0.004166	116	162.93	224.68	3.55E-04	0.0000090
0.166	0.004216	116	162.93	224.68	3.65E-04	0.0000093
0.168	0.004267	117	164.34	226.61	3.65E-04	0.0000093
0.17	0.004318	116	162.93	224.68	3.65E-04	0.0000093
0.172	0.004369	116	162.93	224.68	3.70E-04	0.0000094
0.174	0.004420	116	162.93	224.68	3.70E-04	0.0000094
0.176	0.004470	116	162.93	224.68	3.70E-04	0.0000094
0.178	0.004521	116	162.93	224.68	3.75E-04	0.0000095
0.18	0.004572	116	162.93	224.68	3.75E-04	0.0000095

Sample ID:	Z10ba1	Solvent:	Acetone			
Description of the Sample:	Zorbax C18 Dry Silica					
Diameter of the Sample:	2.5	in	=	6.35	cm	
Area of the Sample:	4.9087	in ²	=	31.67	cm ²	
Normal Pressure:	10	bar				
Mass of the Sample (dry):	27.3	g		Mass of the sample (wet):	41.4 g	
Initial Height of the Sample:	1.1900	cm				
Initial Volume of the Sample:	37.6864	cm ³				
Initial Density of the Sample:	0.7244	g/cm ³				
Horizontal Displacement (inch)	Horizontal Dial Reading (m)	Shear Force (lb)	Shear Stress (kPa)	Normalized Shear Force (kPa)	Vertical Displacement (in)	Change of Vertical Displacement (m)
0	0.000000	0	0.00	0.00	0.00E+00	0.0000000
0.002	0.000051	5	7.02	4.84	0.00E+00	0.0000000
0.004	0.000102	7	9.83	6.78	0.00E+00	0.0000000
0.006	0.000152	60	84.28	58.11	0.00E+00	0.0000000
0.008	0.000203	102	143.27	98.78	0.00E+00	0.0000000
0.01	0.000254	138	193.83	133.64	0.00E+00	0.0000000
0.012	0.000305	163	228.95	157.85	0.00E+00	0.0000000
0.014	0.000356	186	261.25	180.13	2.00E-05	0.0000005
0.016	0.000406	201	282.32	194.65	5.00E-05	0.0000013
0.018	0.000457	213	299.18	206.28	7.00E-05	0.0000018
0.02	0.000508	222	311.82	214.99	1.00E-04	0.0000025
0.022	0.000559	229	321.65	221.77	1.30E-04	0.0000033
0.024	0.000610	236	331.48	228.55	1.50E-04	0.0000038
0.026	0.000660	243	341.32	235.33	1.60E-04	0.0000041
0.028	0.000711	248	348.34	240.17	1.80E-04	0.0000046
0.03	0.000762	254	356.77	245.98	2.10E-04	0.0000053
0.032	0.000813	259	363.79	250.82	2.40E-04	0.0000061
0.034	0.000864	263	369.41	254.70	2.70E-04	0.0000069
0.036	0.000914	266	373.62	257.60	2.70E-04	0.0000069
0.038	0.000965	269	377.83	260.51	3.20E-04	0.0000081
0.04	0.001016	272	382.05	263.41	3.70E-04	0.0000094
0.042	0.001067	275	386.26	266.32	3.90E-04	0.0000099
0.044	0.001118	275	386.26	266.32	4.00E-04	0.0000102
0.046	0.001168	277	389.07	268.26	4.20E-04	0.0000107
0.048	0.001219	278	390.48	269.22	4.40E-04	0.0000112
0.05	0.001270	279	391.88	270.19	4.40E-04	0.0000112
0.052	0.001321	279	391.88	270.19	4.50E-04	0.0000114
0.054	0.001372	279	391.88	270.19	4.50E-04	0.0000114
0.056	0.001422	279	391.88	270.19	4.70E-04	0.0000119
0.058	0.001473	280	393.28	271.16	4.80E-04	0.0000122
0.06	0.001524	279	391.88	270.19	4.85E-04	0.0000123
0.062	0.001575	279	391.88	270.19	4.85E-04	0.0000123
0.064	0.001626	279	391.88	270.19	4.85E-04	0.0000123
0.066	0.001676	279	391.88	270.19	4.85E-04	0.0000123
0.068	0.001727	278	390.48	269.22	5.00E-04	0.0000127
0.07	0.001778	278	390.48	269.22	5.00E-04	0.0000127
0.072	0.001829	278	390.48	269.22	5.20E-04	0.0000132
0.074	0.001880	278	390.48	269.22	5.25E-04	0.0000133
0.076	0.001930	277	389.07	268.26	5.30E-04	0.0000135
0.078	0.001981	278	390.48	269.22	5.35E-04	0.0000136
0.08	0.002032	278	390.48	269.22	5.35E-04	0.0000136
0.082	0.002083	278	390.48	269.22	5.40E-04	0.0000137
0.084	0.002134	277	389.07	268.26	5.45E-04	0.0000138
0.086	0.002184	276	387.67	267.29	5.45E-04	0.0000138
0.088	0.002235	275	386.26	266.32	5.45E-04	0.0000138
0.09	0.002286	275	386.26	266.32	5.50E-04	0.0000140
0.092	0.002337	275	386.26	266.32	5.55E-04	0.0000141
0.094	0.002388	275	386.26	266.32	5.60E-04	0.0000142
0.096	0.002438	275	386.26	266.32	5.60E-04	0.0000142
0.098	0.002489	275	386.26	266.32	5.65E-04	0.0000144
0.1	0.002540	275	386.26	266.32	5.65E-04	0.0000144
0.102	0.002591	275	386.26	266.32	5.65E-04	0.0000144
0.104	0.002642	275	386.26	266.32	5.65E-04	0.0000144
0.106	0.002692	275	386.26	266.32	5.65E-04	0.0000144
0.108	0.002743	275	386.26	266.32	5.65E-04	0.0000144
0.11	0.002794	275	386.26	266.32	5.65E-04	0.0000144
0.112	0.002845	275	386.26	266.32	5.65E-04	0.0000144
0.114	0.002896	275	386.26	266.32	5.65E-04	0.0000144
0.116	0.002946	275	386.26	266.32	5.70E-04	0.0000145
0.118	0.002997	275	386.26	266.32	5.70E-04	0.0000145
0.12	0.003048	275	386.26	266.32	5.75E-04	0.0000146
0.122	0.003099	275	386.26	266.32	5.80E-04	0.0000147
0.124	0.003150	275	386.26	266.32	5.85E-04	0.0000149
0.126	0.003200	275	386.26	266.32	5.85E-04	0.0000149
0.128	0.003251	275	386.26	266.32	5.90E-04	0.0000150
0.13	0.003302	274	384.86	265.35	5.90E-04	0.0000150
0.132	0.003353	274	384.86	265.35	5.90E-04	0.0000150
0.134	0.003404	274	384.86	265.35	5.95E-04	0.0000151
0.136	0.003454	274	384.86	265.35	5.95E-04	0.0000151
0.138	0.003505	274	384.86	265.35	5.95E-04	0.0000151
0.14	0.003556	273	383.45	264.38	5.95E-04	0.0000151
0.142	0.003607	273	383.45	264.38	5.95E-04	0.0000151
0.144	0.003658	273	383.45	264.38	5.95E-04	0.0000151
0.146	0.003708	273	383.45	264.38	6.00E-04	0.0000152
0.148	0.003759	273	383.45	264.38	6.00E-04	0.0000152
0.15	0.003810	273	383.45	264.38	6.05E-04	0.0000154
0.152	0.003861	274	384.86	265.35	6.10E-04	0.0000155
0.154	0.003912	274	384.86	265.35	6.15E-04	0.0000156
0.156	0.003962	273	383.45	264.38	6.20E-04	0.0000157
0.158	0.004013	273	383.45	264.38	6.25E-04	0.0000159
0.16	0.004064	273	383.45	264.38	6.25E-04	0.0000159
0.162	0.004115	274	384.86	265.35	6.30E-04	0.0000160
0.164	0.004166	274	384.86	265.35	6.30E-04	0.0000160
0.166	0.004216	274	384.86	265.35	6.30E-04	0.0000160
0.168	0.004267	273	383.45	264.38	6.30E-04	0.0000160
0.17	0.004318	272	382.05	263.41	6.35E-04	0.0000161
0.172	0.004369	272	382.05	263.41	6.40E-04	0.0000163
0.174	0.004420	273	383.45	264.38	6.40E-04	0.0000163
0.176	0.004470	273	383.45	264.38	6.40E-04	0.0000163
0.178	0.004521	272	382.05	263.41	6.40E-04	0.0000163

Sample ID:	Z30ba1					
Description of the Sample:	Zorbax C18 Dry Silica	Solvent:	Acetone			
Diameter of the Sample:	2.5	in	=	6.35	cm	
Area of the Sample:	4.9087	in ²	=	31.67	cm	
Normal Pressure:	30	bar				
Mass of the Sample (dry):	26.8	g				
Initial Height of the Sample:	1.0400	cm				
Initial Volume of the Sample:	32.9360	cm ³				
Initial Density of the Sample:	0.8137	g/cm ³				
Horizontal Displacement	Horizontal Dial	Shear Force	Shear Stress	Normalized Shear	Vertical	Change of Vertical
(inch)	Reading (m)	(lb)	(kPa)	Force (kPa)	Displacement (in)	Displacement (m)
0.000000	0.000000	0	0.00	0.00	0.000000	0.000000
0.002000	0.000051	102	143.27	32.93	0.000000	0.000000
0.004000	0.000102	151	212.09	48.74	0.000000	0.000000
0.006000	0.000152	186	261.25	60.04	0.000000	0.000000
0.008000	0.000203	259	363.79	83.61	0.000000	0.000000
0.010000	0.000254	326	457.90	105.24	0.000020	0.000005
0.012000	0.000305	387	543.58	124.93	0.000065	0.000017
0.014000	0.000356	441	619.42	142.36	0.000145	0.000037
0.016000	0.000406	497	698.08	160.44	0.000205	0.000052
0.018000	0.000457	539	757.07	173.99	0.000245	0.000062
0.020000	0.000508	575	807.64	185.62	0.000265	0.000067
0.022000	0.000559	609	855.39	196.59	0.000270	0.000069
0.024000	0.000610	643	903.15	207.57	0.000275	0.000070
0.026000	0.000660	670	941.07	216.28	0.000275	0.000070
0.028000	0.000711	695	976.19	224.35	0.000280	0.000071
0.030000	0.000762	718	1008.49	231.78	0.000290	0.000074
0.032000	0.000813	741	1040.80	239.20	0.000305	0.000077
0.034000	0.000864	757	1063.27	244.37	0.000325	0.000083
0.036000	0.000914	775	1088.56	250.18	0.000345	0.000088
0.038000	0.000965	780	1095.58	251.79	0.000350	0.000089
0.040000	0.001016	802	1126.48	258.89	0.000360	0.000091
0.042000	0.001067	819	1150.36	264.38	0.000375	0.000095
0.044000	0.001118	830	1165.81	267.93	0.000385	0.000098
0.046000	0.001168	843	1184.07	272.13	0.000395	0.000100
0.048000	0.001219	855	1200.92	276.00	0.000410	0.000104
0.050000	0.001270	865	1214.97	279.23	0.000425	0.000108
0.052000	0.001321	875	1229.02	282.46	0.000430	0.000109
0.054000	0.001372	882	1238.85	284.72	0.000435	0.000110
0.056000	0.001422	890	1250.08	287.30	0.000440	0.000112
0.058000	0.001473	897	1259.92	289.56	0.000445	0.000113
0.060000	0.001524	904	1269.75	291.82	0.000445	0.000113
0.062000	0.001575	910	1278.18	293.76	0.000445	0.000113
0.064000	0.001626	916	1286.60	295.69	0.000445	0.000113
0.066000	0.001676	921	1293.63	297.31	0.000445	0.000113
0.068000	0.001727	923	1296.44	297.95	0.000445	0.000113
0.070000	0.001778	926	1300.65	298.92	0.000445	0.000113
0.072000	0.001829	931	1307.67	300.54	0.000445	0.000113
0.074000	0.001880	933	1310.48	301.18	0.000445	0.000113
0.076000	0.001930	936	1314.70	302.15	0.000445	0.000113
0.078000	0.001981	937	1316.10	302.47	0.000445	0.000113
0.080000	0.002032	938	1317.50	302.80	0.000445	0.000113
0.082000	0.002083	939	1318.91	303.12	0.000445	0.000113
0.084000	0.002134	939	1318.91	303.12	0.000445	0.000113
0.086000	0.002184	939	1318.91	303.12	0.000445	0.000113
0.088000	0.002235	939	1318.91	303.12	0.000445	0.000113
0.090000	0.002286	936	1314.70	302.15	0.000445	0.000113
0.092000	0.002337	936	1314.70	302.15	0.000445	0.000113
0.094000	0.002388	934	1311.89	301.50	0.000445	0.000113
0.096000	0.002438	935	1313.29	301.83	0.000445	0.000113
0.098000	0.002489	935	1313.29	301.83	0.000445	0.000113
0.100000	0.002540	931	1307.67	300.54	0.000445	0.000113
0.102000	0.002591	930	1306.27	300.21	0.000445	0.000113
0.104000	0.002642	930	1306.27	300.21	0.000445	0.000113
0.106000	0.002692	930	1306.27	300.21	0.000445	0.000113
0.108000	0.002743	929	1304.86	299.89	0.000445	0.000113
0.110000	0.002794	929	1304.86	299.89	0.000445	0.000113
0.112000	0.002845	933	1310.48	301.18	0.000445	0.000113
0.114000	0.002896	930	1306.27	300.21	0.000445	0.000113
0.116000	0.002946	930	1306.27	300.21	0.000445	0.000113
0.118000	0.002997	932	1309.08	300.86	0.000445	0.000113
0.120000	0.003048	932	1309.08	300.86	0.000445	0.000113
0.122000	0.003099	929	1304.86	299.89	0.000445	0.000113
0.124000	0.003150	930	1306.27	300.21	0.000445	0.000113

