Nonwetting Liquid Intrusion Techniques

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OUTLINE

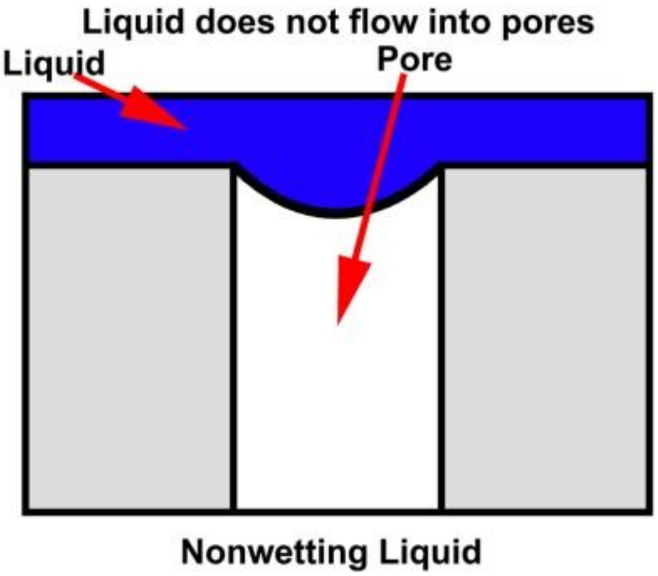
- Basic Principles
- Mercury Intrusion Porosimetry
- Water Intrusion Porosimetry (Aquapore)
- Advanced Water Intrusion Porosimetry (Vacuapore)
- Nonmercury Intrusion Porosimetry
- Comparison of Nonwetting Liquid Intrusion Techniques
- Conclusions

Nonwetting Liquid Intrusion Technique

BASIC PRINCIPLES

Definition of Nonwetting Liquid

Does not spontaneously flow in to pores



BASIC PRINCIPLES

Why are some liquids nonwetting?

ΔG (intrusion)

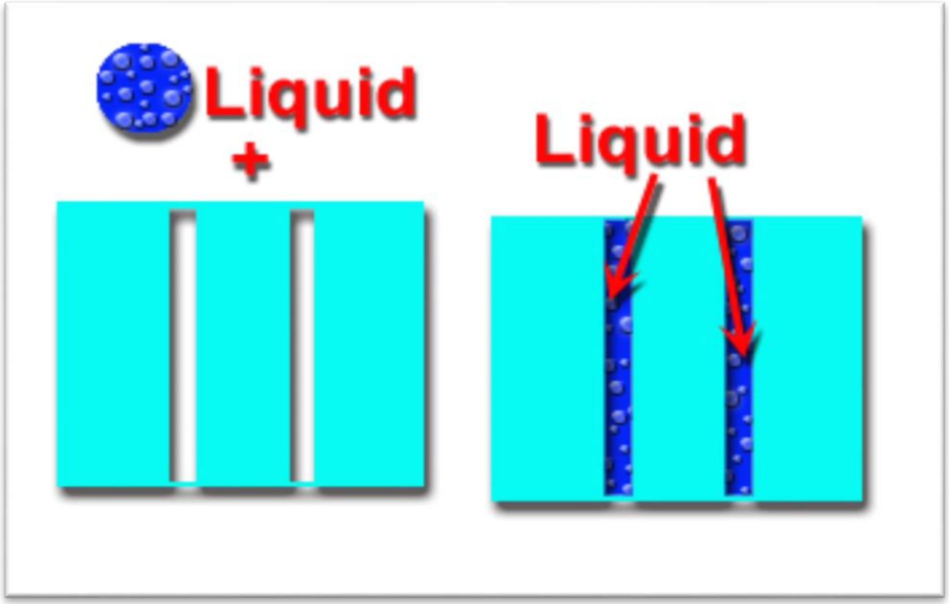
$$\Delta G = A\,(\gamma_{s/l} - \gamma_{s/g})$$

ΔG = change in the free energy of the system

A = Solid/gas area replaced by solid/liquid area

$\gamma_{s/l}$ = solid/liquid interfacial free energy

$\gamma_{s/g}$= solid/gas interfacial free energy



a. Porous material and liquid	**b. Porous material with liquid in pores.**

BASIC PRINCIPLES

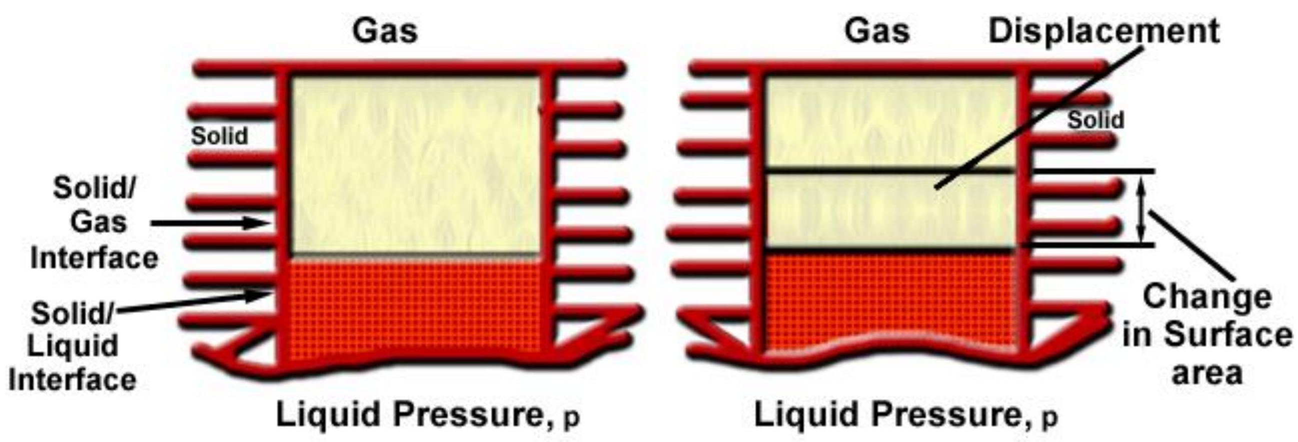
$\Delta G = A(\gamma_{s/l} - \gamma_{s/g})$ $\Delta G > 0$ $(\gamma_{s/l} > \gamma_{s/g})$

