HWRS 505: Vadose Zone Hydrology

Lecture 24

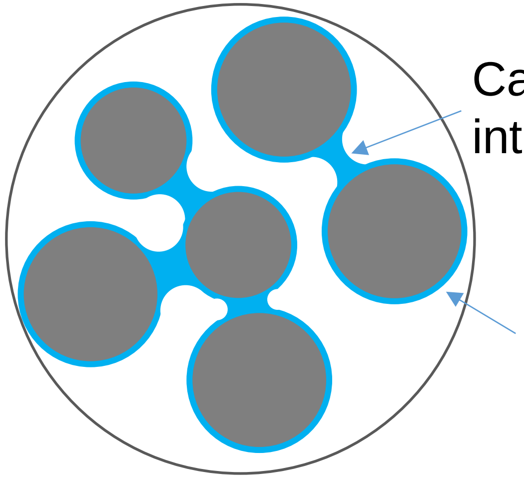
11/21/2024

Today: Fluid-fluid interfacial area

Review of Lecture 23

- Mathematical models for PFAS transport in the vadose zone
  - ✓ Formulating surfactant-induced flow
  - ✓ Formulating adsorption at solid-water and air-water interfaces
- Long-term simulations of PFAS leaching and retention in the vadose zone
  - ✓ w/ vs. w/o air-water interfacial adsorption
  - ✓ Short- vs. long-chain PFAS
  - ✓ Impact of spatial heterogeneity
  - ✓ Implication for remediation strategies

Fluid-Fluid Interfacial Area in Porous Media



How to measure fluid-fluid (e.g., air-water) interfacial area?

- X-ray microtomography (direct imaging)
- Interfacial Partitioning Tracer Test (indirect measurement)

Measuring Fluid-Fluid Interfacial Area

WATER RESOURCES RESEARCH, VOL. 40, W12413, doi:10.1029/2004WR003278, 2004

Interfacial area measurements for unsaturated flow through a porous medium

Katherine A. Culligan,[1,2] Dorthe Wildenschild,[3,4] Britt S. B. Christensen,[4]
William G. Gray,[5] Mark L. Rivers,[6] and Andrew F. B. Tompson[7]

Received 19 April 2004; revised 17 July 2004; accepted 28 September 2004; published 22 December 2004.

[1] Multiphase flow and contaminant transport in porous media are strongly influenced by the presence of fluid-fluid interfaces. Recent theoretical work based on conservation laws and the second law of thermodynamics has demonstrated the need for quantitative interfacial area information to be incorporated into multiphase flow models. We have used synchrotron based X-ray microtomography to investigate unsaturated flow through a glass bead column. Fully three-dimensional images were collected at points on the primary drainage curve and on the secondary imbibition and drainage loops. Analysis of the high-resolution images (17 micron voxels) allows for computation of interfacial areas and saturation. Corresponding pressure measurements are made during the course of the experiments. Results show the fluid-fluid interfacial area increasing as saturation decreases, reaching a maximum at saturations ranging from 20 to 35% and then decreasing as the saturation continues to zero. The findings support results of numerical studies reported in the literature. *INDEX TERMS:* 1875 Hydrology: Unsaturated zone; 1829 Hydrology: Groundwater hydrology; 1894 Hydrology: Instruments and techniques; *KEYWORDS:* interfacial area, porous media, unsaturated flow

Research Communications

ENVIRONMENTAL SCIENCE & TECHNOLOGY / VOL. 31, NO. 3, 1997

Measurement of Specific Fluid—Fluid Interfacial Areas of Immiscible Fluids in Porous Media

K. PRASAD SARIPALLI,† HEONKI KIM,‡
P. SURESH C. RAO,*,‡ AND
MICHAEL D. ANNABLE†
Inter-Disciplinary Program in Hydrologic Science, Department of Environmental Engineering Science and Department of Soil and Water Science, University of Florida, Gainesville, Florida 32611-0290

WATER RESOURCES RESEARCH, VOL. 33, NO. 12, PAGES 2705–2711, DECEMBER 1997

Determination of effective air-water interfacial area in partially saturated porous media using surfactant adsorption

Heonki Kim[1] and P. Suresh C. Rao
Interdisciplinary Program in Hydrologic Science, Soil and Water Science Department
University of Florida, Gainesville

Michael D. Annable
Interdisciplinary Program in Hydrologic Science, Department of Environmental Engineering Sciences
University of Florida, Gainesville

