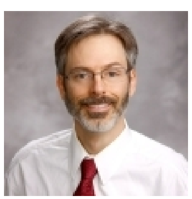
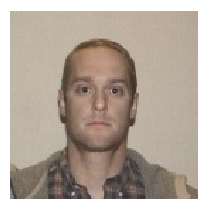
Sandia National Laboratories

SAND2021-3975C

Design of chromatography columns with 3D-graded permeability



PRESENTED BY

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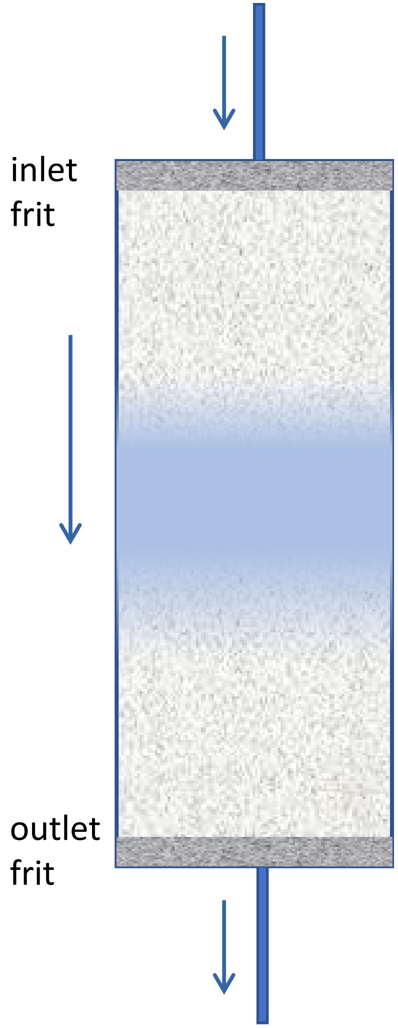
SAND2021-XXXXC

Background and Motivation



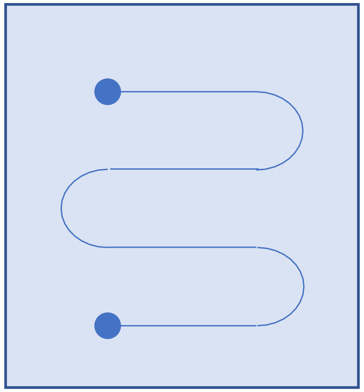
Chromatography often relies on porous media.

Microscopic porosity defines macroscopic permeability, defining flow rate versus pressure.

Mobile phase can travel over varying cross sections or around corners, where flow can be nonuniform.

Examples:

Stainless steel columns with frits
Glass columns with hemispherical ends
Column on a chip



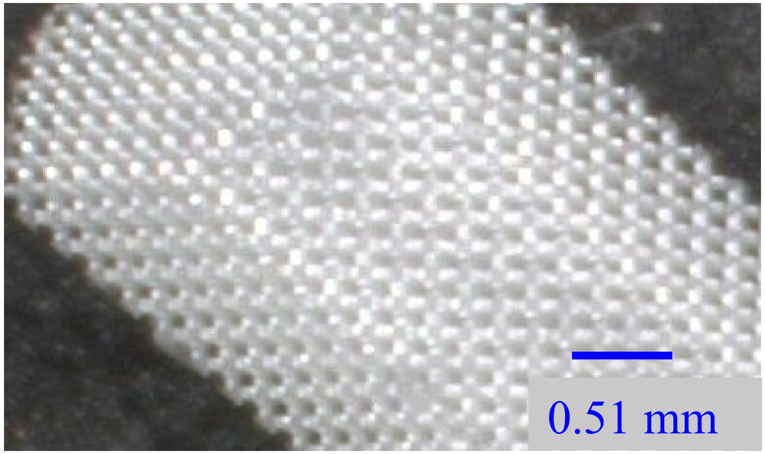
Challenge: Adjust permeability to maintain spatially uniform fluid velocity despite nonuniform geometries.

3D Printing of Porous Material

Additive manufacturing (AM) techniques raise the possibilities that porous media can be fabricated in which the permeability can be arbitrarily specified in three dimensions

By varying laser power and speed, and tuning particle size distribution, Mott Corporation has claimed the ability to spatially vary permeability using metal laser sintering AM methods.[1]

We have previously studied flow through additively manufactured polymer lattices with precisely defined pores.[2]



1. V.P. Palumbo et al. "Porous Devices Made by Laser Additive Manufacturing." US Patent Application 2017/0239726 A1, Mott Corporation, 2017.
2. M. Salloum and D.B. Robinson "A Numerical model of exchange chromatography through 3-D lattice structures", *AIChe J.* vol 64(5), pp. 1874-1884, 2018

Permeability and Porosity, Pressure and Flow

We focus on Darcy's Law:

- Assumes slow flow

$$v = \frac{\kappa}{\mu L} \Delta p$$

v = fluid velocity $\left(\frac{\mathrm{m}}{\mathrm{s}}\right)$
κ = permeability $\left(\mathrm{m}^2\right)$
μ = viscosity (Pa s)
L = length (m)
Δp = pressure drop (Pa)