Sample ID:	Z30ba2	Solvent:	Acetone			
Description of the Sample:	Zorbax C18 Dry Silica					
Diameter of the Sample:	2.5	in	6.35	cm		
Area of the Sample:	4.9087	in ²	31.67	cm		
Normal Pressure:	30	bar				
Mass of the Sample (dry):	26.8	g				
Initial Height of the Sample:	1.0400	cm				
Initial Volume of the Sample:	32.9360	cm ³				
Initial Density of the Sample:	0.8137	g/cm ³				
Horizontal Displacement (inch)	Horizontal Dial Reading (m)	Shear Force (lb)	Shear Stress (kPa)	Normalized Shear Force (kPa)	Vertical Displacement (in)	Change of Vertical Displacement (m)
0.000000	0.000000	0	0.00	0.00	0.000000	0.0000000
0.002000	0.000051	16	22.47	5.16	0.000055	0.0000014
0.004000	0.000102	20	28.09	6.46	0.000095	0.0000024
0.006000	0.000152	23	32.31	7.42	0.000135	0.0000034
0.008000	0.000203	24	33.71	7.75	0.000195	0.0000050
0.010000	0.000254	24	33.71	7.75	0.000235	0.0000060
0.012000	0.000305	53	74.44	17.11	0.000255	0.0000065
0.014000	0.000356	120	168.55	38.74	0.000275	0.0000070
0.016000	0.000406	195	273.89	62.95	0.000280	0.0000071
0.018000	0.000457	261	366.60	84.25	0.000285	0.0000072
0.020000	0.000508	330	463.51	106.53	0.000295	0.0000075
0.022000	0.000559	385	540.77	124.28	0.000305	0.0000077
0.024000	0.000610	440	618.02	142.04	0.000325	0.0000083
0.026000	0.000660	481	675.61	155.27	0.000355	0.0000090
0.028000	0.000711	530	744.43	171.09	0.000385	0.0000098
0.030000	0.000762	568	797.81	183.36	0.000415	0.0000105
0.032000	0.000813	605	849.78	195.30	0.000435	0.0000110
0.034000	0.000864	630	884.89	203.37	0.000455	0.0000116
0.036000	0.000914	656	921.41	211.76	0.000475	0.0000121
0.038000	0.000965	680	955.12	219.51	0.000485	0.0000123
0.040000	0.001016	706	991.64	227.90	0.000495	0.0000126
0.042000	0.001067	718	1008.49	231.78	0.000505	0.0000128
0.044000	0.001118	735	1032.37	237.27	0.000515	0.0000131
0.046000	0.001168	747	1049.23	241.14	0.000535	0.0000136
0.048000	0.001219	763	1071.70	246.30	0.000555	0.0000141
0.050000	0.001270	776	1089.96	250.50	0.000560	0.0000142
0.052000	0.001321	788	1106.82	254.37	0.000565	0.0000144
0.054000	0.001372	801	1125.08	258.57	0.000570	0.0000145
0.056000	0.001422	812	1140.53	262.12	0.000575	0.0000146
0.058000	0.001473	821	1153.17	265.03	0.000575	0.0000146
0.060000	0.001524	829	1164.40	267.61	0.000580	0.0000147
0.062000	0.001575	837	1175.64	270.19	0.000585	0.0000149
0.064000	0.001626	843	1184.07	272.13	0.000595	0.0000151
0.066000	0.001676	850	1193.90	274.39	0.000600	0.0000152
0.068000	0.001727	856	1202.33	276.33	0.000605	0.0000154
0.070000	0.001778	861	1209.35	277.94	0.000610	0.0000155
0.072000	0.001829	865	1214.97	279.23	0.000615	0.0000156
0.074000	0.001880	869	1220.59	280.52	0.000625	0.0000159
0.076000	0.001930	872	1224.80	281.49	0.000635	0.0000161
0.078000	0.001981	874	1227.61	282.14	0.000655	0.0000166
0.080000	0.002032	875	1229.02	282.46	0.000665	0.0000169
0.082000	0.002083	875	1229.02	282.46	0.000670	0.0000170
0.084000	0.002134	874	1227.61	282.14	0.000675	0.0000171
0.086000	0.002184	873	1226.21	281.81	0.000680	0.0000173
0.088000	0.002235	872	1224.80	281.49	0.000685	0.0000174
0.090000	0.002286	870	1221.99	280.84	0.000690	0.0000175
0.092000	0.002337	869	1220.59	280.52	0.000695	0.0000177
0.094000	0.002388	869	1220.59	280.52	0.000700	0.0000178
0.096000	0.002438	868	1219.18	280.20	0.000705	0.0000179
0.098000	0.002489	868	1219.18	280.20	0.000705	0.0000179
0.100000	0.002540	869	1220.59	280.52	0.000710	0.0000180
0.102000	0.002591	868	1219.18	280.20	0.000710	0.0000180
0.104000	0.002642	870	1221.99	280.84	0.000715	0.0000182
0.106000	0.002692	870	1221.99	280.84	0.000725	0.0000184
0.108000	0.002743	870	1221.99	280.84	0.000730	0.0000185
0.110000	0.002794	870	1221.99	280.84	0.000735	0.0000187
0.112000	0.002845	870	1221.99	280.84	0.000740	0.0000188
0.114000	0.002896	870	1221.99	280.84	0.000745	0.0000189
0.116000	0.002946	870	1221.99	280.84	0.000755	0.0000192
0.118000	0.002997	870	1221.99	280.84	0.000765	0.0000194
0.120000	0.003048	870	1221.99	280.84	0.000770	0.0000196
0.122000	0.003099	870	1221.99	280.84	0.000775	0.0000197
0.124000	0.003150	870	1221.99	280.84	0.000780	0.0000198
0.126000	0.003200	870	1221.99	280.84	7.85E-04	0.0000199
0.128000	0.003251	870	1221.99	280.84	0.00079	0.0000201
0.130000	0.003302	870	1221.99	280.84	0.000795	0.0000202
0.132000	0.003353	870	1221.99	280.84	0.0008	0.0000203
0.134000	0.003404	870	1221.99	280.84	0.0008	0.0000203
0.136000	0.003454	870	1221.99	280.84	0.000805	0.0000204
0.138000	0.003505	870	1221.99	280.84	0.000805	0.0000204
0.140000	0.003556	870	1221.99	280.84	0.00081	0.0000206
0.142000	0.003607	870	1221.99	280.84	0.000815	0.0000207

Sample ID:	K10bm1	* New sample		* Stick and slip behavior is observed		
Description of the Sample:	Kromasil C8 Dry Silica	Solvent:	Methanol			
Diameter of the Sample:	2.5	in	=	6.35	cm	
Area of the Sample:	4.9087	in ²	=	31.67	cm	
Normal Pressure:	10	bar				
Mass of the Sample (wet):	40.6	g		Mass of the sample (dry):	21.7	g
Initial Height of the Sample:	1.1400	cm				
Initial Volume of the Sample:	36.1029	cm ³				
Initial Density of the Sample:	1.1246	g/cm ³				
Horizontal Displacement	Horizontal Dial Reading	Shear Force	Shear Stress	Normalized Shear Force	Vertical Displacement	Change of Vertical Displacement
(inch)	(m)	(lb)	(kPa)	(kPa)	(in)	(m)
0	0.000000	0	0.00	0.00	0.00E+00	0.0000000
0.002	0.000051	10	14.05	9.68	6.00E-04	0.0000152
0.004	0.000102	13	18.26	12.59	7.00E-04	0.0000178
0.006	0.000152	19	26.69	18.40	7.50E-04	0.0000190
0.008	0.000203	45	63.21	43.58	9.00E-04	0.0000229
0.01	0.000254	68	95.51	65.85	1.05E-03	0.0000267
0.012	0.000305	90	126.41	87.16	1.40E-03	0.0000356
0.014	0.000356	105	147.48	101.69	1.50E-03	0.0000381
0.016	0.000406	118	165.74	114.27	1.50E-03	0.0000381
0.018	0.000457	128	179.79	123.96	1.50E-03	0.0000381
0.02	0.000508	138	193.83	133.64	1.50E-03	0.0000381
0.022	0.000559	146	205.07	141.39	1.50E-03	0.0000381
0.024	0.000610	145	203.67	140.42	1.50E-03	0.0000381
0.026	0.000660	147	206.47	142.36	1.50E-03	0.0000381
0.028	0.000711	150	210.69	145.26	1.50E-03	0.0000381
0.03	0.000762	147	206.47	142.36	1.55E-03	0.0000394
0.032	0.000813	147	206.47	142.36	1.60E-03	0.0000406
0.034	0.000864	150	210.69	145.26	1.65E-03	0.0000419
0.036	0.000914	146	205.07	141.39	1.70E-03	0.0000432
0.038	0.000965	153	214.90	148.17	1.75E-03	0.0000444
0.04	0.001016	160	224.73	154.95	1.75E-03	0.0000444
0.042	0.001067	151	212.09	146.23	1.75E-03	0.0000444
0.044	0.001118	161	226.14	155.92	1.75E-03	0.0000444
0.046	0.001168	154	216.31	149.14	1.75E-03	0.0000444
0.048	0.001219	154	216.31	149.14	1.75E-03	0.0000444
0.05	0.001270	154	216.31	149.14	1.75E-03	0.0000444
0.052	0.001321	157	220.52	152.04	1.80E-03	0.0000457
0.054	0.001372	158	221.93	153.01	1.80E-03	0.0000457
0.056	0.001422	160	224.73	154.95	1.85E-03	0.0000470
0.058	0.001473	165	231.76	159.79	1.90E-03	0.0000483
0.06	0.001524	163	228.95	157.85	1.95E-03	0.0000495
0.062	0.001575	162	227.54	156.89	2.00E-03	0.0000508
0.064	0.001626	160	224.73	154.95	2.00E-03	0.0000508
0.066	0.001676	160	224.73	154.95	2.05E-03	0.0000521
0.068	0.001727	160	224.73	154.95	2.05E-03	0.0000521
0.07	0.001778	160	224.73	154.95	2.05E-03	0.0000521
0.072	0.001829	160	224.73	154.95	2.05E-03	0.0000521
0.074	0.001880	160	224.73	154.95	2.05E-03	0.0000521
0.076	0.001930	160	224.73	154.95	2.05E-03	0.0000521