Measuring Fluid-Fluid Interfacial Area

X-ray microtomography

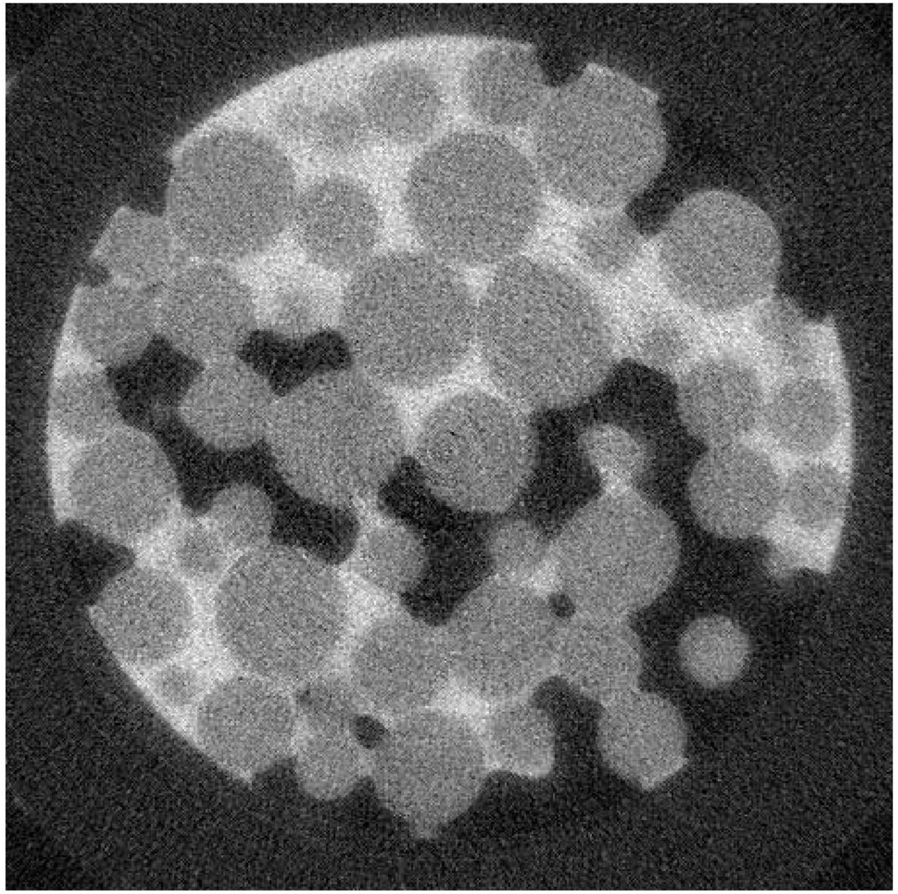


Figure 2. Two-dimensional (2-D) slice through glass bead column. Lightest (white) regions are water, gray regions are beads, and the darkest (black) regions are air.

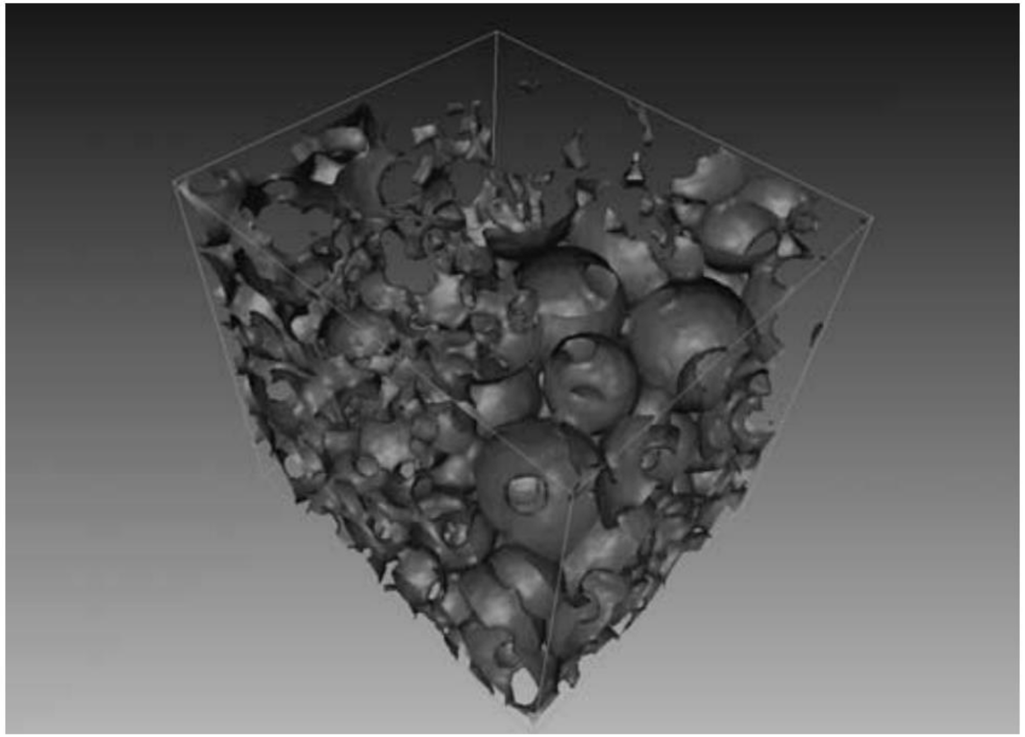


Figure 5a. Total wetting phase surface for GB_32 (s^w = 0.72). See color version of this figure in the HTML.