Permeability is related to porosity ε (pore volume fraction)

- Depends on pore geometry and how it is changed
  - Compaction, sintering, 3D printing, etc.
- Square array of circular pipes, fixed spacing W:
  $\kappa = \frac{W^2 \varepsilon}{8\pi}$ for $0 < \varepsilon < 0.79 = \pi/4$
- Packed spheres, diameter D: Kozeny-Carman equation
  $\kappa = \frac{D^2 \varepsilon^3}{150(1-\varepsilon)^2}$
- See Erdim et al., Powder Tech. 283 488 (2015)

Case Study

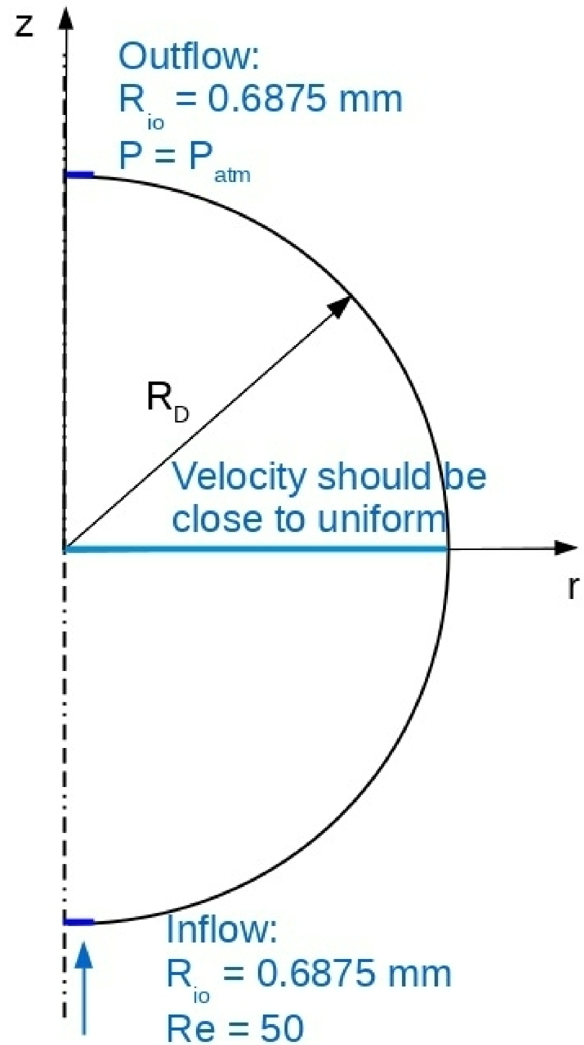
Spherical Columns (or Hemispherical Ends)

Inert porous frits abruptly change flow diameter at inlet and outlet in cylindrical columns.
- Sharp corners cause large stresses around the device inlet.

Curved regions such as spherical shapes could decrease stress concentrations in high-pressure chromatography, and increase the amount of active porous material.

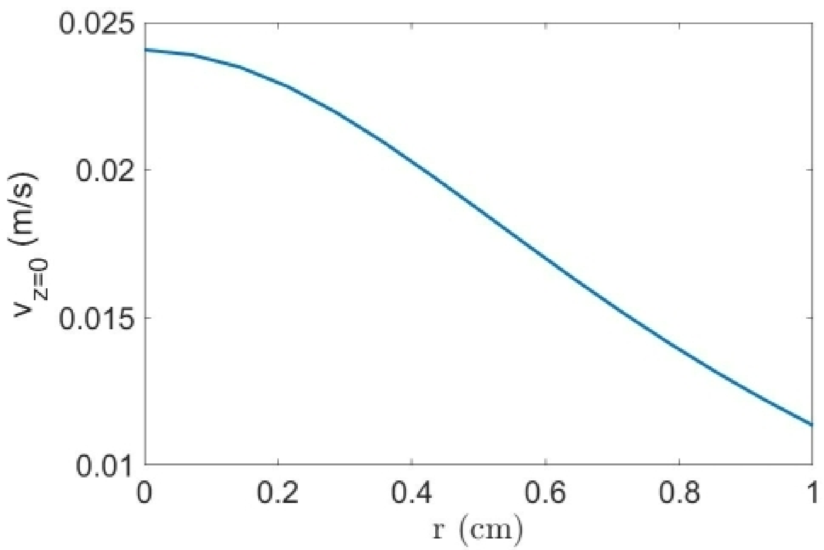
We would like to study the feasibility of graded permeability of spherical porous columns by computing optimal permeability distributions.

Spherical Column Geometry



We start by studying a full sphere of axi-symmetric model geometry.