Sample ID	K20bm1		* Stick and slip behavior is observed				
Description of the Sample:	Kromasil C8 Dry Silica	Solvent:	Methanol				* New sample
Diameter of the Sample:	2.5	in	=	6.35	cm		
Area of the Sample:	4.9087	in ²	=	31.67	cm		
Normal Pressure:	20	bar					
Mass of the Sample (wet):	41.7	g		Mass of the	21.2	g	
				sample (dry):			
Initial Height of the Sample:	1.2400	cm					
Initial Volume of the Sample:	39.2698	cm ³					
Initial Density of the Sample:	1.0619	g/cm ³					
Horizontal Displacement	Horizontal Dial Reading	Shear	Shear	Normalized	Vertical	Change of Vertical	
		Force	Stress	Shear Force	Displacement	Displacement	
(inch)	(m)	(lb)	(kPa)	(kPa)	(in)	(m)	
0	0.000000	0	0.00	0.00	0.00E+00	0.0000000	
0.002	0.000051	6	8.43	2.91	2.50E-04	0.0000063	
0.004	0.000102	12	16.86	5.81	8.00E-04	0.0000203	
0.006	0.000152	48	67.42	23.24	8.50E-04	0.0000216	
0.008	0.000203	85	119.39	41.16	1.00E-03	0.0000254	
0.01	0.000254	115	161.53	55.68	1.25E-03	0.0000317	
0.012	0.000305	140	196.64	67.79	1.55E-03	0.0000394	
0.014	0.000356	170	238.78	82.32	1.70E-03	0.0000432	
0.016	0.000406	188	264.06	91.03	1.80E-03	0.0000457	
0.018	0.000457	208	292.15	100.72	1.85E-03	0.0000470	
0.02	0.000508	229	321.65	110.89	2.00E-03	0.0000508	
0.022	0.000559	242	339.91	117.18	2.20E-03	0.0000559	
0.024	0.000610	257	360.98	124.44	2.35E-03	0.0000597	
0.026	0.000660	265	372.22	128.32	2.70E-03	0.0000686	
0.028	0.000711	275	386.26	133.16	2.85E-03	0.0000724	
0.03	0.000762	284	398.90	137.52	3.05E-03	0.0000775	
0.032	0.000813	290	407.33	140.42	3.25E-03	0.0000825	
0.034	0.000864	300	421.38	145.26	3.65E-03	0.0000927	
0.036	0.000914	307	431.21	148.65	3.95E-03	0.0001003	
0.038	0.000965	288	404.52	139.45	4.25E-03	0.0001079	
0.04	0.001016	278	390.48	134.61	4.55E-03	0.0001156	
0.042	0.001067	294	412.95	142.36	5.05E-03	0.0001283	
0.044	0.001118	284	398.90	137.52	5.65E-03	0.0001435	
0.046	0.001168	285	400.31	138.00	5.85E-03	0.0001486	
0.048	0.001219	298	418.57	144.30	6.30E-03	0.0001600	
0.05	0.001270	291	408.74	140.91	6.55E-03	0.0001664	
0.052	0.001321	289	405.93	139.94	6.65E-03	0.0001689	
0.054	0.001372	296	415.76	143.33	6.95E-03	0.0001765	
0.056	0.001422	304	427.00	147.20	7.35E-03	0.0001867	
0.058	0.001473	301	422.78	145.75	7.65E-03	0.0001943	
0.06	0.001524	307	431.21	148.65	7.85E-03	0.0001994	
0.062	0.001575	308	432.61	149.14	8.00E-03	0.0002032	
0.064	0.001626	313	439.64	151.56	8.20E-03	0.0002083	
0.066	0.001676	316	443.85	153.01	8.35E-03	0.0002121	
0.068	0.001727	320	449.47	154.95	8.60E-03	0.0002184	
0.07	0.001778	332	466.32	160.76	8.75E-03	0.0002222	

Sample ID:	K20bm2	* Stick and slip behavior is observed * Old sample from previous K10bm1				
Description of the Sample:	Kromasil C8 Dry Silica	Solvent:	Methanol			
Diameter of the Sample:	2.5	in	=	6.35	cm	
Area of the Sample:	4.9087	in ²	=	31.67	cm	
Normal Pressure:	20	bar				
Mass of the Sample (wet):	35.27	g	Mass of the	18.96	g	
		sample (dry):				
Initial Height of the Sample:	1.3900	cm				
Initial Volume of the Sample:	44.0202	cm ³				
Initial Density of the Sample:	0.8012	g/cm ³				
Horizontal Displacement	Horizontal Dial Reading	Shear Force	Shear Stress	Normalized Shear Force	Vertical Displacement	Change of Vertical Displacement
(inch)	(m)	(lb)	(kPa)	(kPa)	(in)	(m)
0	0.000000	0	0.00	0.00	0.00E+00	0.0000000
0.002	0.000051	13	18.26	6.29	2.00E-05	0.0000005
0.004	0.000102	17	23.88	8.23	8.00E-05	0.0000020
0.006	0.000152	22	30.90	10.65	1.50E-04	0.0000038
0.008	0.000203	22	30.90	10.65	1.70E-04	0.0000043
0.01	0.000254	26	36.52	12.59	1.75E-04	0.0000044
0.012	0.000305	28	39.33	13.56	1.75E-04	0.0000044
0.014	0.000356	30	42.14	14.53	1.75E-04	0.0000044
0.016	0.000406	33	46.35	15.98	1.75E-04	0.0000044
0.018	0.000457	45	63.21	21.79	1.75E-04	0.0000044
0.02	0.000508	109	153.10	52.78	1.75E-04	0.0000044
0.022	0.000559	162	227.54	78.44	1.75E-04	0.0000044
0.024	0.000610	206	289.35	99.75	1.75E-04	0.0000044
0.026	0.000660	237	332.89	114.76	1.75E-04	0.0000044
0.028	0.000711	267	375.03	129.29	1.75E-04	0.0000044
0.03	0.000762	290	407.33	140.42	1.75E-04	0.0000044
0.032	0.000813	295	414.35	142.84	1.75E-04	0.0000044
0.034	0.000864	288	404.52	139.45	1.80E-04	0.0000046
0.036	0.000914	288	404.52	139.45	1.80E-04	0.0000046
0.038	0.000965	257	360.98	124.44	1.80E-04	0.0000046
0.04	0.001016	256	359.57	123.96	1.85E-04	0.0000047
0.042	0.001067	256	359.57	123.96	1.90E-04	0.0000048
0.044	0.001118	256	359.57	123.96	1.95E-04	0.0000050
0.046	0.001168	256	359.57	123.96	2.00E-04	0.0000051
0.048	0.001219	256	359.57	123.96	2.00E-04	0.0000051
0.05	0.001270	256	359.57	123.96	2.00E-04	0.0000051
0.052	0.001321	256	359.57	123.96	2.00E-04	0.0000051
0.054	0.001372	256	359.57	123.96	2.05E-04	0.0000052
0.056	0.001422	256	359.57	123.96	2.05E-04	0.0000052
0.058	0.001473	256	359.57	123.96	2.05E-04	0.0000052

Sample ID:	K30bm1	* Stick and slip behavior is observed * New sample				
Description of the Sample:	Kromasil C8 Dry Silica	Solvent:	Methanol			
Diameter of the Sample:	2.5	in	=	6.35	cm	
Area of the Sample:	4.9087	in ²	=	31.67	cm	
Normal Pressure:	30	bar				
Mass of the Sample (Wet):	43.7	g	Mass of the	22.8	g	
Sample (Dry):						
Initial Height of the Sample:	1.3200	cm				
Initial Volume of the Sample:	41.8034	cm ³				
Initial Density of the Sample:	1.0454	g/cm ³				
Horizontal Displacement	Horizontal Dial Reading	Shear Force	Shear Stress	Normalized Shear Force	Vertical Displacement	Change of Vertical Displacement
(inch)	(m)	(lb)	(kPa)	(kPa)	(in)	(m)
0	0.000000	0	0.00	0.00	0.00E+00	0.0000000
0.002	0.000051	12	16.86	3.87	0.00E+00	0.0000000
0.004	0.000102	25	35.11	8.07	0.00E+00	0.0000000
0.006	0.000152	32	44.95	10.33	0.00E+00	0.0000000
0.008	0.000203	39	54.78	12.59	-1.00E-05	-0.0000003
0.01	0.000254	92	129.22	29.70	-1.50E-05	-0.0000004
0.012	0.000305	146	205.07	47.13	-1.50E-05	-0.0000004
0.014	0.000356	183	257.04	59.07	-1.00E-05	-0.0000003
0.016	0.000406	230	323.06	74.25	0.00E+00	0.0000000
0.018	0.000457	267	375.03	86.19	1.50E-05	0.0000004
0.02	0.000508	301	422.78	97.17	3.00E-05	0.0000008
0.022	0.000559	330	463.51	106.53	6.00E-05	0.0000015
0.024	0.000610	356	500.03	114.92	1.00E-04	0.0000025
0.026	0.000660	378	530.93	122.02	1.20E-04	0.0000030
0.028	0.000711	399	560.43	128.80	1.40E-04	0.0000036
0.03	0.000762	420	589.93	135.58	1.70E-04	0.0000043
0.032	0.000813	439	616.61	141.71	2.50E-04	0.0000063
0.034	0.000864	436	612.40	140.75	3.20E-04	0.0000081
0.036	0.000914	395	554.81	127.51	3.40E-04	0.0000086
0.038	0.000965	390	547.79	125.90	3.50E-04	0.0000089
0.04	0.001016	400	561.84	129.12	3.60E-04	0.0000091
0.042	0.001067	404	567.45	130.42	3.70E-04	0.0000094
0.044	0.001118	404	567.45	130.42	3.80E-04	0.0000097
0.046	0.001168	428	601.16	138.16	3.80E-04	0.0000097
0.048	0.001219	419	588.52	135.26	3.85E-04	0.0000098
0.05	0.001270	429	602.57	138.49	4.00E-04	0.0000102
0.052	0.001321	471	661.56	152.04	4.10E-04	0.0000104
0.054	0.001372	452	634.87	145.91	4.20E-04	0.0000107
0.056	0.001422	456	640.49	147.20	4.25E-04	0.0000108
0.058	0.001473	483	678.42	155.92	4.30E-04	0.0000109
0.06	0.001524	477	669.99	153.98	4.40E-04	0.0000112
0.062	0.001575	470	660.16	151.72	4.50E-04	0.0000114
0.064	0.001626	478	671.39	154.30	4.65E-04	0.0000118
0.066	0.001676	512	719.15	165.28	5.00E-04	0.0000127
0.068	0.001727	490	688.25	158.18	5.10E-04	0.0000130
0.07	0.001778	487	684.03	157.21	5.20E-04	0.0000132

Interface Direct Shear Testing Mohr Coulomb Failure Envelope Data									
Zorbax C18 Silica Particles					Kromasil C8 Silica Particles				
Solvent: Methanol		Solvent: Methanol (Spray Graphite Lubricant on the Steel Plate)			Solvent: Acetone			Solvent: Methanol	
Applied	Peak Shear	Applied	Peak Shear	Applied	Peak Shear	Applied	Peak Shear	Applied	Peak Shear
Normal Stress (kPa)	Stress (kPa)	Normal Stress (kPa)	Stress (kPa)	Normal Stress (kPa)	Stress (kPa)	Normal Stress (kPa)	Stress (kPa)	Normal Stress (kPa)	Stress (kPa)
253.38	92.70	3040.59	1026.75	506.76	174.17	1013.53	210.69		
253.38	96.92	2027.06	634.87	506.76	181.19	2027.06	431.21		
506.76	179.79			506.76	179.79	2027.06	414.35		
506.76	191.02			1013.53	393.28	3040.59	616.61		
1013.53	390.48			3040.59	1318.91				
1013.53	387.67			3040.59	1229.02				
1013.53	376.43								
2027.06	796.40								
3040.59	1182.66								
* The Peak Shear Stress above is the Peak Shear Stress at failure during Interface Direct Shear Tests									

Appendix B

Interface Direct Shear Test Data:

Volumetric Strain vs. Normal Stress Response

Sample ID Zz 5bm1				
Initial Sample Height			1 34	
Applied Normal Pressure (bar)	Vertical Dial Gage x 10E-4 (in)	Change in Height x 10E-4 (in)	cm	
0	0 00	0 00	Volumetric Strain (cm/cm)	
1	20 80	20 80	0 0000	
2 5	29 70	29 70	0 0056	

Sample ID Z5bm1				
Initial Sample Height			1 34	
Applied Normal Pressure (bar)	Vertical Dial Gage x 10E-4 (in)	Change in Height x 10E-4 (in)	cm	
0	0 00	0 00	Volumetric Strain (cm/cm)	
1	11 90	11 90	0 0000	
2	20 55	20 55	0 0039	
3	28 40	28 40	0 0054	
4	31 60	31 60	0 0060	
5	36 10	36 10	0 0068	

Sample ID Z10bm2				
Initial Sample Height			1 14	
Applied Normal Pressure (bar)	Vertical Dial Gage x 10E-4 (in)	Change in Height x 10E-4 (in)	cm	
0	0 00	0 00	Volumetric Strain (cm/cm)	
1	18 95	18 95	0 0000	
2	25 00	25 00	0 0042	
3	28 30	28 30	0 0056	
4	32 15	32 15	0 0063	
5	34 05	34 05	0 0072	
6	37 60	37 60	0 0076	
7	39 20	39 20	0 0084	
8	41 80	41 80	0 0087	
9	42 75	42 75	0 0093	
10	44 80	44 80	0 0100	

Sample ID Zz 5bm2				
Initial Sample Height			0 94	
Applied Normal Pressure (bar)	Vertical Dial Gage x 10E-4 (in)	Change in Height x 10E-4 (in)	cm	
0	0 00	0 00	Volumetric Strain (cm/cm)	
1	10 10	10 10	0 0000	
2 5	20 70	20 70	0 0027	
			0 0056	

Sample ID Z10bm1				
Initial Sample Height			1 54	
Applied Normal Pressure (bar)	Vertical Dial Gage x 10E-4 (in)	Change in Height x 10E-4 (in)	cm	
0	0 00	0 00	Volumetric Strain (cm/cm)	
1	32 45	32 45	0 0000	
2	44 20	44 20	0 0054	
3	53 60	53 60	0 0073	
4	61 00	61 00	0 0088	
5	67 10	67 10	0 0101	
6	71 10	71 10	0 0111	
7	75 50	75 50	0 0117	
8	78 85	78 85	0 0125	
9	79 15	79 15	0 0130	
10	80 65	80 65	0 0131	
			0 0133	

Sample ID Z10bm3				
Initial Sample Height			1 34	
Applied Normal Pressure (bar)	Vertical Dial Gage x 10E-4 (in)	Change in Height x 10E-4 (in)	cm	
0	0 00	0 00	Volumetric Strain (cm/cm)	
1	13 55	13 55	0 0000	
2	19 95	19 95	0 0026	
3	23 50	23 50	0 0038	
4	26 70	26 70	0 0045	
5	28 35	28 35	0 0051	
6	30 45	30 45	0 0054	
7	32 60	32 60	0 0058	
8	33 80	33 80	0 0062	
9	35 80	35 80	0 0064	
10	37 80	37 80	0 0068	
			0 0072	

Sample ID Z30bm1							
Initial Sample Height 114cm							
Applied Normal	Vertical Dial Gage	Change in Height	Volumetric	Applied Normal	Vertical Dial Gage	Change in Height	Volumetric
Pressure (bar)	x 10E-4 (m)	x 10E-4 (m)	Strain (cm/cm)	Pressure (bar)	x 10E-4 (m)	x 10E-4 (m)	Strain (cm/cm)
0	0 00	0 00	0 0000	15	80 00	80 00	0 0178
1	31 80	31 80	0 0071	14	79 70	79 70	0 0178
2	38 00	38 00	0 0085	13	79 40	79 40	0 0177
3	43 80	43 80	0 0098	12	79 25	79 25	0 0177
4	50 15	50 15	0 0112	11	78 30	78 30	0 0174
5	52 30	52 30	0 0117	10	77 95	77 95	0 0174
6	54 20	54 20	0 0121	9	77 10	77 10	0 0172
7	56 45	56 45	0 0126	8	76 30	76 30	0 0170
8	58 70	58 70	0 0131	7	75 30	75 30	0 0168
9	62 10	62 10	0 0138	6	74 35	74 35	0 0166
10	64 00	64 00	0 0143	5	73 35	73 35	0 0163
9	62 10	62 10	0 0138	4	72 30	72 30	0 0161
8	62 10	62 10	0 0138	3	70 45	70 45	0 0157
7	62 10	62 10	0 0138	2	67 30	67 30	0 0150
6	62 00	62 00	0 0138	3	68 00	68 00	0 0152
5	61 80	61 80	0 0138	4	68 00	68 00	0 0152
4	60 00	60 00	0 0134	5	68 70	68 70	0 0153
3	58 30	58 30	0 0130	6	69 60	69 60	0 0155
2	56 30	56 30	0 0125	7	70 65	70 65	0 0157
3	56 40	56 40	0 0126	8	71 55	71 55	0 0159
4	56 70	56 70	0 0126	9	72 60	72 60	0 0162
5	57 90	57 90	0 0129	10	73 35	73 35	0 0163
6	59 05	59 05	0 0132	11	74 50	74 50	0 0166
7	60 50	60 50	0 0135	12	75 10	75 10	0 0167
8	61 05	61 05	0 0136	13	76 30	76 30	0 0170
9	62 20	62 20	0 0139	14	77 45	77 45	0 0173
10	63 60	63 60	0 0142	15	77 95	77 95	0 0174
11	65 10	65 10	0 0145	16	78 70	78 70	0 0175
12	65 80	65 80	0 0147	17	79 35	79 35	0 0177
13	67 50	67 50	0 0150	18	80 45	80 45	0 0179
14	69 05	69 05	0 0154	19	81 45	81 45	0 0181
15	70 20	70 20	0 0156	20	82 90	82 90	0 0185
16	72 10	72 10	0 0161	21	83 50	83 50	0 0186
17	75 10	75 10	0 0167	22	84 05	84 05	0 0187
18	76 10	76 10	0 0170	23	84 75	84 75	0 0189
19	76 90	76 90	0 0171	24	85 90	85 90	0 0191
20	80 05	80 05	0 0178	25	86 60	86 60	0 0193
19	80 00	80 00	0 0178	26	87 40	87 40	0 0195
18	80 00	80 00	0 0178	27	88 70	88 70	0 0198
17	80 00	80 00	0 0178	28	89 80	89 80	0 0200
16	80 00	80 00	0 0178	29	90 70	90 70	0 0202
				30	93 15	93 15	0 0208

Sample ID: Z5ba1				
Initial Sample Height		1 54	cm	
Applied Normal Pressure (bar)	Vertical Dial Gage x 10E-4 (in)	Change in Height x 10E-4 (in)	Volumetric Strain (cm/cm)	
0	0.00	0.00	0.0000	
1	16.60	16.60	0.0027	
2	22.60	22.60	0.0037	
3	26.70	26.70	0.0044	
4	30.20	30.20	0.0050	
5	32.70	32.70	0.0054	

Sample ID: Z5ba2				
Initial Sample Height		1 19	cm	
Applied Normal Pressure (bar)	Vertical Dial Gage x 10E-4 (in)	Change in Height x 10E-4 (in)	Volumetric Strain (cm/cm)	
0	0.00	0.00	0.0000	
1	28.85	28.85	0.0062	
2	33.75	33.75	0.0072	
3	38.40	38.40	0.0082	
4	42.60	42.60	0.0091	
5	45.70	45.70	0.0098	

Sample ID: Z5ba3				
Initial Sample Height		1.24	cm	
Applied Normal Pressure (bar)	Vertical Dial Gage x 10E-4 (in)	Change in Height x 10E-4 (in)	Volumetric Strain (cm/cm)	
0	0.00	0.00	0.0000	
1	4.25	4.25	0.0009	
2	9.70	9.70	0.0021	
3	13.80	13.80	0.0029	
4	17.30	17.30	0.0037	
5	20.10	20.10	0.0043	

Sample ID: Z10ba1				
Initial Sample Height		1 19	cm	
Applied Normal Pressure (bar)	Vertical Dial Gage x 10E-4 (in)	Change in Height x 10E-4 (in)	Volumetric Strain (cm/cm)	
0	0.00	0.00	0.0000	
1	13.30	13.30	0.0028	
2	18.15	18.15	0.0039	
3	21.40	21.40	0.0046	
4	25.95	25.95	0.0055	
5	28.35	28.35	0.0061	
6	30.60	30.60	0.0065	
7	33.45	33.45	0.0071	
8	34.35	34.35	0.0073	
9	36.30	36.30	0.0077	
10	39.20	39.20	0.0084	

Sample ID Z20bml1				
Initial Sample Height		0.84 cm		
Applied Normal Pressure (bar)	Vertical Dial Gage x 10E-4 (in)	Change in Height x 10E-4 (in)	Volumetric Strain (cm/cm)	
0	0	0	0.0000	
1	19.85	19.85	0.0048	
2	28.15	28.15	0.0069	
3	34.8	34.8	0.0085	
4	39.55	39.55	0.0097	
5	43.55	43.55	0.0106	
6	47.3	47.3	0.0116	
7	50.8	50.8	0.0124	
8	53.7	53.7	0.0131	
9	56.8	56.8	0.0139	
10	58.8	58.8	0.0144	
11	60.8	60.8	0.0148	
12	62.7	62.7	0.0153	
13	64.55	64.55	0.0158	
14	66.6	66.6	0.0163	
15	69.75	69.75	0.0170	
16	72.6	72.6	0.0177	
17	73.8	73.8	0.0180	
18	75	75	0.0183	
19	75.9	75.9	0.0185	
20	81.1	81.1	0.0198	

Sample ID: Z30bml1**				
Initial Sample Height			0.87	cm
Applied Normal Pressure (bar)	Vertical Dial Gage x 10E-4 (in)	Change in Height x 10E-4 (in)	Volumetric Strain (cm/cm)	
0	0	0	0.0000	
1	3.15	3.15	0.0008	
2	12.9	12.9	0.0032	
3	18.5	18.5	0.0045	
4	23.7	23.7	0.0058	
5	27.85	27.85	0.0068	
6	32.55	32.55	0.0079	
7	35.7	35.7	0.0087	
8	39.1	39.1	0.0095	
9	40.9	40.9	0.0100	
10	42.6	42.6	0.0104	
11	46.3	46.3	0.0113	
12	47.5	47.5	0.0116	
13	49.85	49.85	0.0122	
14	52.2	52.2	0.0127	
15	54.25	54.25	0.0132	
16	55.05	55.05	0.0134	
17	55.65	55.65	0.0136	
18	56.2	56.2	0.0137	
19	56.85	56.85	0.0139	
20	57.8	57.8	0.0141	
21	58.65	58.65	0.0143	
22	59.15	59.15	0.0144	
23	60.15	60.15	0.0147	
24	60.95	60.95	0.0149	
25	61.9	61.9	0.0151	
26	64	64	0.0156	
27	65.25	65.25	0.0159	
28	66.4	66.4	0.0162	
29	68.8	68.8	0.0168	
30	--	--	--	

** Air line broke, no shearing data

Sample ID Z30bml2				
Initial Sample Height		1.32 cm		
Applied Normal Pressure (bar)	Vertical Dial Gage x 10E-4 (in)	Change in Height x 10E-4 (in)	Volumetric Strain (cm/cm)	
0	0	0	0.0000	
1	20.7	20.7	0.0051	
2	29.7	29.7	0.0073	
3	35.7	35.7	0.0087	
4	40.05	40.05	0.0098	
5	45.8	45.8	0.0112	
6	48	48	0.0117	
7	52.4	52.4	0.0128	
8	57	57	0.0139	
9	58.6	58.6	0.0143	
10	59.7	59.7	0.0146	
11	62.4	62.4	0.0152	
12	70.6	70.6	0.0172	
13	71.55	71.55	0.0175	
14	72.7	72.7	0.0178	
15	73.4	73.4	0.0179	
16	73.8	73.8	0.0180	
17	75.05	75.05	0.0183	
18	75.8	75.8	0.0185	
19	76.75	76.75	0.0187	
20	80.75	80.75	0.0197	
21	81.65	81.65	0.0199	
22	82	82	0.0200	
23	82.9	82.9	0.0202	
24	83.75	83.75	0.0205	
25	84.75	84.75	0.0207	
26	85.8	85.8	0.0210	
27	87.1	87.1	0.0213	
28	88.15	88.15	0.0215	
29	89.65	89.65	0.0219	
30	96.2	96.2	0.0235	