Gulligan et al (2004). WRR

Measuring Fluid-Fluid Interfacial Area

Interfacial Partitioning Tracer Test

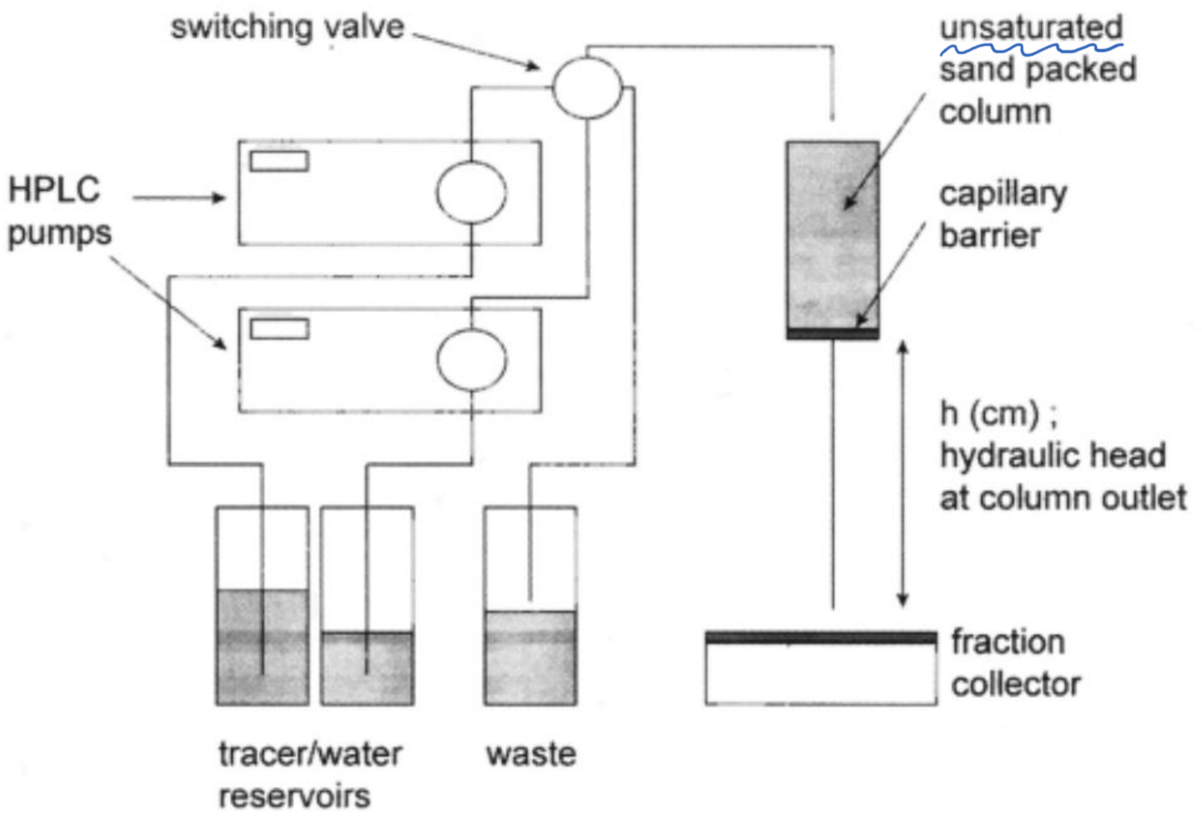


Figure 1. Schematic diagram of the experimental apparatus used for the miscible displacement experiments in unsaturated sand columns.

Kim et al. (1997) WRR

<u>**Idea**</u>: Use the retardation factor computed from the breakthrough curve to infer the air-water interfacial area in the porous medium.

Measuring Fluid-Fluid Interfacial Area

Interfacial Partitioning Tracer Test

Tracer transport

Advection Dispersion

$$\frac{\partial(\theta C)}{\partial t} + \rho_b \frac{\partial C_s}{\partial t} + \frac{\partial C_{aw}}{\partial t} + \frac{\partial}{\partial z}(\theta v C) - \frac{\partial}{\partial z}\left(\theta D \frac{\partial C}{\partial z}\right) = 0,$$

Storage in the aqueous phase

Storage in the solid-phase adsorption

Storage in the air-water interfacial adsorption

Assuming steady-state water flow and linear solid-phase and air-water interfacial adsorption

$$\theta \neq \theta(t), \theta \neq \theta(z), v \neq v(t), v \neq v(z)$$

$$C_s = K_d C$$

$$C_{aw} = K_{aw} A_{aw} C$$

$$\Rightarrow \left(1 + \frac{\rho_b K_d}{\theta} + \frac{1}{\theta} K_{aw} A_{aw}\right) \frac{\partial C}{\partial t} + v \frac{\partial C}{\partial z} - \frac{\partial}{\partial z}\left(D \frac{\partial C}{\partial z}\right) = 0$$

$$\Rightarrow R \frac{\partial C}{\partial t} + v \frac{\partial C}{\partial z} - \frac{\partial}{\partial z}\left(D \frac{\partial C}{\partial z}\right) = 0$$