<u>For a nonwetting liquid:</u>

- Surface free energy of the liquid with solid
  > Surface free energy of solid with vapor
- Nonwetting liquid does not enter pores

BASIC PRINCIPLES

Intrusion of Nonwetting Liquid due to pressure

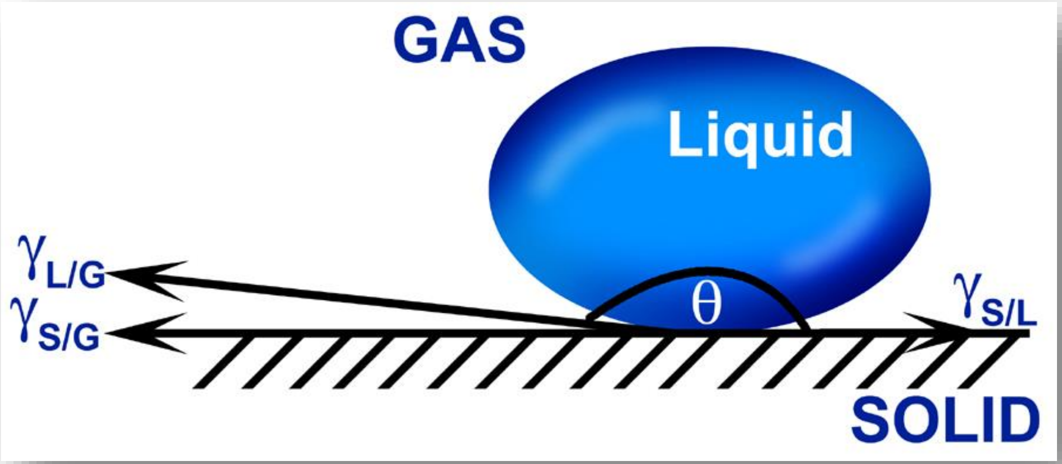


Displacement of gas by the liquid in the pore

BASIC PRINCIPLES

Intrusion of Nonwetting Liquid

Equilibrium between surface free energies associated with a nonwetting liquid



Equilibrium between surface tensions

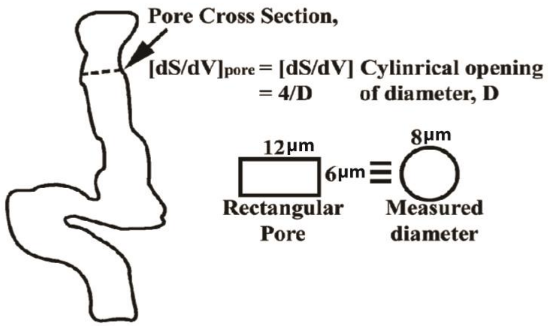
$$\theta > 90$$

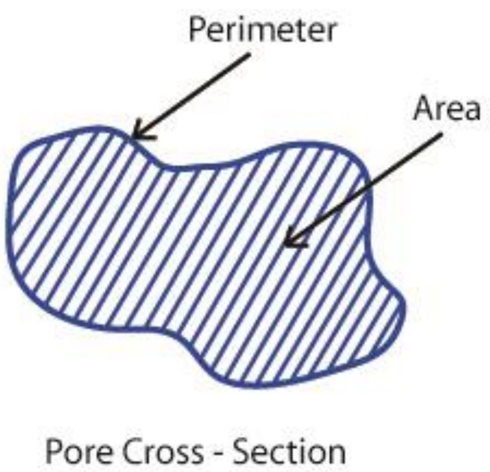
$$\gamma_{s/l} - \gamma_{s/g} + \gamma_{l/g} \cos\theta = 0$$

BASIC PRINCIPLES

Pore diameter, D

$$(dS/dV)_{pore} = (dS/dV)_{\text{circular opening of diameter, D}}$$
$$= 4/D$$





[dS /dV] = [Perimeter / Area]
(pore) (pore cross-section)