Sample ID K10bm1			
Initial Sample Height		1 14	cm
Applied Normal	Vertical Dial Gage	Change in Height	Volumetric
Pressure (bar)	x 10E-4 (in)	x 10E-4 (in)	Strain (cm/cm)
0	0	0	0 0000
1	20 5	20 5	0 0050
2	25 6	25 6	0 0063
3	31 7	31 7	0 0077
4	34 85	34 85	0 0085
5	36 35	36 35	0 0089
6	38 8	38 8	0 0095
7	41 5	41 5	0 0101
8	43 1	43 1	0 0105
9	46	46	0 0112
10	50 9	50 9	0 0124

Sample ID K30bm1			
Initial Sample Height		1 32	cm
Applied Normal	Vertical Dial Gage	Change in Height	Volumetric
Pressure (bar)	x 10E-4 (in)	x 10E-4 (in)	Strain (cm/cm)
0	0	0	0 0000
1	29 15	29 15	0 0071
2	38 05	38 05	0 0093
3	53 3	53 3	0 0130
4	57 45	57 45	0 0140
5	61 55	61 55	0 0150
6	64 25	64 25	0 0157
7	67 1	67 1	0 0164
8	69 9	69 9	0 0171
9	72 8	72 8	0 0178
10	75 8	75 8	0 0185
11	76 95	76 95	0 0188
12	78 2	78 2	0 0191
13	79 75	79 75	0 0195
14	81 25	81 25	0 0198
15	82 7	82 7	0 0202
16	83 6	83 6	0 0204
17	84 3	84 3	0 0206
18	85 25	85 25	0 0208
19	86 1	86 1	0 0210
20	87 55	87 55	0 0214
21	89 4	89 4	0 0218
22	90 7	90 7	0 0222
23	92 4	92 4	0 0226
24	93 5	93 5	0 0228
25	94 7	94 7	0 0231
26	95 8	95 8	0 0234
27	97 25	97 25	0 0238
28	98 15	98 15	0 0240
29	98 95	98 95	0 0242
30	99 3	99 3	0 0243

Sample ID K20bm1			
Initial Sample Height		1 24	cm
Applied Normal	Vertical Dial Gage	Change in Height	Volumetric
Pressure (bar)	x 10E-4 (in)	x 10E-4 (in)	Strain (cm/cm)
0	0	0	0 0000
1	10 35	10 35	0 0025
2	16	16	0 0039
3	20 7	20 7	0 0051
4	23 25	23 25	0 0057
5	24 95	24 95	0 0061
6	26 7	26 7	0 0065
7	28 45	28 45	0 0069
8	31 25	31 25	0 0076
9	32 3	32 3	0 0079
10	33 1	33 1	0 0081
11	34 7	34 7	0 0085
12	35 4	35 4	0 0086
13	36 6	36 6	0 0089
14	38 3	38 3	0 0094
15	40 7	40 7	0 0099
16	41 3	41 3	0 0101
17	42 3	42 3	0 0103
18	43 3	43 3	0 0106
19	44 45	44 45	0 0109
20	46 4	46 4	0 0113

Sample ID K20bm2			
Initial Sample Height		1 39	cm
Applied Normal	Vertical Dial Gage	Change in Height	Volumetric
Pressure (bar)	x 10E-4 (in)	x 10E-4 (in)	Strain (cm/cm)
0	0	0	0 0000
1	21 7	21 7	0 0053
2	36 5	36 5	0 0089
3	45 9	45 9	0 0112
4	48 5	48 5	0 0118
5	53 75	53 75	0 0131
6	55 7	55 7	0 0136
0	0	0	0 0000
2	16 4	16 4	0 0040
4	23 55	23 55	0 0058
6	27 8	27 8	0 0068
7	32 8	32 8	0 0080
8	33 5	33 5	0 0082
9	37 7	37 7	0 0092
10	38 6	38 6	0 0094
11	41 2	41 2	0 0101
12	42 5	42 5	0 0104
13	43 6	43 6	0 0106
14	44 7	44 7	0 0109
15	48 45	48 45	0 0118
16	50 6	50 6	0 0124
17	51 3	51 3	0 0125
18	52 6	52 6	0 0128
19	53 3	53 3	0 0130
20	57 65	57 65	0 0141

Appendix C

Fixed-Ring Consolidation Tests

with

Falling Head Permeability Testing Data

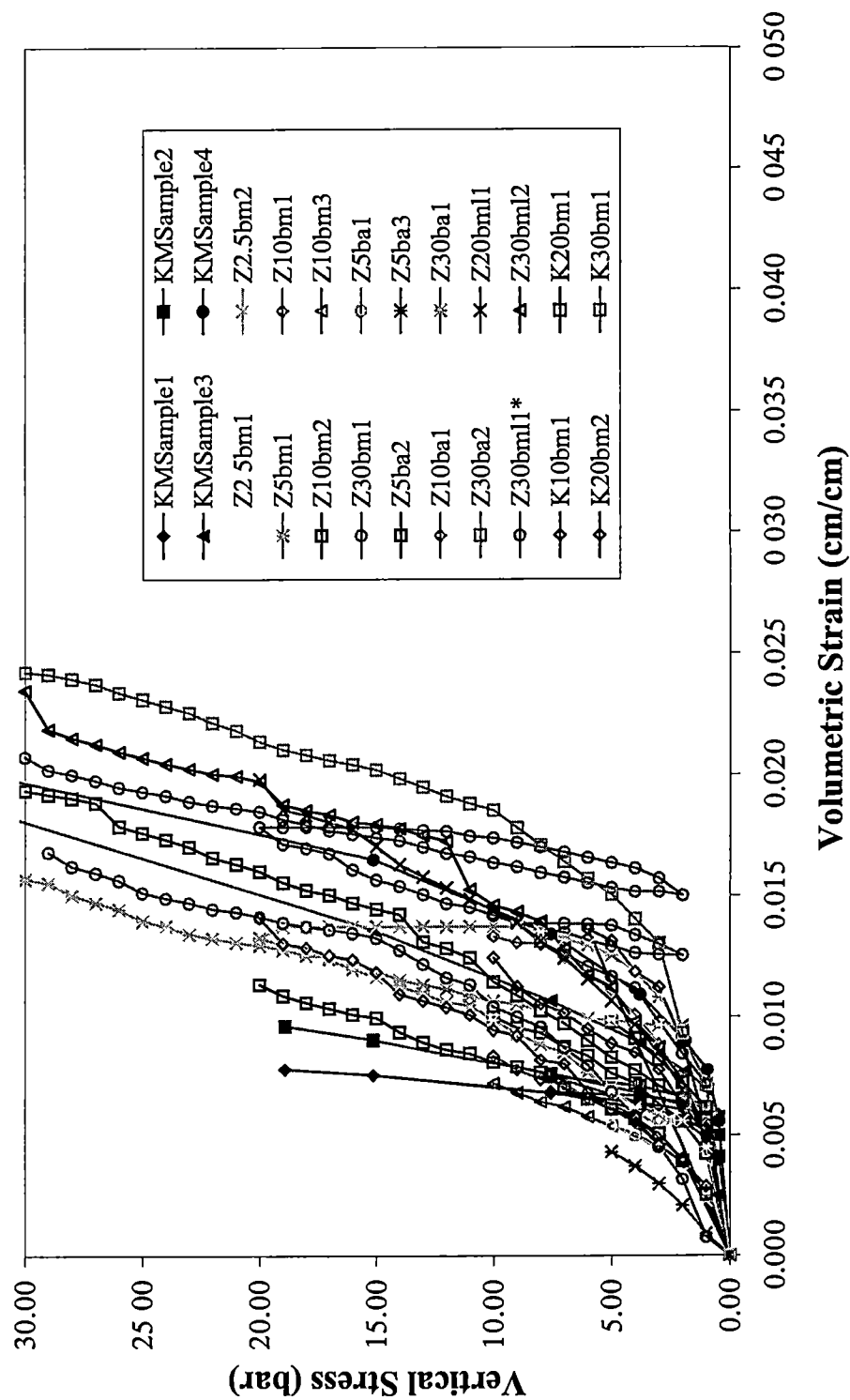
KMSample1									
Sample ID									
Initial height =	0.91	inch							
Mass of the sample (Wet) =	68.10	g							
Mass of the sample (Dry) =	61.00	g							
Diameter of the sample =	2.50	inch						6.35	cm
Area of the sample =	4.91	inch ²						31.67	cm ²
Volume of the sample =	4.48	inch ³						73.43	cm ³
Initial dry density of the sample =	0.83	g/cm ³							
Specific gravity of the sample =	1.57								
Density of the solvent =	0.79	g/cm ³							
Initial void ratio of the sample =	0.6129								
Vertical stress (ton/ft ²)	Vertical stress (bar)	Void ratio	Normalized Void Ratio	Volumetric strain (cm/cm)	Kozeny-Carman Permeability				
					(cm/s)	(m ²)			(cm ²)
0.00	0.00	0.5333	1.0000	0.0000	--	--	--	--	--
0.50	0.47	0.5272	0.9886	0.0040	3.27E-05	2.91E-14	3.27E-05	2.91E-14	2.91E-10
1.00	0.95	0.5259	0.9862	0.0048	3.24E-05	2.89E-14	3.24E-05	2.89E-14	2.89E-10
2.00	1.89	0.5248	0.9840	0.0056	3.23E-05	2.87E-14	3.23E-05	2.87E-14	2.87E-10
1.00	0.95	0.5252	0.9848	0.0053	3.23E-05	2.88E-14	3.23E-05	2.88E-14	2.88E-10
0.50	0.47	0.5257	0.9857	0.0050	3.24E-05	2.88E-14	3.24E-05	2.88E-14	2.88E-10
1.00	0.95	0.5254	0.9851	0.0052	3.24E-05	2.88E-14	3.24E-05	2.88E-14	2.88E-10
2.00	1.89	0.5247	0.9839	0.0056	3.22E-05	2.87E-14	3.22E-05	2.87E-14	2.87E-10
4.00	3.78	0.5240	0.9825	0.0061	3.21E-05	2.86E-14	3.21E-05	2.86E-14	2.86E-10
8.00	7.56	0.5229	0.9804	0.0068	3.19E-05	2.84E-14	3.19E-05	2.84E-14	2.84E-10
4.00	3.78	0.5231	0.9809	0.0067	3.20E-05	2.85E-14	3.20E-05	2.85E-14	2.85E-10
2.00	1.89	0.5236	0.9818	0.0063	3.21E-05	2.85E-14	3.21E-05	2.85E-14	2.85E-10
1.00	0.95	0.5240	0.9825	0.0061	3.21E-05	2.86E-14	3.21E-05	2.86E-14	2.86E-10
0.50	0.47	0.5244	0.9832	0.0058	3.22E-05	2.87E-14	3.22E-05	2.87E-14	2.87E-10
1.00	0.95	0.5243	0.9831	0.0059	3.22E-05	2.86E-14	3.22E-05	2.86E-14	2.86E-10
2.00	1.89	0.5240	0.9826	0.0061	3.21E-05	2.86E-14	3.21E-05	2.86E-14	2.86E-10
4.00	3.78	0.5236	0.9818	0.0063	3.21E-05	2.85E-14	3.21E-05	2.85E-14	2.85E-10
8.00	7.56	0.5229	0.9805	0.0068	3.20E-05	2.85E-14	3.20E-05	2.85E-14	2.85E-10
16.00	15.12	0.5218	0.9784	0.0075	3.18E-05	2.83E-14	3.18E-05	2.83E-14	2.83E-10
20.00	18.91	0.5214	0.9776	0.0078	3.17E-05	2.82E-14	3.17E-05	2.82E-14	2.82E-10