R is defined as the retardation factor. All the parameters can be determined *a prior* except for A_{aw}

$$R \equiv 1 + \frac{\rho_b K_d}{\theta} + \frac{1}{\theta} K_{aw} A_{aw}$$

Measuring Fluid-Fluid Interfacial Area

Interfacial Partitioning Tracer Test

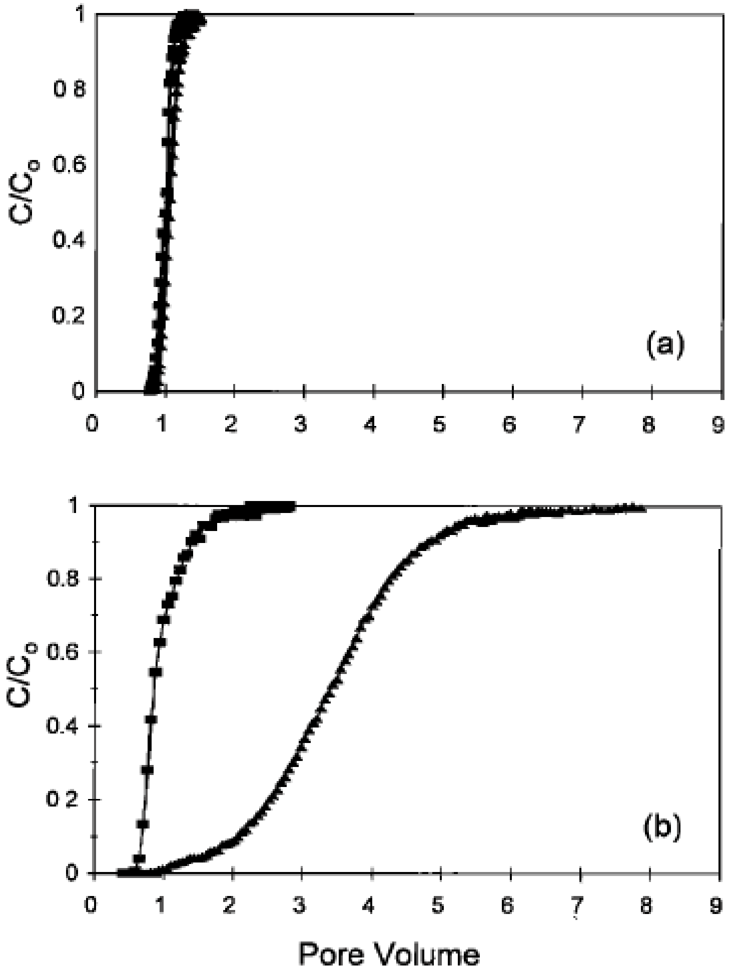


Figure 3. Breakthrough curves of SDBS and bromide (a) under water-saturated conditions, average volumetric water content, 0.36, and (b) average volumetric water content, 0.11: squares, bromide; triangles, SDBS.