BASIC PRINCIPLES

- Intrusion pressure

$$(P - P_g) = -(4\,\gamma_{l/g} \cos\theta)/D$$

- Intrusion pressure yields pore diameter
- Intrusion volume yields pore volume

PMI Mercury Instrusion Porosimetry

Intrusion Pressure

Evacuated

$P_g = 0$

$$P = -(4\,\gamma_{l/g} \cos\theta)/D$$

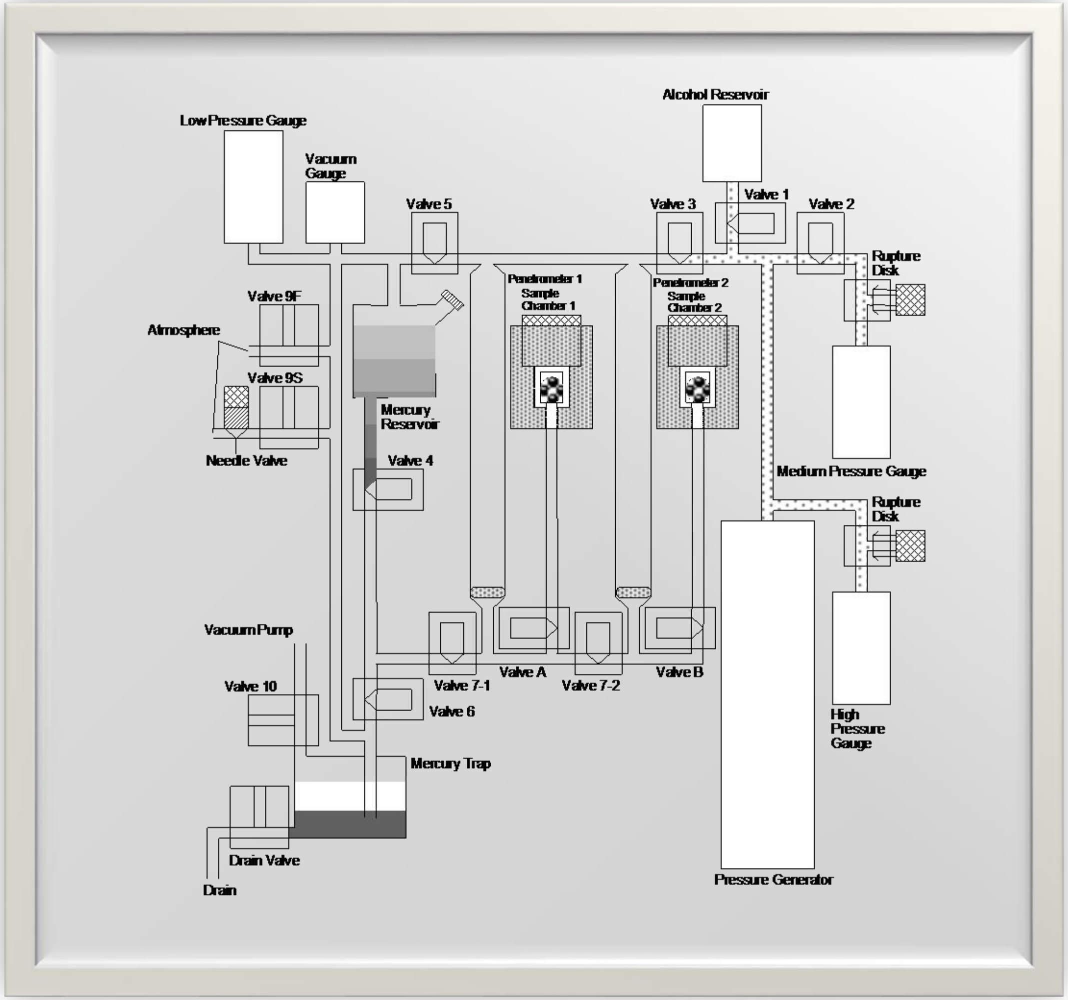
Intrusion Pressure on Mercury, P, psi	Gas Pressure in Pore, pg , 0.01 psi	Measurable Pore Diameters, µm
60,000	Negligible	0.003,6
30,000	Negligible	0.007,1
1,000	Negligible	0.213
100	Negligible	2.13
15	Negligible	14.2
10 (Sub-atmospheric)	Negligible	21.3
1	Negligible	213
0.5	Neglected (2%)	425

Difficult to control pressure below 1 psi

Mercury Instrusion Porosimetry

PMI Mercury Intrusion Porosimeter

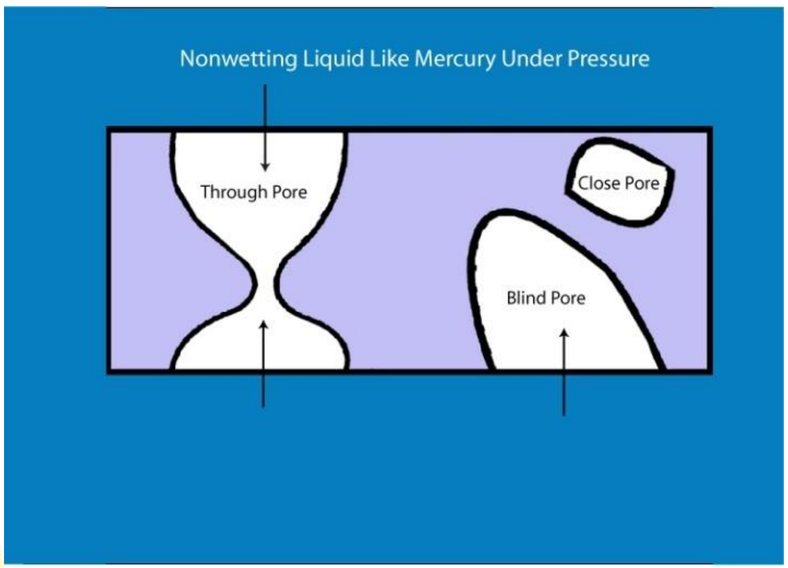
- Complex
- Stainless steel sample chamber
- Minimal Hg exposure