KMSample2									
Sample ID	Initial height =	0.91	in						
	Mass of the sample (Wet) =	69.10	g						
	Mass of the sample (Dry) =	61.30	g						
	Diameter of the sample =	2.50	in	=		6.35	cm		
	Area of the sample =	4.91	in ²	=		31.67	cm ²		
	Volume of the sample =	4.48	in ³	=		73.43	cm ³		
	Initial dry density of the sample =	0.83	g/cm ³						
	Specific gravity of the sample =	1.57							
	Density of the solvent =	0.79	g/cm ³						
	Initial void ratio of the sample =	0.6129							
Vertical stress (ton/ft ²)	Vertical stress (bar)	Void ratio		Normalized Void Ratio		Volumetric strain (cm/cm)		Kozeny-Carman Permeability (cm/s) (m ²) (cm ³)	
0.00	0.00	0.5333		1.0000		0.0000		--	--
0.50	0.47	0.5270		0.9883		0.0041		3.26E-05	2.91E-14
1.00	0.95	0.5260		0.9863		0.0048		3.25E-05	2.89E-14
2.00	1.89	0.5248		0.9840		0.0056		3.23E-05	2.87E-14
1.00	0.95	0.5252		0.9847		0.0053		3.23E-05	2.88E-14
0.50	0.47	0.5257		0.9857		0.0050		3.24E-05	2.88E-14
1.00	0.95	0.5254		0.9851		0.0052		3.24E-05	2.88E-14
2.00	1.89	0.5247		0.9840		0.0056		3.23E-05	2.87E-14
4.00	3.78	0.5236		0.9817		0.0064		3.21E-05	2.85E-14
8.00	7.56	0.5219		0.9786		0.0075		3.18E-05	2.83E-14
4.00	3.78	0.5225		0.9797		0.0071		3.19E-05	2.84E-14
2.00	1.89	0.5232		0.9811		0.0066		3.20E-05	2.85E-14
1.00	0.95	0.5239		0.9823		0.0062		3.21E-05	2.85E-14
0.50	0.47	0.5245		0.9835		0.0057		3.22E-05	2.87E-14
1.00	0.95	0.5242		0.9830		0.0059		3.22E-05	2.86E-14
2.00	1.89	0.5238		0.9821		0.0062		3.21E-05	2.86E-14
4.00	3.78	0.5229		0.9806		0.0068		3.20E-05	2.85E-14
8.00	7.56	0.5217		0.9782		0.0076		3.18E-05	2.83E-14
16.00	15.12	0.5195		0.9740		0.0090		3.14E-05	2.80E-14
20.00	18.91	0.5186		0.9724		0.0096		3.13E-05	2.78E-14

KM Samples 3									
Sample ID	Initial height =	0 61	inch						
	Mass of the sample (Wet) =	49 80	g						
	Mass of the sample (Dry) =	39 90	g						
	Diameter of the sample =	2 50	inch	=	6 35	cm			
	Area of the sample =	4 91	inch ²	=	31 67	cm ²			
	Volume of the sample =	3 01	inch ³	=	49 36	cm ³			
	Initial dry density of the sample =	0 81	g/cm ³						
	Specific gravity of the sample =	1 57							
	Density of the solvent =	0 79	g/cm ³						
	Initial void ratio of the sample =	0 53							
Vertical stress (ton/ft ²)	Vertical stress (bar)	Void ratio	Normalized Void Ratio	Volumetric strain (cm/cm)	Measured Falling Head Permeability (cm/s)	(m ²)	Carmen-Kozeny Permeability (cm/s)	(m ²)	Permeability (cm ²)
0 00	0 00	0 5319	1 0000	0 0000	--	--	--	--	--
0 50	0 47	0 5223	0 9819	0 0025	--	--	--	--	--
1 00	0 95	0 5213	0 9802	0 0069	--	--	--	--	--
2 00	1 89	0 5201	0 9779	0 0077	--	--	--	--	--
4 00	3 78	0 5182	0 9744	0 0089	3 27E-05	2 91E-14	3 12E-05	2 78E-14	2 78E-10
8 00	7 56	0 5156	0 9693	0 0106	3 10E-05	2 76E-14	3 08E-05	2 74E-14	2 74E-10
16 00	15 12	0 5111	0 9609	0 0136	2 80E-05	2 49E-14	3 01E-05	2 68E-14	2 68E-10
32 00	30 25	0 5041	0 9478	0 0181	2 72E-05	2 42E-14	2 90E-05	2 58E-14	2 58E-10

Sample ID	KMSample4									
Initial height =	0.60	inch								
Mass of the sample (Wet) =	49.10	g								
Mass of the sample (Dry) =	35.90	g								
Diameter of the sample =	2.50	inch	=				6.35	cm		
Area of the sample =	4.91	inch ²	=				31.67	cm ²		
Volume of the sample =	2.93	inch ³	=				47.94	cm ³		
Initial dry density of the sample =	0.75	g/cm ³								
Specific gravity of the sample =	1.57									
Density of the solvent =	0.79	g/cm ³								
Initial void ratio of the sample =	0.5338									
Vertical stress (ton/ft ²)	Vertical stress (bar)	Void ratio	Normalized Void Ratio	Volumetric strain (cm/cm)	Measured Falling Head Permeability (cm/s)	(m ²)	(cm ²)	Kozeny-Carman Permeability (cm/s)	(m ²)	(cm ²)
0.00	0.00	0.5338	1.0000	0.0000	--	--	--	--	--	--
0.50	0.47	0.5252	0.9840	0.0056	--	--	--	--	--	--
1.00	0.95	0.5219	0.9778	0.0077	--	--	--	--	--	--
2.00	1.89	0.5200	0.9742	0.0090	--	--	--	--	--	--
4.00	3.78	0.5171	0.9687	0.0109	3.37E-05	3.00E-14	3.00E-10	3.10E-05	2.76E-14	2.76E-10
8.00	7.56	0.5132	0.9614	0.0134	3.18E-05	2.83E-14	2.83E-10	3.04E-05	2.71E-14	2.71E-10
16.00	15.12	0.5085	0.9526	0.0165	2.76E-05	2.46E-14	2.46E-10	2.97E-05	2.64E-14	2.64E-10
32.00	30.25	0.5035	0.9433	0.0197	2.59E-05	2.30E-14	2.30E-10	2.89E-05	2.57E-14	2.57E-10

Vertical Stress vs. Volumetric Strain



Appendix D

ABAQUS Version 5.8 Input Files

Uncoupled Mechanical Analysis using Zorbax Spherical C18 packing material
File name: porous1c.inp

```
*HEADING
THE CHROMATOGRAPHY PROBLEM WITH FRICTION SURFACE (KPA, M, DAYS)
**This is a model used to simulate a 5 3cm by 10 6cm column used in the HPLC column
**There is a restraint on top of both the column and steel section to prevent movement along the y-direction
**A piston is used to induce 3 4 mm displacement (bottom) into the column
**The packing material inside the column is assumed to behave like a porous elastic material
**Units Length=m, Stress=kPa
*RESTART,WRITE
**
**Defining the coordinates of all the nodes used to model the HPLC column and the steel column
*NODE,SYSTEM=R
1, 0, 0 001
6, 0 025, 0 001
321, 0, 0 16
326, 0 025, 0 16
2001, 0 025, 0
2002, 0 03, 0
2321, 0 025, 0 16
2322, 0 03, 0 16
**
**Defining the nodes of the internal section of the column
*NGEN, NSET=TOP
321, 326, 1
*NGEN, NSET=BOTTOM
1, 6, 1
*NGEN, NSET=SIDE
6, 326, 10
*NGEN, NSET=CENTER
1, 321, 10
*NFill, NSET=INTNODE
BOTTOM, TOP, 32, 10
**
**Defining the nodes of the contacting steel friction section located beside the column
*NGEN, NSET=SFRICIN
2001, 2321, 10
*NGEN, NSET=SFRICOUT
2002, 2322, 10
*NGEN, NSET=SFRICBOT
2001, 2002, 1
*NGEN, NSET=SFRICTOP
2321, 2322, 1
**
**Defining elements of the internal section of the column
*ELEMENT, TYPE=CAX4
1, 1, 2, 12, 11
*ELGEN, ELSET=BOTTOM
1, 5, 1
*ELSET, ELSET=TOP, GENERATE
311, 315, 1
*ELGEN, ELSET=INTERNAL
1, 5, 1, 1, 32, 10, 10
*ELSET, ELSET=SIDE, GENERATE
5, 315, 10
*ELSET, ELSET=CENTER, GENERATE
1, 311, 10
**
```

```

**Defining elements of the contacting steel friction section located beside the column
*ELEMENT, TYPE=CAX4, ELSET=SFRIC
2001, 2001, 2002, 2012, 2011
*ELGEN, ELSET=SFRIC
2001, 1, 1, 1, 32, 10, 10
**
**Defining the solid material properties of the internal section of the column
*SOLID SECTION, ELSET=INTERNAL, MATERIAL=SILICA
**Defining the material properties of the column
**The material is assumed to behave like a porous elastic material
**Note that Poisson ratio is 0.3
*MATERIAL, NAME=SILICA
*POROUS ELASTIC, SHEAR=POISSON
0.01, 0.3, 100.0
*DRUCKER PRAGER HARDENING
1.1, 0
*DRUCKER PRAGER, SHEAR CRITERION=LINEAR
45.51, 1.0, 0
**
*EQUATION
2
326, 1, 1, 2321, 1, -1
**Defining the solid section properties of the steel friction section located beside the column
*SOLID SECTION, ELSET=SFRIC, MATERIAL=STEEL
**Modulus of Elasticity used in the steel section is 29 E6 ksi
**which has been converted to 2e-11 kPa
**The Poisson ratio of the steel is assumed to be 0.3
*MATERIAL, NAME=STEEL
*ELASTIC
2.9E11, 0.3
**
**Defining the contact surfaces between the internal section
**and the friction steel section beside the column
*SURFACE DEFINITION, NAME=SSOILSUR, TRIM=YES
SIDE
*SURFACE DEFINITION, NAME=SFRICSUR
SFRIC
*CONTACT PAIR, INTERACTION=SDFRIC
SSOILSUR, SFRICSUR
*SURFACE INTERACTION, NAME=SDFRIC
**The interface coefficient of friction is estimated to be 0.39 for Zorbax spherical C18 packing and the polished
**stainless steel plate (interface direct shear tests)
*FRICTION
0.3874
**
**Defining the boundary conditions of the section
**Both the top of the column and friction section is prevented from moving axially
*BOUNDARY
TOP, 2
SFRICTOP, 2
**
**Defining the initial loading conditions of the internal section
*INITIAL CONDITIONS, TYPE=RATIO
INTNODE, 0.61, 0, 0.61, 0.16
*INITIAL CONDITIONS, TYPE=STRESS, GEOSTATIC
INTERNAL, -10, 0, -10, 0.16, 0.43
**
**Defining the loading onto the internal section
**Step 1 *****
*STEP

```

```

*GEOSTATIC
*DLOAD
BOTTOM, P1, 10
*EL PRINT
S
E
VOIDR
*NODE FILE
U, RF
*CONTACT PRINT, MASTER=SFRICSUR, SLAVE=SSOILSUR, SUMMARY=YES
*PRINT, CONTACT=YES
*END STEP
**Step 2*****
*STEP, INC=100
*STATIC
0 025, 1 0, 0 001, 0 1
*BOUNDARY
BOTTOM, 2, 2, 0 0034
*END STEP