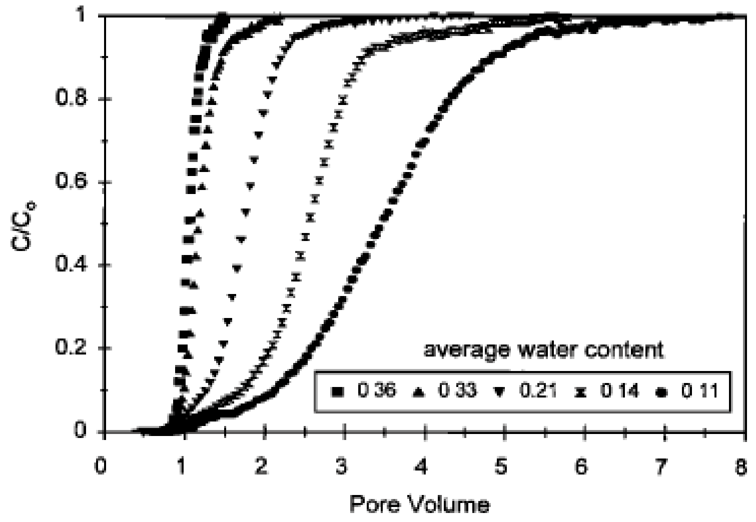
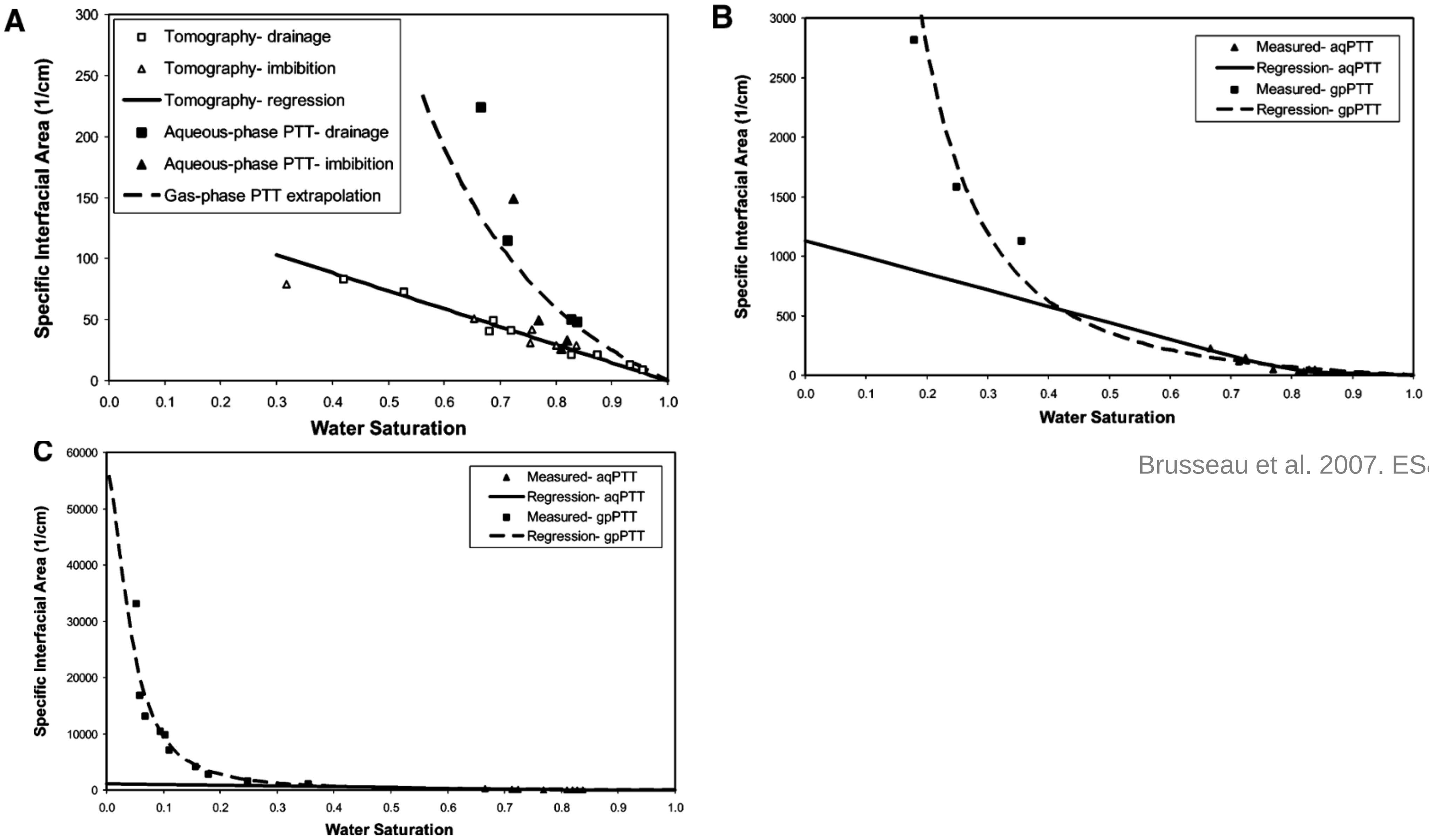


Figure 4. Comparison of SDBS breakthrough curves at different water contents.