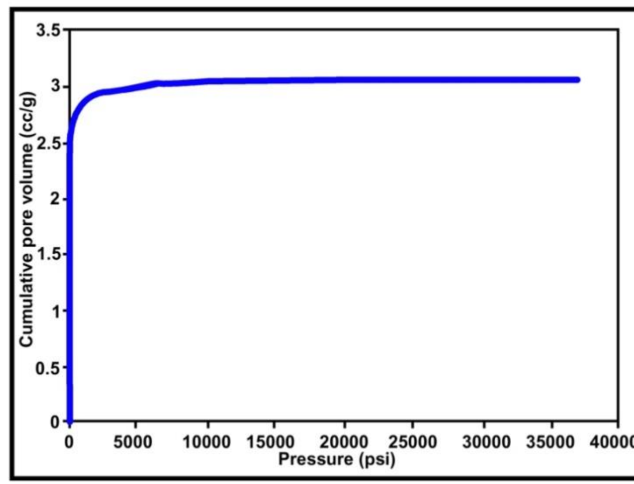


PMI Mercury Instrusion Porosimetry

THROUGH & BLIND PORE VOLUME

- Nonwetting liquid enters through and blind pores
- Through & blind pore volumes measured



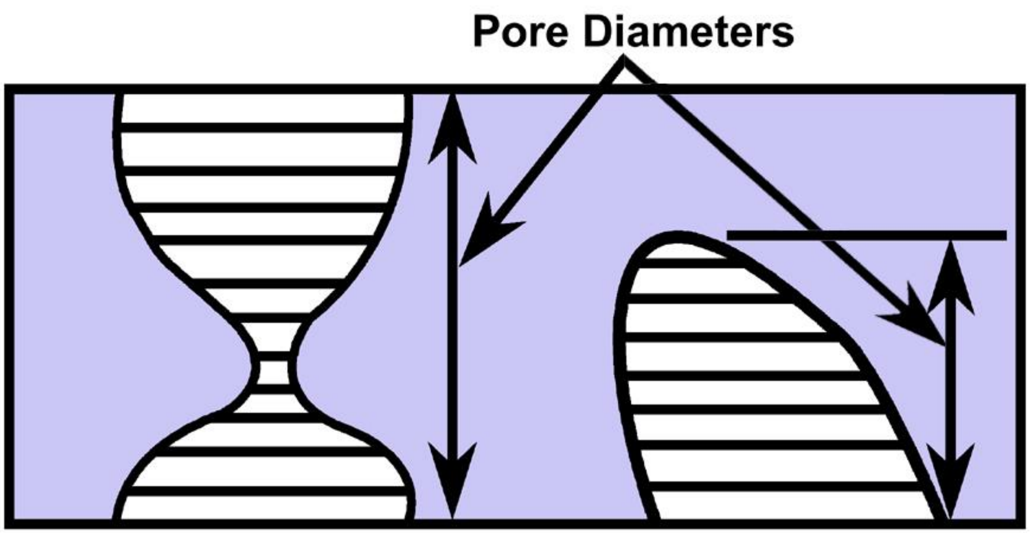


- With bulk or true density Yields porosity (percentage pore Volume)

PMI Mercury Instrusion Porosimetry

THROUGH & BLIND PORE DIAMETER

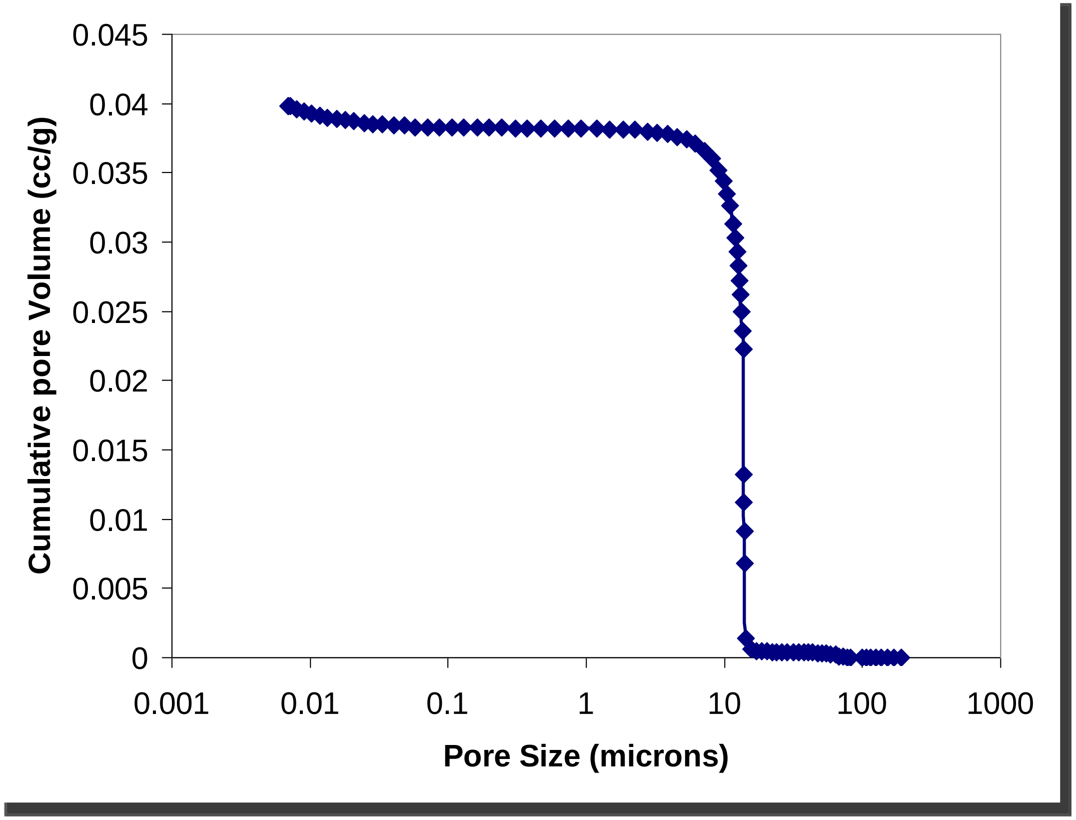
All pore diameters of through and blind pores computed from intrusion pressure



Measurable pore diameters

PMI Mercury Instrusion Porosimetry

VARIATION OF THROUGH & BLIND PORE VOLUME WITH DIAMETER



Typical variation of cumulative pore volume with pore diameter.