```

**Coupled Mechanical-Seepage Steady-State Analysis using Kromasil Spherical C8
packing material (Loading rate: 1 minute)
File name: coup1.inp**

```

*HEADING
THE CHROMATOGRAPHY PROBLEM WITH FRICTION SURFACE (KPA, M, DAYS)
**This is a model used to simulate a 5 3cm by 10 6cm column used in the HPLC column
**There is a restraint on top of both the column and steel section to prevent movement along the y-direction
**A piston is used to induce 3 4 mm displacement (bottom) into the column, while the solvent is free to flow out of
**the column through the flange on top of the column
**The material is assumed to behave like a porous elastic material
**Units Length=m, Stress=kPa
*RESTART,WRITE
**
**Defining the coordinates of all the nodes used to model the column
*NODE,SYSTEM=R
1, 0 , 0 001
6, 0 025, 0 001
321, 0 , 0 16
326, 0 025, 0 16
2001, 0 025, 0
2002, 0 03, 0
2321, 0 025, 0 16
2322, 0 03, 0 16
**
**Defining the nodes of the internal section of the column
*NGEN, NSET=TOP
321, 326, 1
*NGEN, NSET=BOTTOM
1, 6, 1
*NGEN, NSET=SIDE
6, 326, 10
*NGEN, NSET=CENTER
1, 321, 10
*NFill, NSET=INTNODE
BOTTOM, TOP, 32, 10
**
**Defining the nodes of the contacting steel friction section located beside the column
*NGEN, NSET=SFRICIN
2001, 2321, 10
*NGEN, NSET=SFRICOUT
2002, 2322, 10
*NGEN, NSET=SFRICBOT
2001, 2002, 1
*NGEN, NSET=SFRICTOP
2321, 2322, 1
**
**Defining elements of the internal section of the column
*ELEMENT, TYPE=CAX4P
1, 1, 2, 12, 11
*ELGEN, ELSET=BOTTOM
1, 5, 1
*ELSET, ELSET=TOP, GENERATE
311, 315, 1
*ELGEN, ELSET=INTERNAL
1, 5, 1, 1, 32, 10, 10
*ELSET, ELSET=SIDE, GENERATE
5, 315, 10

```

```

*ELSET, ELSET=CENTER, GENERATE
1, 311, 10
**
**Defining elements of the contacting steel friction section located beside the column
*ELEMENT, TYPE=CAX4P, ELSET=SFRIC
2001, 2001, 2002, 2012, 2011
*ELGEN, ELSET=SFRIC
2001, 1, 1, 1, 32, 10, 10
**
**Defining the solid material properties of the internal section of the column
*SOLID SECTION, ELSET=INTERNAL, MATERIAL=SILICA
**Defining the material properties of the column
**The material is assumed to behave like a porous elastic material
**Note that Poisson ratio is 0.3
*MATERIAL, NAME=SILICA
*POROUS ELASTIC, SHEAR=POISSON
0.01, 0.3, 100.0
*DRUCKER PRAGER HARDENING
1, 1, 0
*DRUCKER PRAGER, SHEAR CRITERION=LINEAR
45.51, 1.0, 0
** Defining the permeability of the packing material
**Permeability in m/day, specific weight of methanol in kN/m^3
*PERMEABILITY, TYPE=ISO, SPECIFIC=7.7499
7.89e-6, 0.1819
7.62e-6, 0.1919
1.16e-5, 0.2019
1.73e-5, 0.2119
2.54e-5, 0.2219
3.65e-5, 0.2319
5.18e-5, 0.2419
7.25e-5, 0.2519
1.00e-4, 0.2619
1.36e-4, 0.2719
1.84e-4, 0.2819
2.45e-4, 0.2919
3.24e-4, 0.3019
4.25e-4, 0.3119
5.52e-4, 0.3219
7.11e-4, 0.3319
9.09e-4, 0.3419
1.15e-3, 0.3519
1.46e-3, 0.3619
1.82e-3, 0.3719
2.27e-3, 0.3819
2.81e-3, 0.3919
3.47e-3, 0.4019
4.25e-3, 0.4119
5.18e-3, 0.4219
6.29e-3, 0.4319
7.60e-3, 0.4419
9.15e-3, 0.4519
1.10e-2, 0.4619
1.31e-2, 0.4719
1.56e-2, 0.4819
1.85e-2, 0.4919
2.18e-2, 0.5019
2.57e-2, 0.5119
3.01e-2, 0.5219
3.53e-2, 0.5319

```

```

*PERMEABILITY, TYPE=SATURATION
1 0,1 0
*PERMEABILITY, TYPE=VELOCITY
1 0
**
*EQUATION
2
326, 1, 1, 2321, 1, -1
**
**Defining the solid section properties of the steel friction section located beside the column
*SOLID SECTION, ELSET=SFRIC, MATERIAL=STEEL
**Modulus of Elasticity used in the steel section is 29 E6 ksi
**which has been converted to 2e-11 kPa.
**The Poisson ratio of the steel is assumed to be 0.3
*MATERIAL, NAME=STEEL
*ELASTIC
2 E11, 0.3
**The steel is assumed to have a low permeable layer
*PERMEABILITY, TYPE=ISO, SPECIFIC = 7.7499
1 e-9
**
**Defining the contact surfaces between the internal section
**and the friction steel section beside the column
*SURFACE DEFINITION, NAME=SSOILSUR, TRIM=YES
SIDE
*SURFACE DEFINITION, NAME=SFRICSUR
SFRIC
*CONTACT PAIR, INTERACTION=SDFRIC
SSOILSUR, SFRICSUR
*SURFACE INTERACTION, NAME=SDFRIC
**The interface coefficient of friction of the Kromasil is estimated to be 0.21
**where the friction angle is approximately 12 degrees
*FRICTION
0.2056
**
**Defining the boundary conditions of the section
**Both the top of the column and friction section is prevented from moving axially
**The fluid (solvent) inside the column is free to flow out of the column through the top
*BOUNDARY
TOP, 2
TOP, 8
SFRICTOP, 2
**
**Defining the initial load conditions of the internal section
*INITIAL CONDITIONS, TYPE=SATURATION
INTNODE, 1 0
*INITIAL CONDITIONS, TYPE=PORE PRESSURE
INTNODE, -100, 0, 0, 0.16
*INITIAL CONDITIONS, TYPE=RATIO
INTNODE, 0.5319, 0, 0.5319, 0.16
*INITIAL CONDITIONS, TYPE=RATIO
SFRICIN, 1 e-5, 0, 1 e-5, 0.16
*INITIAL CONDITIONS, TYPE=RATIO
SFRICOUT, 1 e-5, 0, 1 e-5, 0.16
*INITIAL CONDITIONS, TYPE=STRESS, GEOSTATIC
INTERNAL, -10, 0, -10, 0.16, 0.43
**
**Defining the loading onto the internal section
**Step 1 *****
*STEP

```

```

*GEOSTATIC
*DLOAD
BOTTOM, P1, 10
*EL PRINT
S
E
SAT
POR
VOIDR
**MONITOR, NODE=161,DOF=2,FREQUENCY=1
*MONITOR, NODE=161,DOF=8,FREQUENCY=1
*NODE FILE
U, RF
*CONTACT PRINT, MASTER=SFRICSUR, SLAVE=SSOILSUR, SUMMARY=YES
*PRINT, CONTACT=YES
*END STEP
**Step 2*****
*STEP, INC=100
**The packing material is consolidated in 1 mm
*SOILS, UTOL=1300 0
7 0e-8,6 94e-4,0 001,0 1
*BOUNDARY
BOTTOM, 2, 2, 0 0034
*END STEP

```

**Coupled Mechanical-Seepage Transient Analysis using Kromasil Spherical C8
packing material (Loading rate: 1 minute)
File name: coup10.inp**

```

*HEADING
THE CHROMATOGRAPHY PROBLEM WITH FRICTION SURFACE (KPA, M, DAYS)
**This is a model used to simulate a 5 3cm by 10 6cm column used in the HPLC column
**There is a restraint on top of both the column and steel section to prevent movement along the y-direction
**A piston is used to induce 3 4 mm displacement (bottom) into the column, while the solvent is free to flow out of the
**column through the flange on top of the column
**The packing material is assumed to behave like a porous elastic material
**Units Length=m, Stress=kPa
*RESTART,WRITE
**
**Defining the coordinates of all the nodes used to model the column
*NODE,SYSTEM=R
1, 0, 0 001
6, 0 025, 0 001
321, 0, 0 16
326, 0 025, 0 16
2001, 0 025, 0
2002, 0 03, 0
2321, 0 025, 0 16
2322, 0 03, 0 16
**
**Defining the nodes of the internal section of the column
*NGEN, NSET=TOP
321, 326, 1
*NGEN, NSET=BOTTOM
1, 6, 1
*NGEN, NSET=SIDE
6, 326, 10
*NGEN, NSET=CENTER
1, 321, 10
*NFill, NSET=INTNODE
BOTTOM, TOP, 32, 10
**
**Defining the nodes of the contacting steel friction section located beside the column
*NGEN, NSET=SFRICIN
2001, 2321, 10
*NGEN, NSET=SFRICOUT
2002, 2322, 10
*NGEN, NSET=SFRICBOT
2001, 2002, 1
*NGEN, NSET=SFRICTOP
2321, 2322, 1
**
**Defining elements of the internal section of the column
*ELEMENT, TYPE=CAX4P
1, 1, 2, 12, 11
*ELGEN, ELSET=BOTTOM
1, 5, 1
*ELSET, ELSET=TOP, GENERATE
311, 315, 1
*ELGEN, ELSET=INTERNAL
1, 5, 1, 1, 32, 10, 10
*ELSET, ELSET=SIDE, GENERATE
5, 315, 10

```

```

*ELSET, ELSET=CENTER, GENERATE
1, 311, 10
**
**Defining elements of the contacting steel friction section located beside the column
*ELEMENT, TYPE=CAX4P, ELSET=SFRIC
2001, 2001, 2002, 2012, 2011
*ELGEN, ELSET=SFRIC
2001, 1, 1, 1, 32, 10, 10
**
**Defining the solid material properties of the internal section of the column
*SOLID SECTION, ELSET=INTERNAL, MATERIAL=SILICA
**Defining the material properties of the column
**The material is assumed to behave like a porous elastic material
**Note that Poisson ratio is 0.3
*MATERIAL, NAME=SILICA
*POROUS ELASTIC, SHEAR=POISSON
0.01, 0.3, 100.0
*DRUCKER PRAGER HARDENING
1, 1, 0
*DRUCKER PRAGER, SHEAR CRITERION=LINEAR
45, 51, 1, 0, 0
**Defining the permeability w r t void ratio of the packing material
** Permeability in m/day, specific weight of methanol in kN/m^3
*PERMEABILITY, TYPE=ISO, SPECIFIC=7.7499
1.0968e-2, 0.46188
1.1367e-2, 0.46388
1.1780e-2, 0.46588
1.2205e-2, 0.46788
1.2644e-2, 0.46988
1.3096e-2, 0.47188
1.3563e-2, 0.47388
1.4044e-2, 0.47588
1.4540e-2, 0.47788
1.5052e-2, 0.47988
1.5579e-2, 0.48188
1.6122e-2, 0.48388
1.6682e-2, 0.48588
1.7259e-2, 0.48788
1.7854e-2, 0.48988
1.8466e-2, 0.49188
1.9097e-2, 0.49388
1.9747e-2, 0.49588
2.0416e-2, 0.49788
2.1105e-2, 0.49988
2.1814e-2, 0.50188
2.2544e-2, 0.50388
2.3296e-2, 0.50588
2.4070e-2, 0.50788
2.4866e-2, 0.50988
2.5685e-2, 0.51188
2.6527e-2, 0.51388
2.7394e-2, 0.51588
2.8286e-2, 0.51788
2.9203e-2, 0.51988
3.0146e-2, 0.52188
3.1116e-2, 0.52388
3.2113e-2, 0.52588
3.3138e-2, 0.52788
3.4192e-2, 0.52988
3.5275e-2, 0.53188