For a constant permeability $K_0=10^{-12}$ m/s, the resulting midplane velocity profile is:

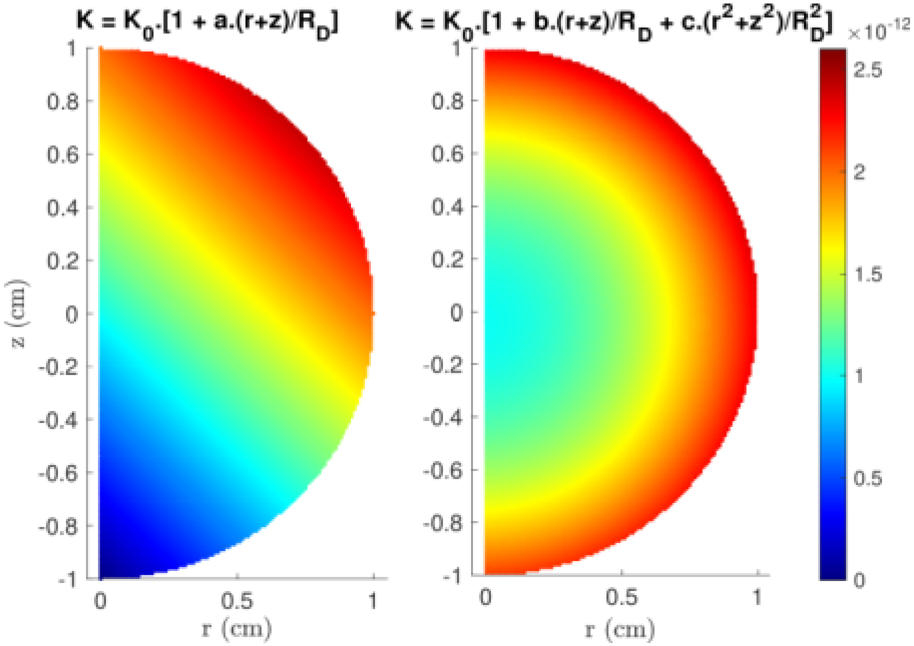


We seek a graded permeability that establishes a uniform flow velocity mid-way between the inlet and outlet.

Spherical Column with Graded Permeability

Parametric Optimization

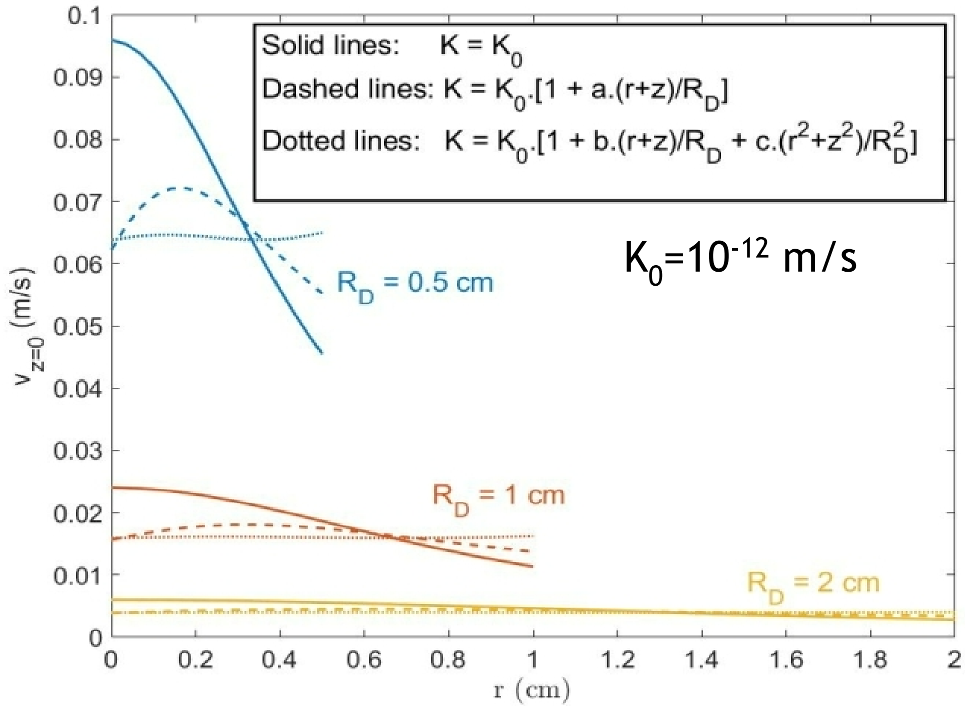
We assume linear and quadratic permeability profiles. ($K_0=10^{-12}$ m/s)



$R_D = 1$cm

The contribution of the linear term vanishes when a quadratic term exists.

A quadratic term is necessary to obtain a nearly uniform velocity profile.



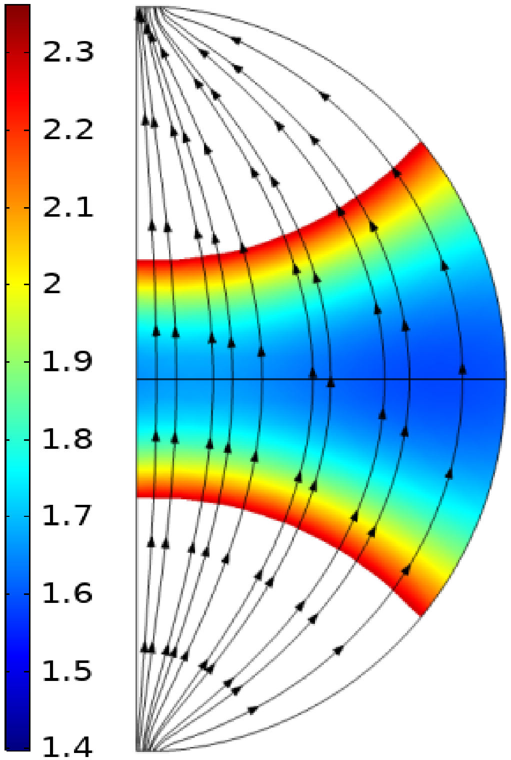
$K_0=10^{-12}$ m/s

Spherical Column with Graded Permeability

Parametric Optimization – Transit Time

Although a uniform velocity profile is obtained in the sphere mid-plane, the transit time along the flow streamlines is still not uniform.