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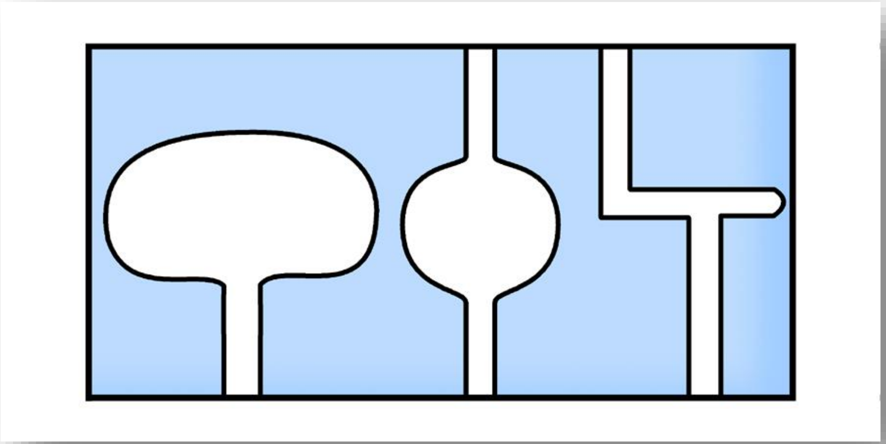
LIMITATIONS OF PORE DIAMETER

- Pores < 0.0035 mm not ensured because the pressure is limited to 60,000 psi.
- Pores > 500 µm not measurable because pressure is too low to be precisely detectable
- Certain pore diameters in complex pore configurations not measurable