```

```

*PERMEABILITY, TYPE=SATURATION
1 0,1 0
*PERMEABILITY, TYPE=VELOCITY
1 0
**
*EQUATION
2
326, 1, 1, 2321, 1, -1
**
**Defining the solid section properties of the steel friction section located beside the column
*SOLID SECTION, ELSET=SFRIC, MATERIAL=STEEL
**Modulus of Elasticity used in the steel section is 29 E6 ksi
**which has been converted to 2e-11 kPa
**The Poisson ratio of the steel is assumed to be 0.3
*MATERIAL, NAME=STEEL
*ELASTIC
2 E11, 0.3
*PERMEABILITY, TYPE=ISO, SPECIFIC=7.7499
1 e-9
**
**Defining the contact surfaces between the internal section
**and the friction steel section beside the column
*SURFACE DEFINITION, NAME=SSOILSUR, TRIM=YES
SIDE
*SURFACE DEFINITION, NAME=SFRICSUR
SFRIC
*CONTACT PAIR, INTERACTION=SDFRIC
SSOILSUR, SFRICSUR
*SURFACE INTERACTION, NAME=SDFRIC
**The interface coefficient of friction of the Kromasil is estimated to be 0.21
**where the friction angle is approximately 12 degrees
*FRICTION
0.2056
**
**Defining the boundary conditions of the section
**Both the top of the column and friction section is prevented from moving axially
**The fluid (solvent) inside the column is free to flow out of the column through the top
*BOUNDARY
TOP, 2
TOP, 8
SFRICTOP, 2
**
**Defining the initial load conditions of the internal section
*INITIAL CONDITIONS, TYPE=SATURATION
INTNODE, 1 0
*INITIAL CONDITIONS, TYPE=PORE PRESSURE
INTNODE, 0, 0, 0, 0.16
*INITIAL CONDITIONS, TYPE=RATIO
SFRICIN, 1 e-5, 0, 1 e-5, 0.16
*INITIAL CONDITIONS, TYPE=RATIO
SFRICOUT, 1 e-5, 0, 1 e-5, 0.16
*INITIAL CONDITIONS, TYPE=RATIO
INTNODE, 0.5319, 0, 0.5319, 0.16
*INITIAL CONDITIONS, TYPE=STRESS, GEOSTATIC
INTERNAL, -10, 0, -10, 0.16, 0.43
**
**Defining the loading onto the internal section
**Step 1*****
*STEP
*GEOSTATIC

```

```

0 025, 1 0, 0 001, 0 1
*DLOAD
BOTTOM, P1, 10
*EL PRINT, ELSET=INTERNAL
S
E
SAT
POR
VOIDR
*EL PRINT, ELSET=SFRIC
S
E
*MONITOR, NODE=161, DOF=8, FREQUENCY=1
**MONITOR, NODE=161, DOF=2, FREQUENCY=1
*NODE PRINT, NSET=INTNODE
U
*CONTACT PRINT, MASTER=SFRIC SUR, SLAVE=SSOIL SUR, SUMMARY=YES
*PRINT, CONTACT=YES
*END STEP
**Step 2*****
*STEP, INC=100
**The packing material is consolidated for 1 min, where the maximum allowable pore pressure dissipation for each
**increment is 1,300 kPa
*SOILS, CONSOLIDATION, UTOL=1300
7 e-8, 6 944e-4,,,
*BOUNDARY
BOTTOM, 2, 2, 0 0034
*EL PRINT, ELSET=INTERNAL
S
E
SAT
POR
VOIDR
*EL PRINT, ELSET=SFRIC
S
E
*NODE PRINT, NSET=INTNODE
U
*CONTACT PRINT, MASTER=SFRIC SUR, SLAVE=SSOIL SUR, SUMMARY=YES
*PRINT, CONTACT=YES
*END STEP

```

Coupled Mechanical-Seepage Transient Analysis using Kromasil Spherical C8 packing material (Loading rate: 1 minute, remaining at 3.4mm for 2 minute)
File name: coup11.inp

```

*HEADING
THE CHROMATOGRAPHY PROBLEM WITH FRICTION SURFACE (KPA, M, DAYS)
**This is a model used to simulate a 5 3cm by 10 6cm column used in the HPLC column
**There is a restraint on top of both the column and steel section to prevent movement along the y-direction
**A piston is used to induce 3 4mm displacement (bottom) into the column
**The packing material is assumed to behave like a porous elastic material
**Units Length=m, Stress=kPa
*RESTART,WRITE
**
**Defining the coordinates of all the nodes used to model the column
*NODE,SYSTEM=R
1, 0 , 0 001
6, 0 025, 0 001
321, 0 , 0 16
326, 0 025, 0 16
2001, 0 025, 0
2002, 0 03, 0
2321, 0 025, 0 16
2322, 0 03, 0 16
**
**Defining the nodes of the internal section of the column
*NGEN, NSET=TOP
321, 326, 1
*NGEN, NSET=BOTTOM
1, 6, 1
*NGEN, NSET=SIDE
6, 326, 10
*NGEN, NSET=CENTER
1, 321, 10
*NFill, NSET=INTNODE
BOTTOM, TOP, 32, 10
**
**Defining the nodes of the contacting steel friction section located beside the column
*NGEN, NSET=SFRICIN
2001, 2321, 10
*NGEN, NSET=SFRICOUT
2002, 2322, 10
*NGEN, NSET=SFRICBOT
2001, 2002, 1
*NGEN, NSET=SFRICTOP
2321, 2322, 1
**
**Defining elements of the internal section of the column
*ELEMENT, TYPE=CAX4P
1, 1, 2, 12, 11
*ELGEN, ELSET=BOTTOM
1, 5, 1
*ELSET, ELSET=TOP, GENERATE
311, 315, 1
*ELGEN, ELSET=INTERNAL
1, 5, 1, 1, 32, 10, 10
*ELSET, ELSET=SIDE, GENERATE
5, 315, 10
*ELSET, ELSET=CENTER, GENERATE

```

```

1, 311, 10
**
**Defining elements of the contacting steel friction section located beside the column
*ELEMENT, TYPE=CAX4P, ELSET=SFRIC
2001, 2001, 2002, 2012, 2011
*ELGEN, ELSET=SFRIC
2001, 1, 1, 1, 32, 10, 10
**
**Defining the solid material properties of the internal section of the column
*SOLID SECTION, ELSET=INTERNAL, MATERIAL=SILICA
**Defining the material properties of the column
**The material is assumed to behave like a porous elastic material
**Note that Poisson ratio is 0.3
*MATERIAL, NAME=SILICA
*POROUS ELASTIC, SHEAR=POISSON
0 01, 0 3, 100 0
*DRUCKER PRAGER HARDENING
1 1, 0
*DRUCKER PRAGER, SHEAR CRITERION=LINEAR
45 51, 1 0, 0
** Permeability in m/day, specific weight of methanol in kN/m^3
*PERMEABILITY, TYPE=ISO, SPECIFIC=7 7499
1 0968e-2, 0 46188
1 1367e-2, 0 46388
1 1780e-2, 0 46588
1 2205e-2, 0 46788
1 2644e-2, 0 46988
1 3096e-2, 0 47188
1 3563e-2, 0 47388
1 4044e-2, 0 47588
1 4540e-2, 0 47788
1.5052e-2, 0 47988
1 5579e-2, 0 48188
1 6122e-2, 0 48388
1 6682e-2, 0 48588
1 7259e-2, 0 48788
1 7854e-2, 0 48988
1 8466e-2, 0 49188
1 9097e-2, 0 49388
1 9747e-2, 0 49588
2 0416e-2, 0 49788
2 1105e-2, 0 49988
2 1814e-2, 0 50188
2 2544e-2, 0 50388
2 3296e-2, 0 50588
2 4070e-2, 0 50788
2 4866e-2, 0 50988
2 5685e-2, 0 51188
2 6527e-2, 0 51388
2 7394e-2, 0 51588
2 8286e-2, 0 51788
2 9203e-2, 0 51988
3 0146e-2, 0 52188
3 1116e-2, 0 52388
3 2113e-2, 0 52588
3 3138e-2, 0 52788
3 4192e-2, 0 52988
3 5275e-2, 0 53188
*PERMEABILITY, TYPE=SATURATION
1 0,1 0

```

```

*PERMEABILITY, TYPE=VELOCITY
1 0
**
*EQUATION
2
326, 1, 1, 2321, 1, -1
**
**Defining the solid section properties of the steel friction section located beside the column
*SOLID SECTION, ELSET=SFRIC, MATERIAL=STEEL
**Modulus of Elasticity used in the steel section is 29 E6 ksi
**which has been converted to 2e-11 kPa
*MATERIAL, NAME=STEEL
*ELASTIC
2 E11, 0 3
*PERMEABILITY, TYPE=ISO, SPECIFIC=7 7499
1 e-9
**
**Defining the contact surfaces between the internal section
**and the friction steel section beside the column
*SURFACE DEFINITION, NAME=SSOILSUR, TRIM=YES
SIDE
*SURFACE DEFINITION, NAME=SFRICSUR
SFRIC
*CONTACT PAIR, INTERACTION=SDFRIC
SSOILSUR, SFRICSUR
*SURFACE INTERACTION, NAME=SDFRIC
**The interface coefficient of friction of the Kromasil is estimated to be 0 21
**where the friction angle is approximately 12 degrees
*FRICTION
0 2056
**
**Defining the boundary conditions of the section
**Both the top of the column and friction section is prevented from moving axially
**The fluid (solvent) inside the column is free to flow out of the column through the top
*BOUNDARY
TOP, 2
TOP, 8
SFRICTOP, 2
**
**Defining the initial load conditions of the internal section
*INITIAL CONDITIONS, TYPE=SATURATION
INTNODE, 1 0
*INITIAL CONDITIONS, TYPE=PORE PRESSURE
INTNODE, 0, 0, 0, 0 16
*INITIAL CONDITIONS, TYPE=RATIO
SFRICIN, 1 e-5, 0, 1 e-5, 0 16
*INITIAL CONDITIONS, TYPE=RATIO
SFRICOUT, 1 e-5, 0, 1 e-5, 0 16
*INITIAL CONDITIONS, TYPE=RATIO
INTNODE, 0 5319, 0, 0 5319, 0 16
*INITIAL CONDITIONS, TYPE=STRESS, GEOSTATIC
INTERNAL, -10, 0, -10, 0 16, 0 43
**
**Defining the loading onto the internal section
**Step 1*****
*STEP
*GEOSTATIC
0 025, 1 0, 0 001, 0 1
*DLOAD
BOTTOM, P1, 10

```

```

*EL PRINT, ELSET=INTERNAL
S
E
SAT
POR
VOIDR
*EL PRINT, ELSET=SFRIC
S
E
*MONITOR, NODE=161, DOF=8, FREQUENCY=1
**MONITOR, NODE=161, DOF=2, FREQUENCY=1
*NODE PRINT, NSET=INTNODE
U
*CONTACT PRINT, MASTER=SFRICSUR, SLAVE=SSOILSUR, SUMMARY=YES
*PRINT, CONTACT=YES
*END STEP
**Step 2*****
*STEP, INC=100
**The packing material is consolidated for 1 minute, where the maximum pore pressure dissipation allowed in each
**increment is 1,300 kPa
*SOILS, CONSOLIDATION, UTOL=1300
7 e-8,6 944e-4,,,
**The piston is pushed 3 4mm from the bottom within 1 minute
*BOUNDARY
BOTTOM, 2, 2, 0 0034
*EL PRINT, ELSET=INTERNAL
S
E
SAT
POR
VOIDR
*EL PRINT, ELSET=SFRIC
S
E
*NODE PRINT, NSET=INTNODE
U
*CONTACT PRINT, MASTER=SFRICSUR, SLAVE=SSOILSUR, SUMMARY=YES
*PRINT, CONTACT=YES
*END STEP
**step3*****
*STEP, INC=100
**Holding the piston at its final position for 2 minutes
*SOILS, CONSOLIDATION, UTOL=1300
7 e-8,1 389e-3,,,
*END STEP

```

Vita

Bee Gaik Yew was born in Penang, Malaysia on September 14, 1974. She attended primary school and high school there. In Fall 1996, she transferred from Inti College, Subang Jaya, Malaysia to the University of Tennessee, Knoxville to further her education. She was awarded membership in the Honor Society of Phi Kappa Phi, National Honor Society of Golden Key, Honor Society of National Dean Lists, the Engineering Honor Society of Tau Beta Pi, and the Civil Engineering Honor Society of Chi Epsilon. She graduated from the University of Tennessee Summa Cum Laude with a B.S. degree in Civil and Environmental Engineering in Spring 1998. She also passed Fundamental of Engineering examination in Spring 1998.

In May 1998, she enrolled in the graduate program in the Department of Civil and Environmental Engineering at the University of Tennessee, Knoxville and accepted a graduate research assistantship from the Chemistry department. She was awarded a graduate school travel grant and presented selected results from this research at the Fourth International Conference on Constitutive Laws for Engineering Materials: Experiment, Theory, Computation and Applications, in Troy, NY, on July 27 – July 30, 1999. She received her M.S. degree in Civil Engineering, with a concentration in Geotechnical Engineering from the University of Tennessee, Knoxville in May, 2000.