Streamlines and velocity field (cm/s)

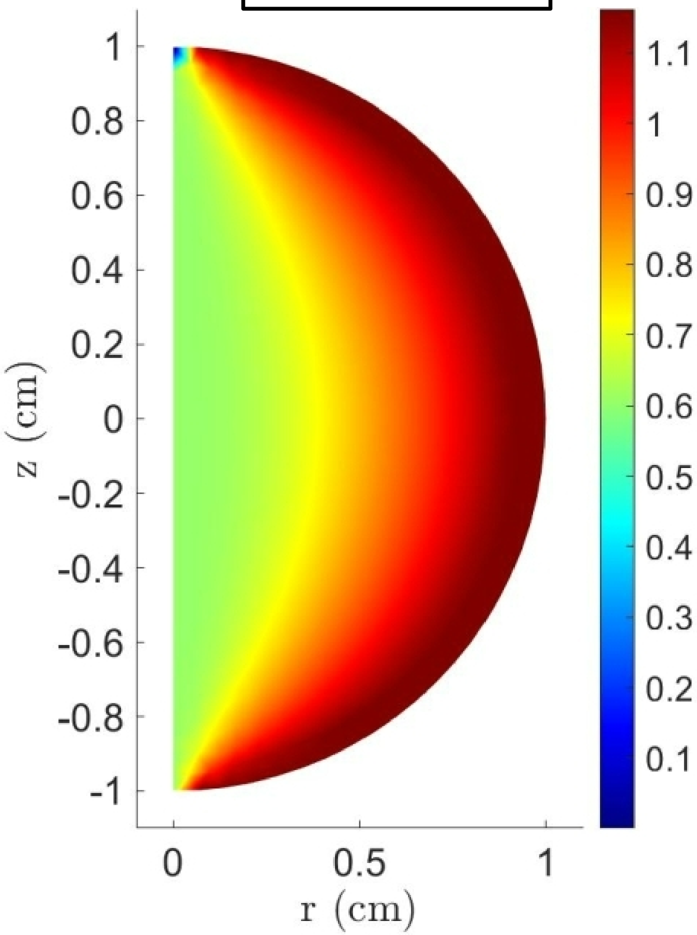


We define the transit time τ as the time taken by a fluid element to travel along a streamline.

We also seek a uniform transit time among all of the streamlines.

This could allow a chromatography peak to remain sharp at the outlet.

Transit time (s)



Spherical Column with Graded Permeability

Iterative Non-Parametric Optimization

In non-parametric optimization, we do not impose any functional form of the permeability field.

We obtain the optimal solution iteratively by adjusting the permeability field model input according to the velocity profile and transit time output.

We start with a constant permeability $K=K_0$ and repeat the following until convergence:

$$K(r,z)_i = K(r,z)_{i-1} \cdot \frac{max[v(r)_{i-1}]}{v(r)_{i-1}} \cdot \frac{\tau(r,z)_{i-1}}{max[\tau(r,z)_{i-1}]}$$