PMI Mercury Instrusion Porosimetry

THROUGH & BLIND PORE VOLUME DISTRIBUTION

- Pore volume distribution function

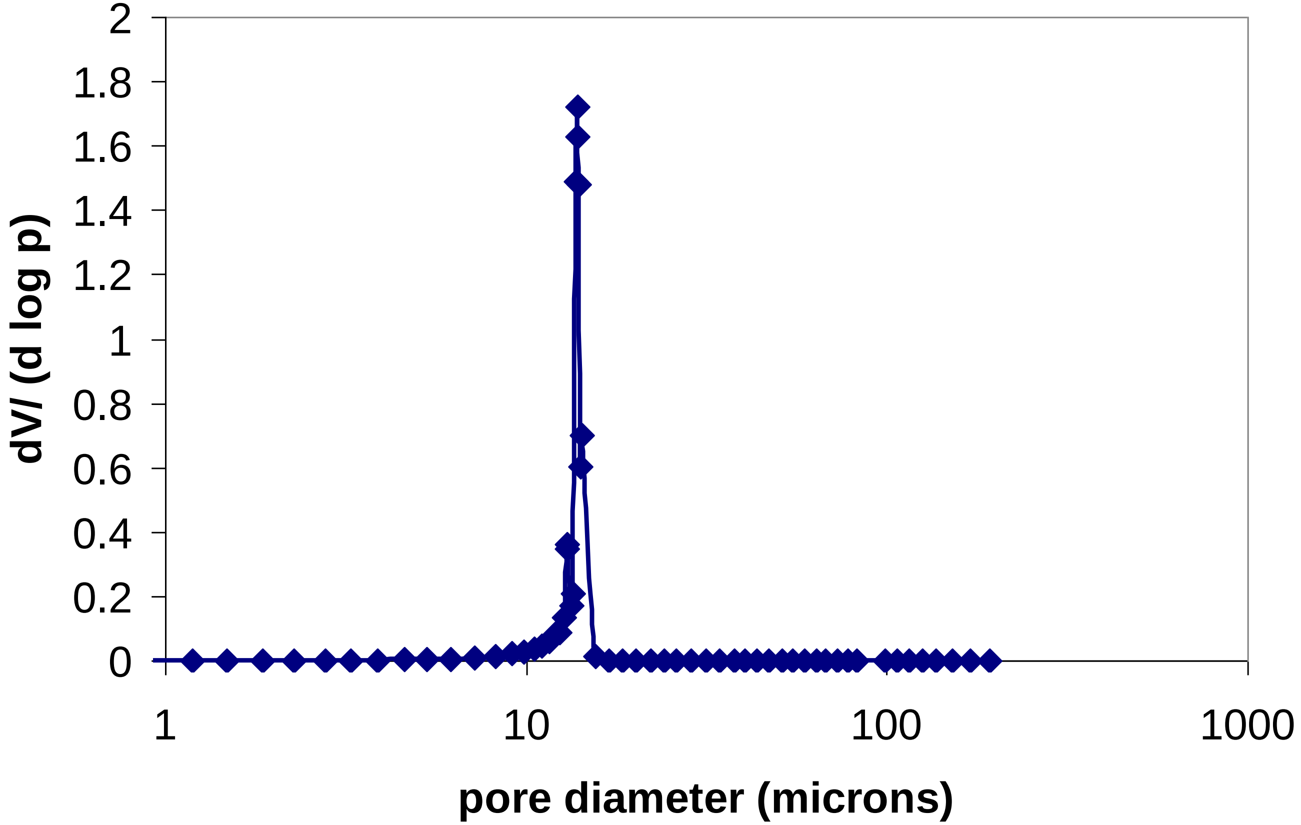
$$f_v(\log D) = -\frac{dV}{d\log D}$$

- Area under the curve yields pore volume

$$\int dV = -\int (f_v)\, d\log D$$

PMI Mercury Instrusion Porosimetry

THROUGH & BLIND PORE VOLUME DISTRIBUTION



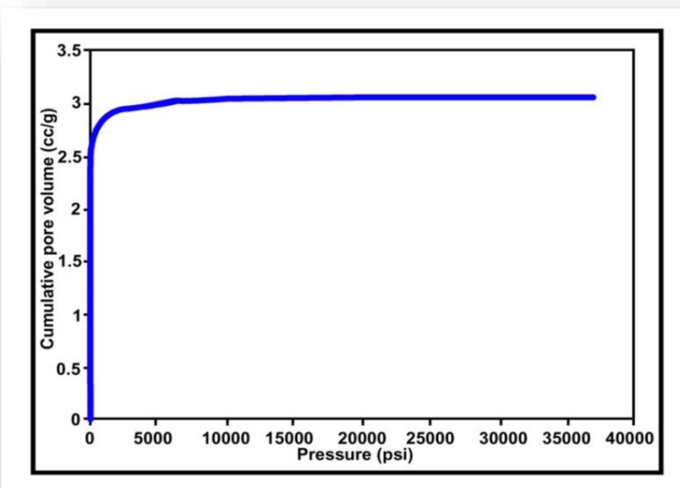
PMI Mercury Instrusion Porosimetry

THROUGH & BLIND PORE SURFACE AREA

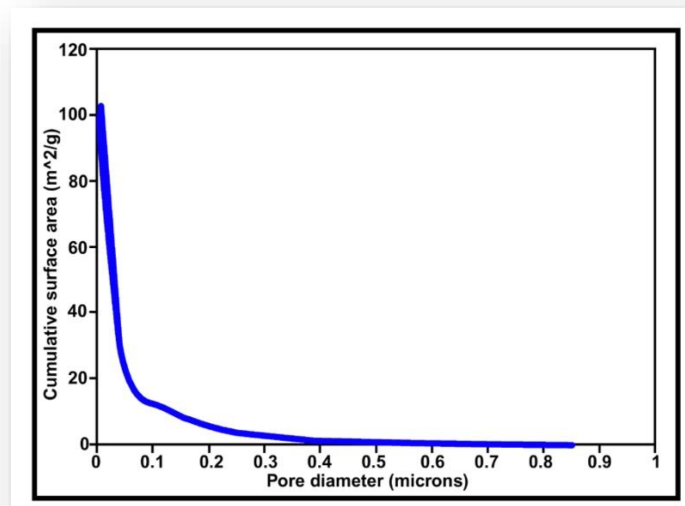
Integration of the basic relation,

$p = (-\gamma_{l/g} \cos \theta)(dS/dV)$:

$$\int dS = \left[\frac{1}{-\gamma_{l/g} \cdot \cos\theta}\right] \int P\, dV$$



Intrusion Volume and Pressure

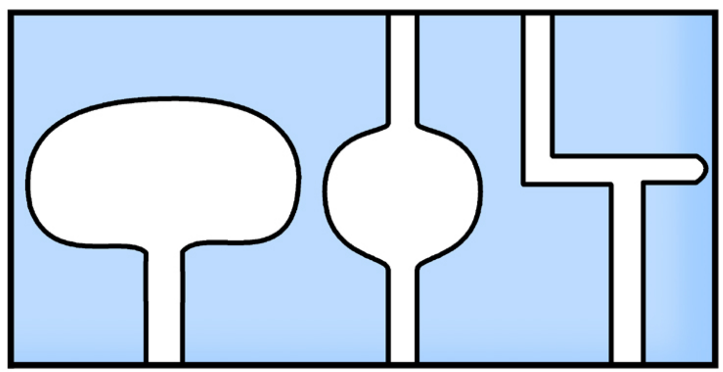


Cumulative Surface Area

PMI Mercury Instrusion Porosimetry

SURFACE AREA –LIMITATIONS: NOT PRECISE

- Small pores need high pressures & large corrections due to compressibility
- Integration over volume of small pores not precise
- Small pores, large contribution to surface area, more error



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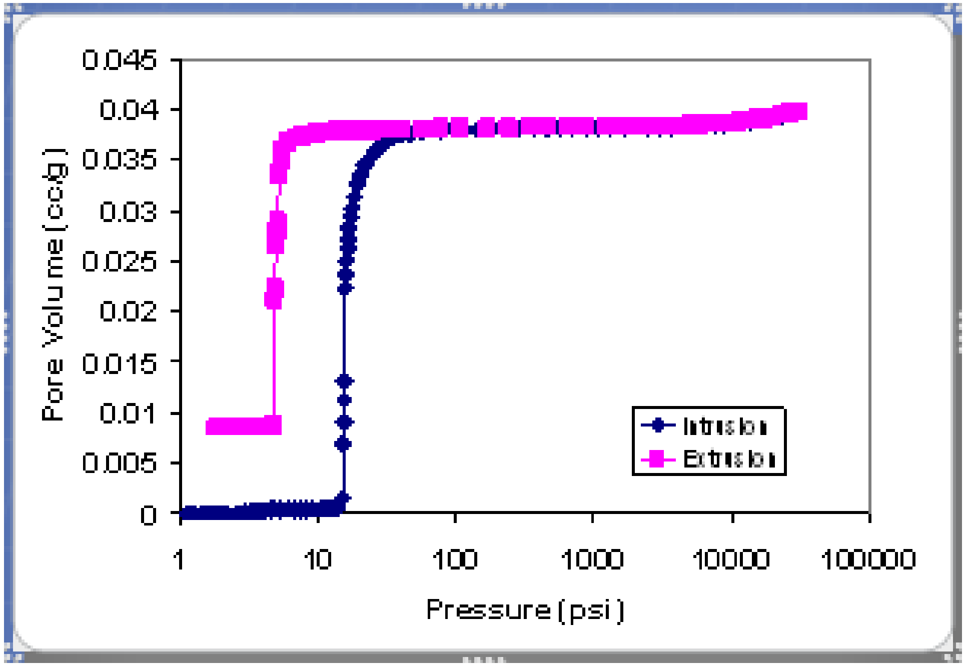
EXTRUSION VOLUME AND HYSTERESIS