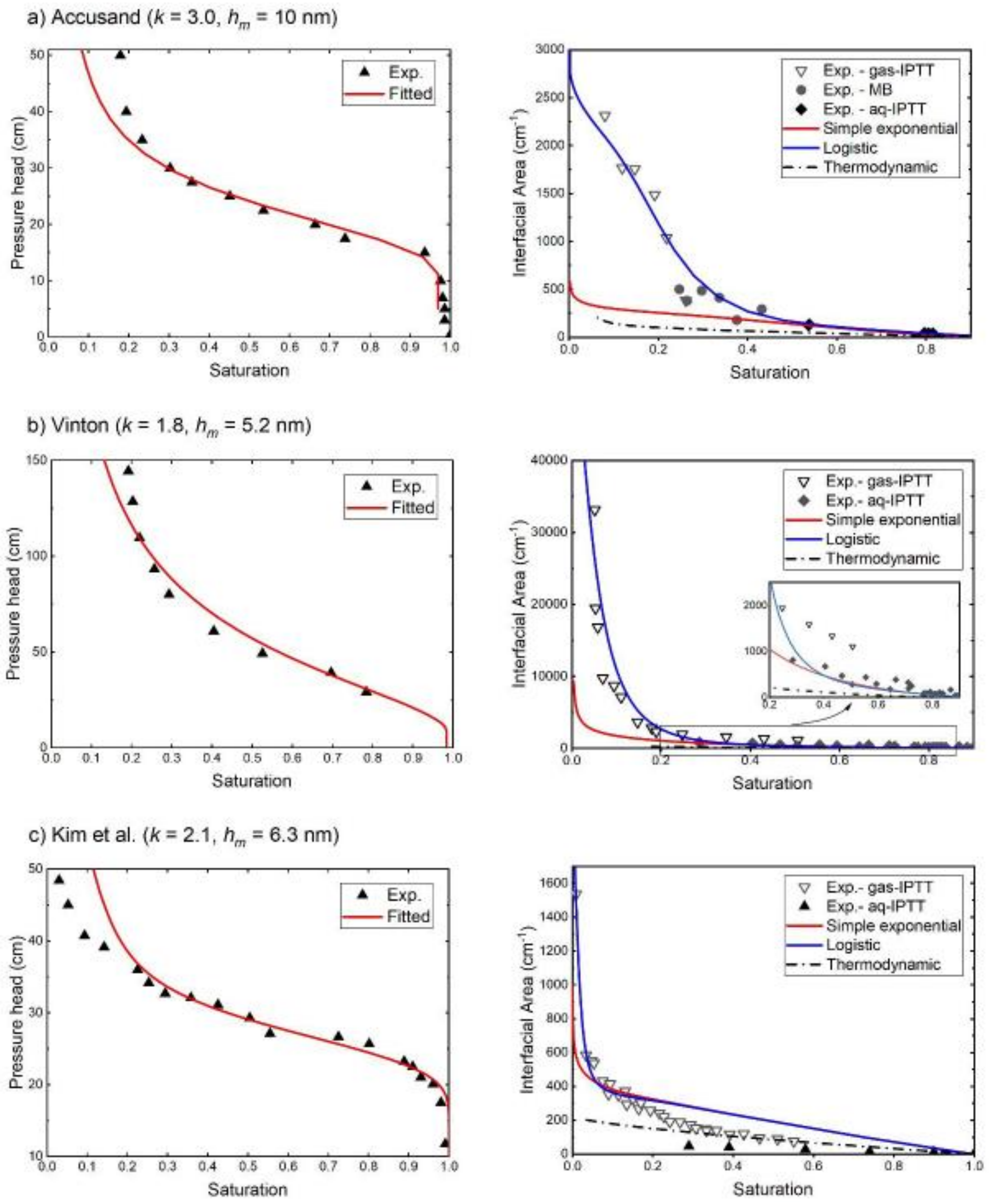
Kim et al. (1997) WRR

Measuring Fluid-Fluid Interfacial Area



Brusseau et al. 2007. ES&T

Measuring Fluid-Fluid Interfacial Area



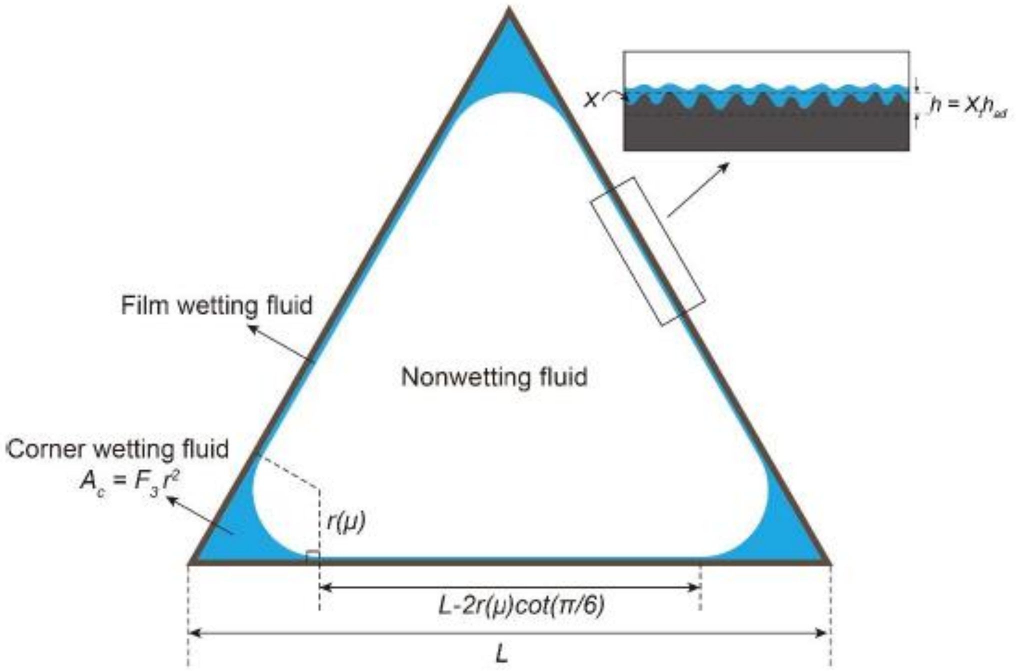


Figure 3. Cross-sectional scheme of a partially-filled equilateral triangular pore and the distribution of corner and film water.

Jiang, Guo, Brusseau. 2020. WRR

Measuring Fluid-Fluid Interfacial Area

Why is fluid-fluid interfacial area important?

✓ Many physical/chemical/biological processes take place at the fluid-fluid interfaces
  - PFAS fate and transport in the vadose zone is an important example.