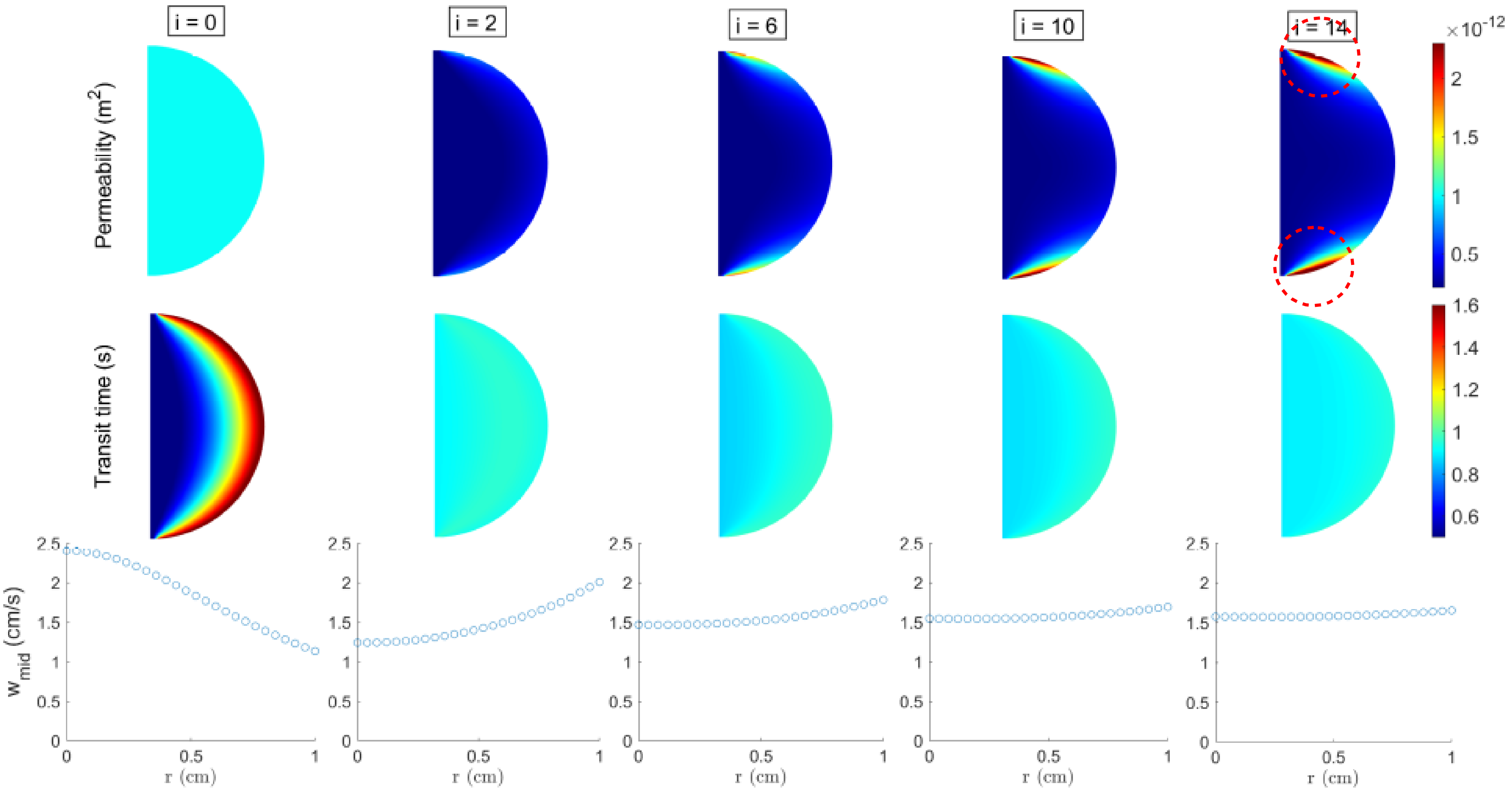
This algorithm adjusts the local value of the permeability according to the local value of the velocity and transit time.

Spherical Column with Graded Permeability

Non-Parametric Optimization Results

An optimal solution is obtained within 14 iterations with uniform velocity and transit time.

Uniformity is obtained by grading the permeability only near the sphere inlet and outlet.



Spherical Column with Graded Permeability

Retention Time

Analytes spend a fraction of time bound reversibly to the solid.

- Their velocities v_r are proportional to fluid velocity, but slower.
- Also proportional to fraction of analyte in fluid.

If analytes diffuse into micropores in solid (solid absorbs analyte):

$$\frac{v_r}{v} = \frac{\varepsilon}{\varepsilon + C(1-\varepsilon)}$$

where *C* is a solid-fluid equilibrium constant.

MAIN POINT: retention time L/v_r may not be simply proportional to transit time.

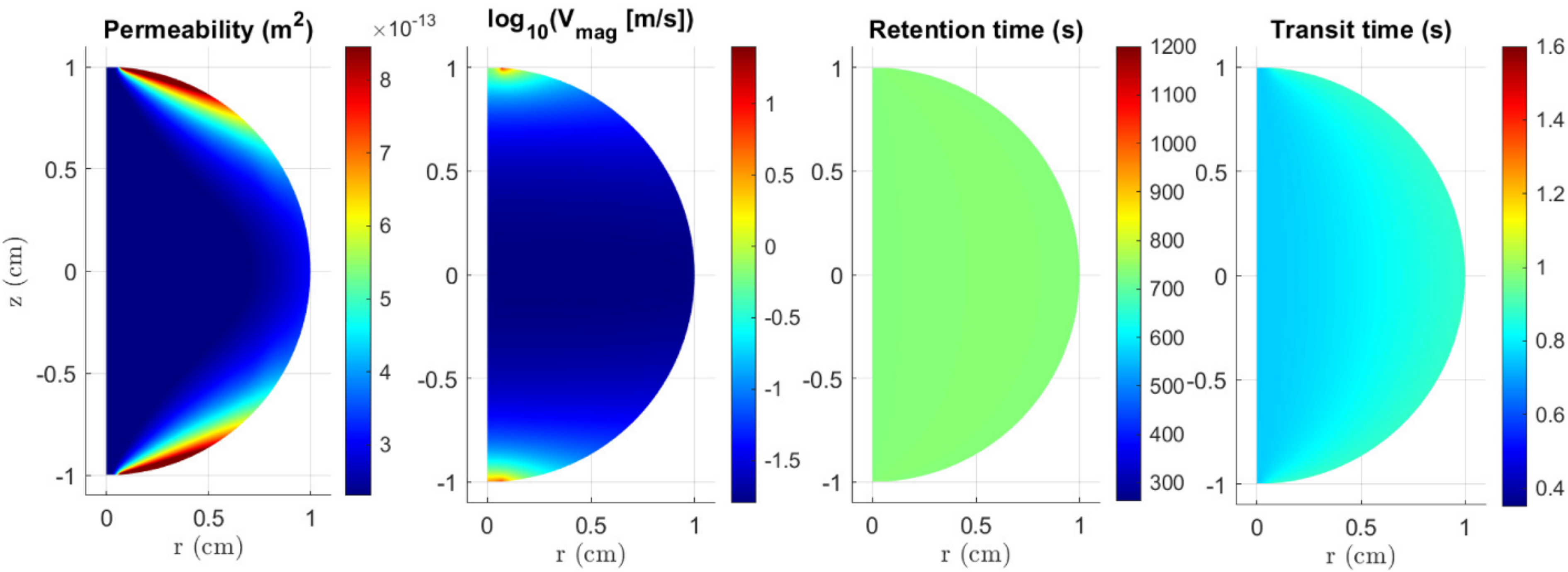
Spherical Column with Graded Permeability