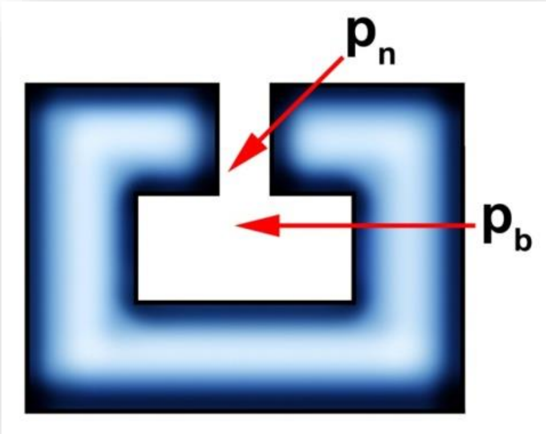
Hysteresis in the intrusion-extrusion cycle

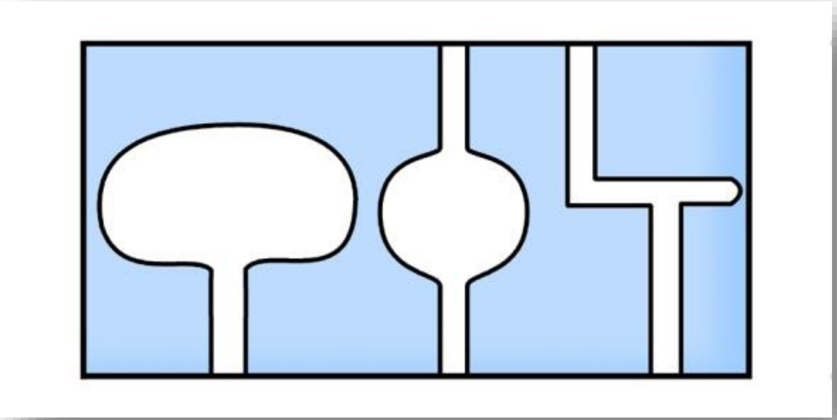
Intrusion-extrusion loop does not close and some liquid is trapped in the sample.

PMI Mercury Instrusion Porosimetry

POSSIBLE REASON FOR HYSTERESIS

- Not fully understood
- Inkbottle effect
- Other complex pore configurations
- The different receding contact angle





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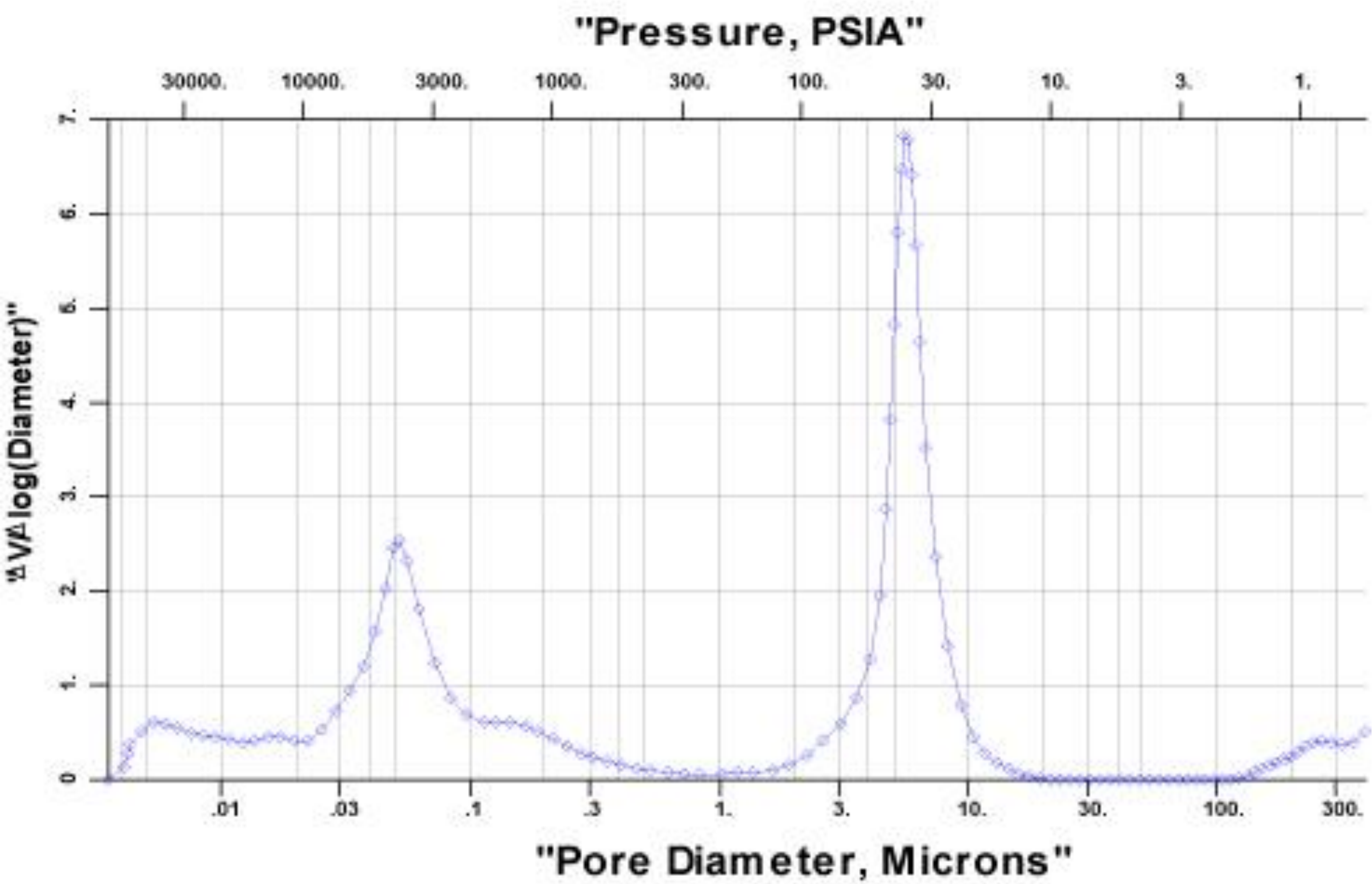
PARTICLE SIZE OF POWDERS