✓ It is critical for a complete description of multiphase flow theory in porous media

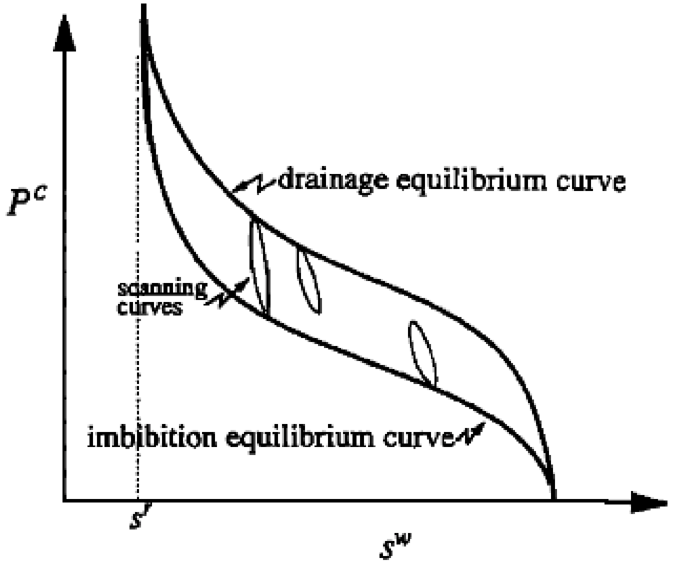


Fig. 5. Standard equilibrium plot of capillary pressure versus saturation.

Hassanizadeh & Gray (1993) WRR

Measuring Fluid-Fluid Interfacial Area

WATER RESOURCES RESEARCH, VOL. 29, NO. 10, PAGES 3389–3405, OCTOBER 1993

Thermodynamic Basis of Capillary Pressure in Porous Media

S. MAJID HASSANIZADEH

National Institute of Public Health and Environmental Protection, Bilthoven, Netherlands

WILLIAM G. GRAY

Department of Civil Engineering and Geological Sciences, University of Notre Dame, Notre Dame, Indiana

Important features of multiphase flow in porous media that distinguish it from single-phase flow are the presence of interfaces between the fluid phases and of common lines where three phases come in contact. Despite this fact, mathematical descriptions of these flows have been lacking in rigor, consisting primarily of heuristic extensions of Darcy's law that include a hysteretic relation between capillary pressure and saturation and a relative permeability coefficient. As a result, the standard capillary pressure concept appears to have physically unrealistic properties. The present paper employs microscopic mass and momentum balance equations for phases and interfaces to develop an understanding of capillary pressure at the microscale. Next, the standard theories and approaches that define capillary pressure at the macroscale are described and their shortcomings are discussed. Finally, an approach is presented whereby capillary pressure is shown to be an intrinsic property of the system under study. In particular, the presence of interfaces and their distribution within a multiphase system are shown to be essential to describing the state of the system. A thermodynamic approach to the definition of capillary pressure provides a theoretically sound alternative to the definition of capillary pressure as a simple hysteretic function of saturation.

WATER RESOURCES RESEARCH, VOL. 32, NO. 8, PAGES 2345–2358, AUGUST 1996

A functional relationship between capillary pressure, saturation, and interfacial area as revealed by a pore-scale network model

Paul C. Reeves and Michael A. Celia

Water Resources Program, Department of Civil Engineering and Operations Research, Princeton University
Princeton, New Jersey

Abstract. The constitutive relationships required for the parameterization of multiphase flow and transport problems are of critical importance to hydrologic modeling. Recently, a hypothesis has been developed that predicts a functional relationship between capillary pressure, saturation, and interfacial area. A network model was developed to test this hypothesis. Microscale physical processes were simulated and volume averaging was used to derive the macroscopic measures of saturation and fluid-fluid interfacial area per volume of porous media. Results indicate that a smooth, though complex, functional relationship exists at the continuum scale. These results have direct relevance to constitutive theory and the modeling of nonaqueous phase liquid dissolution processes.