Optimization for Retention Time

We let C=1 and relate porosity to permeability by the Kozeny-Carman equation.

Other nonlinear relationships are easy to implement.

Retention time can be made quite uniform.



The optimal permeability resembles that for transit time.

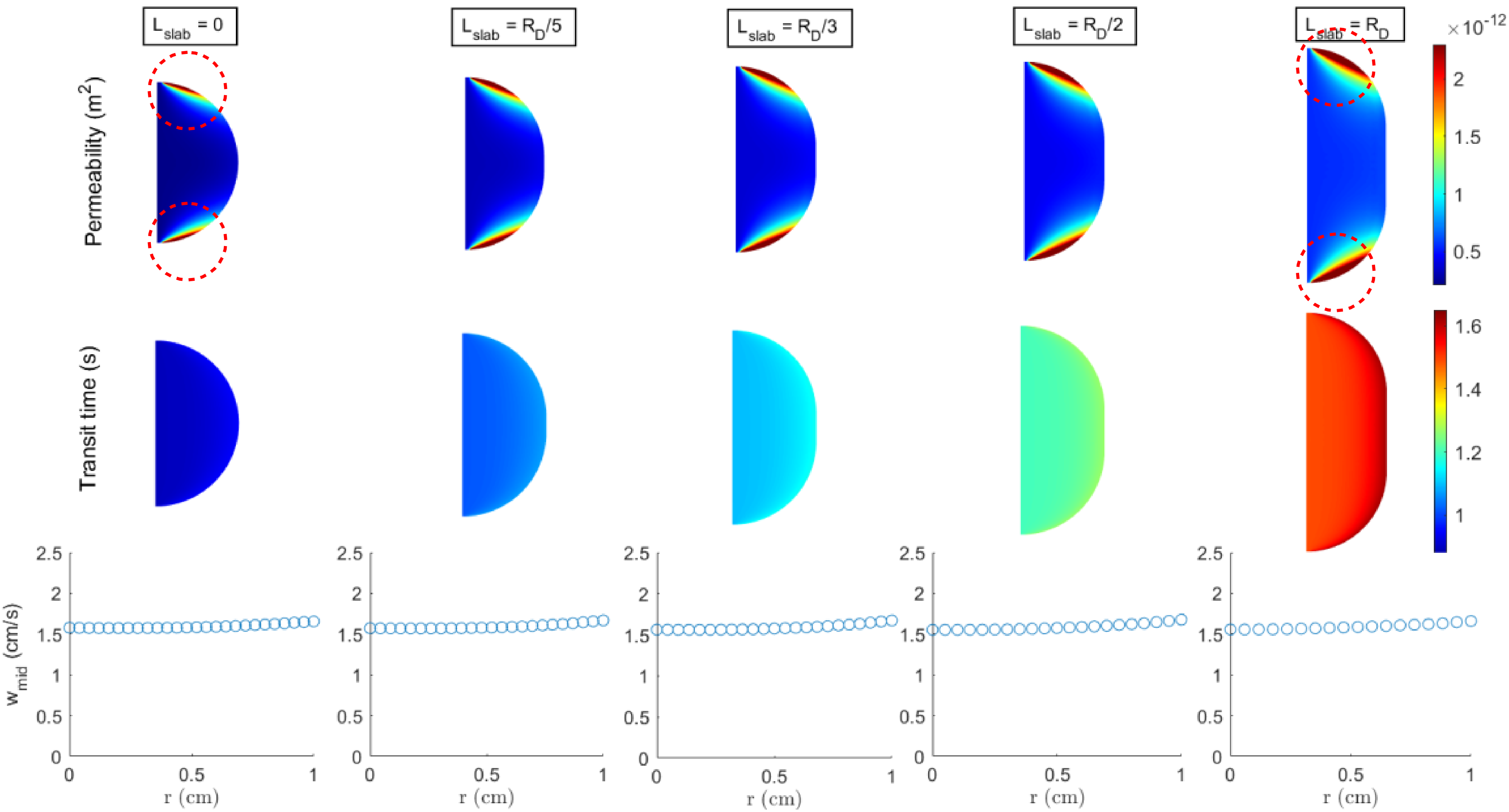
The optimal velocity is almost uniform in the radial direction.