Measuring Fluid-Fluid Interfacial Area

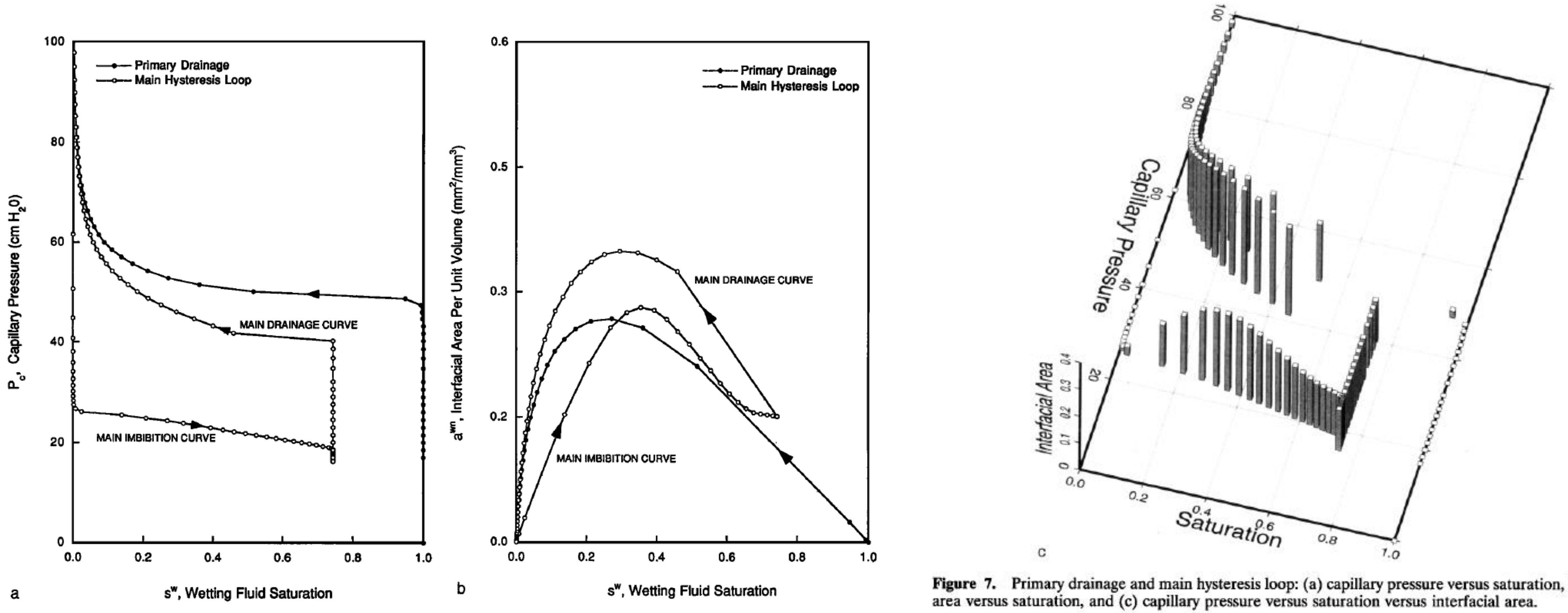


Figure 7. Primary drainage and main hysteresis loop: (a) capillary pressure versus saturation, (b) interfacial area versus saturation, and (c) capillary pressure versus saturation versus interfacial area.

Reeves & Celia (1996) WRR

Measuring Fluid-Fluid Interfacial Area

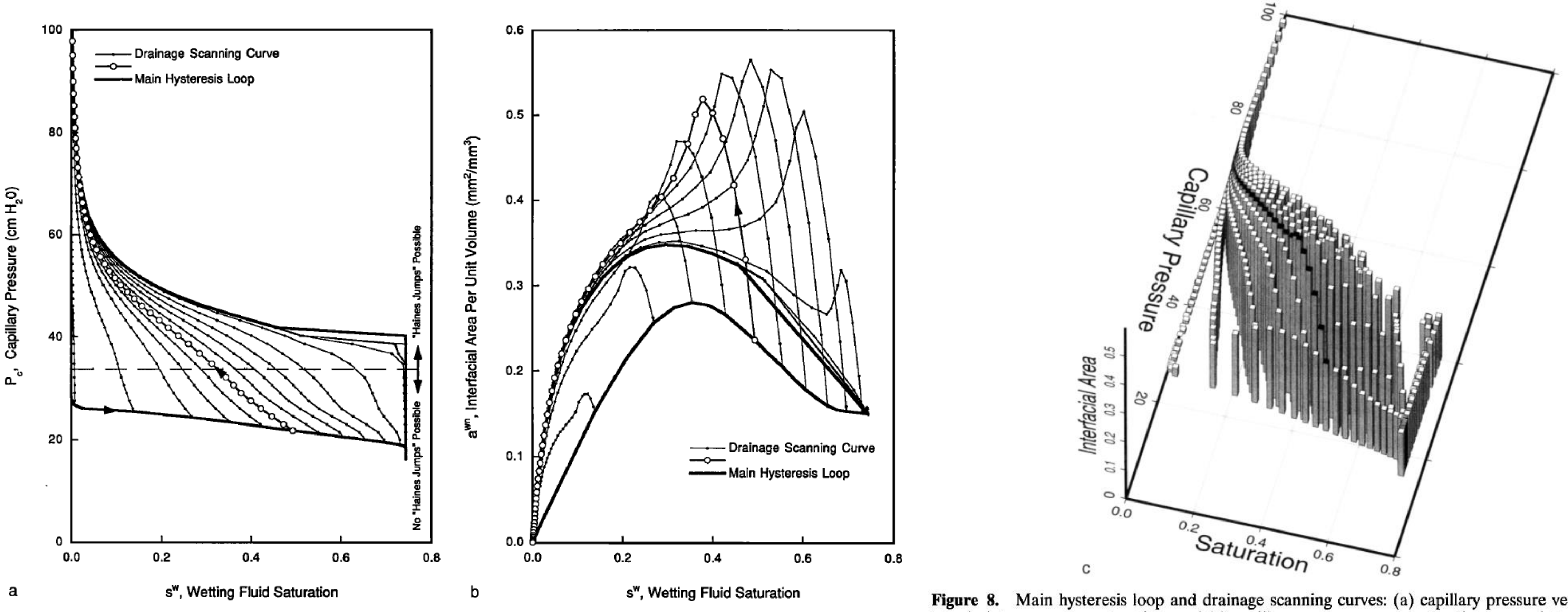


Figure 8. Main hysteresis loop and drainage scanning curves: (a) capillary pressure versus saturation, (b) interfacial area versus saturation, and (c) capillary pressure versus saturation versus interfacial area.

Reeves & Celia (1996) WRR