When we have optimized for uniform retention time, the transit time is also quite uniform, but slightly less so.

Spherical Column with Graded Permeability

Effect of an Inserted Slab

Similar permeability field trend is obtained for a slab inside the sphere which simulates a more cylindrical geometry (e.g. chromatography column)



Trust-region Newton method

Sandia has implemented more advanced optimization codes available that can efficiently accommodate a broader range of flow models and constraints.

Flow models implemented include Darcy's law and Stokes-Brinkman, allowing open channels to form.

T. Borrvall, J. Petersson. "Topology Optimization of Fluids in Stokes Flow." Int. J. Numer. Meth. Fluids 41, 77–107, 2003.

C. J. Lin and J. J. More. "Newton's Method for Large Bound-Constrained Optimization Problems." SIAM J Optim. 9 (4) 1100-1127, 1999.

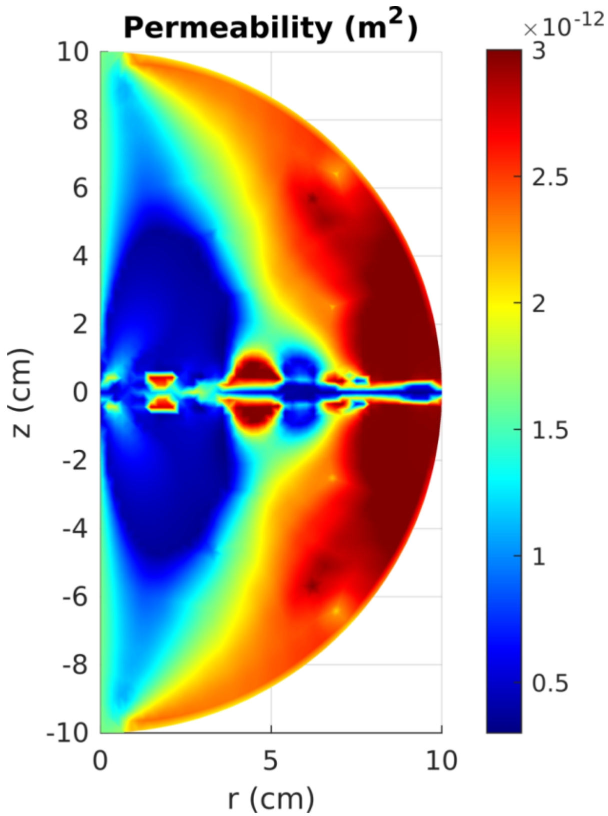
B. Jared et al. "Additive manufacturing: Toward holistic design." Scripta Materialia 125 141-147, 2017.

M. A. Heroux, R. A. Bartlett et al. "An overview of the Trilinos project." ACM Trans. Math. Softw. 31(3), 397-423, 2005.

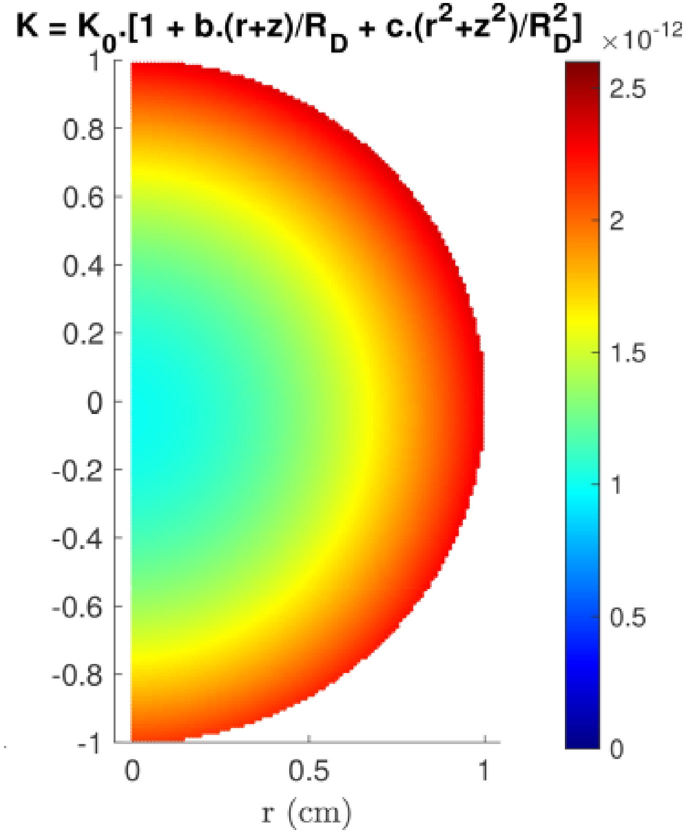
Spherical Column with Graded Permeability

Trust-region Newton method vs. Parametric

Trust-region Newton method produces a permeability field that is qualitatively similar to the one produces by parametric optimization, but with finer detail.



Trust-region Newton result for uniform midplane and axial velocity



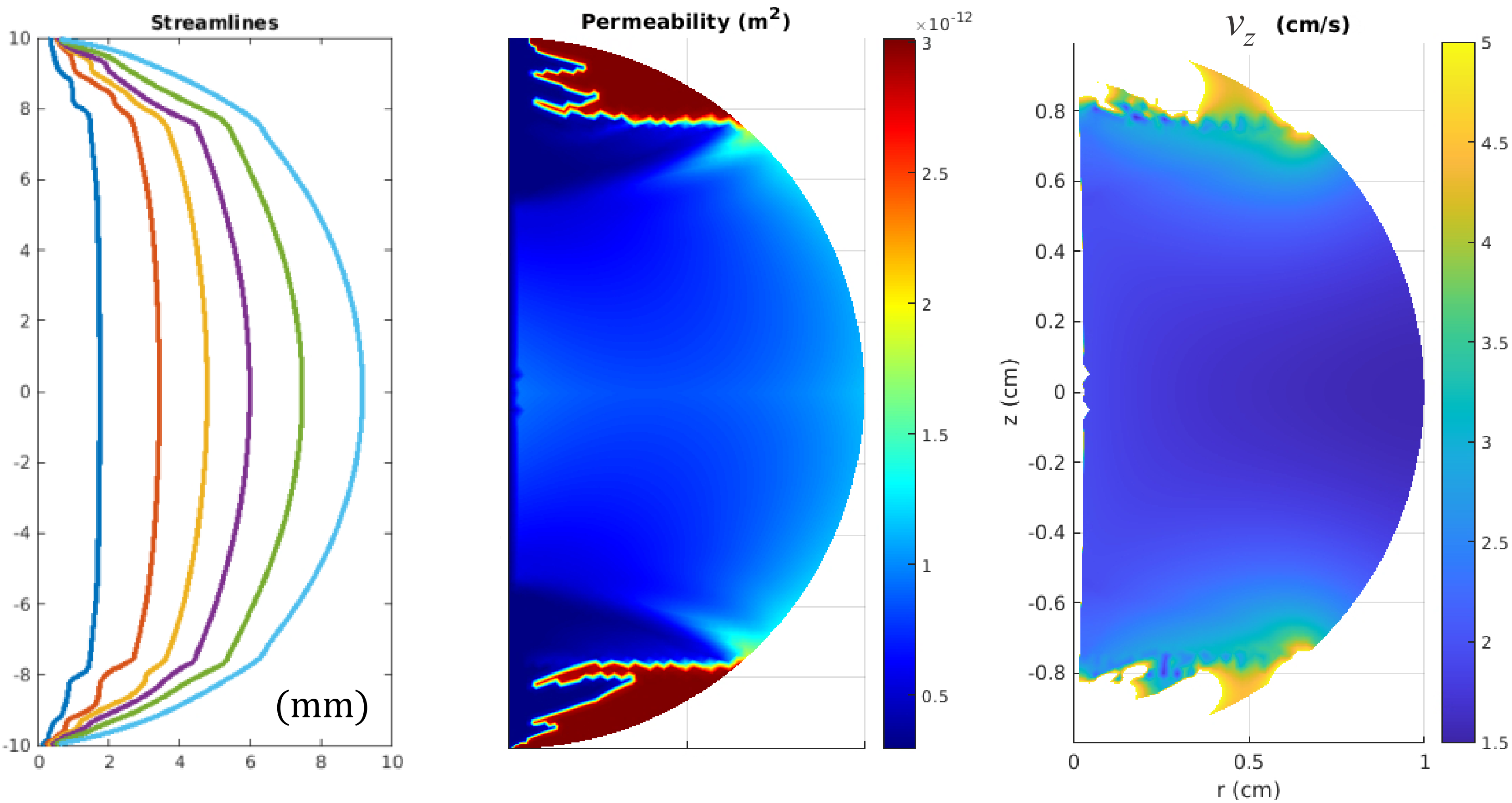
Parametric optimization for uniform midplane velocity

Spherical Column with Graded Permeability

Trust-region Newton: Optimizing velocity fields

Trust-region Newton can pursue a specified analytical velocity field (even if nonphysical!).

We specify a constant axial velocity v_z, and radial velocity $v_r = \frac{rz}{R^2 - z^2} v_z$ over 75% of length.



Algorithm is constrained to find physical solutions, and approaches a v_z of about 2 cm/s over a large area. Using a more physically validated target velocity field may improve results.

Conclusions

Additive manufacturing techniques may enable novel architectures for porous media.

Optimized graded permeability can achieve uniform flow velocity, transit time, and/or retention time in chromatography columns.

Several optimization methods yield solutions that improve flow uniformity in spherical columns.

Spherical columns with uniform transit or retention time could be easily manufactured by simply grading permeability in regions near the inlet and outlet.

Adding a slab in the middle of a spherical column approximately preserves the optimal graded permeability field.

Acknowledgements and Contact Info

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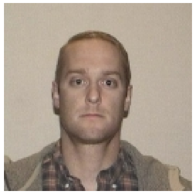

Drew Kouri

Thank you for your attention!