Two peaks



PMI Mercury Instrusion Porosimetry

APPLICATIONS

Wide range of materials can be tested

Examples: Rock, textiles, ceramics, polymeric materials, food, pharmaceutical products

Water Instrusion Porosimetry

THE PMI AQUAPORE

- Water nonwetting to
  hydrophobic materials
- No evacuation
- Water directly pressurized
- No toxic material
- Simple inexpensive instrument

Water Instrusion Porosimetry

INTRUSION PRESSURE IN AQUAPORE

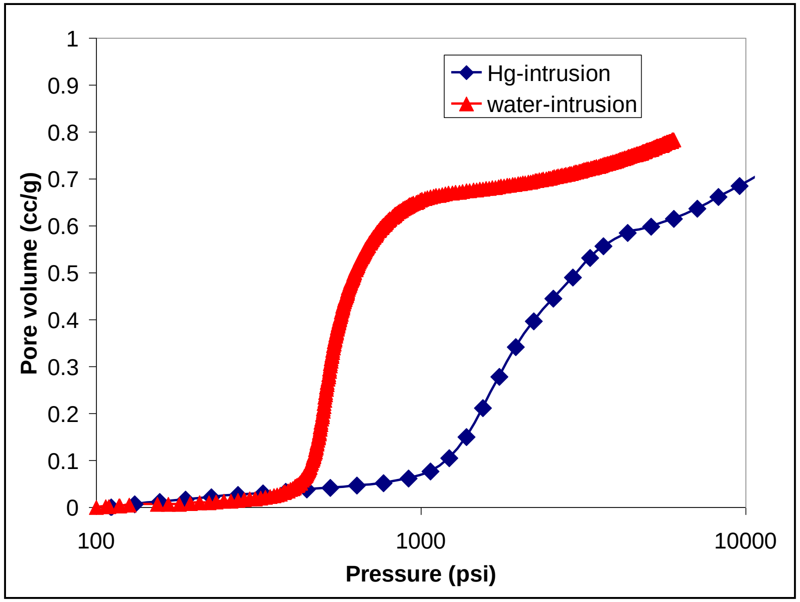
$(P - P_g) = -(4\,\gamma_{l/g} \cos\theta) / D$, P_g = atmospheric pressure

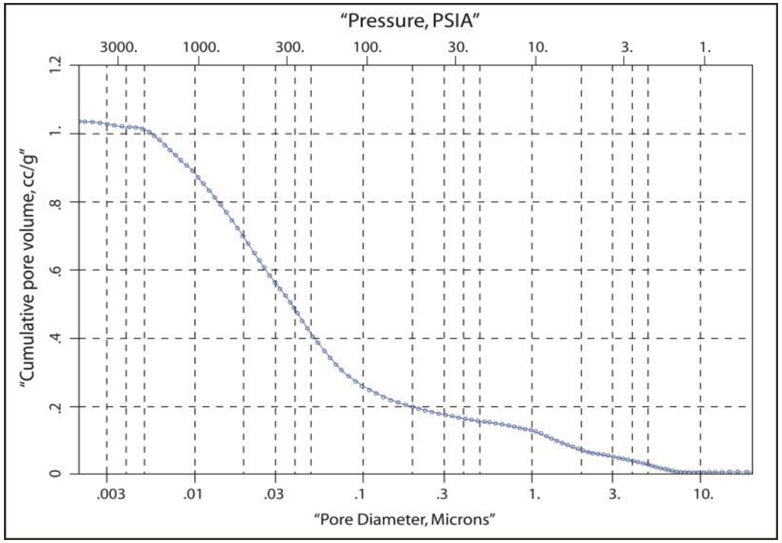
Intrusion Pressure on Water, P, psi	Differential Pressure (P-Pg) psi	Error in pore volume # Due to 1 Atm. Gas pressure in pore (Pg)	Computed Pore Diameter µm
20,014.7	20,000	Negligible	0.001
10,014.7	10,000	Negligible	0.002
5,014.7	5,000	Negligible	0.004
2,014.7	2,000	Negligible	0.010
1,014.7	1,000	Negligible	0.021
114.7	100	13%	0.209
24.7	10	60%	2.09
15.7	1	94%	20.9

Volume occupied by trapped air & measured at higher pressures as the volume of smaller pores

The PMI Aquapore

Through and Blind Pore Volume

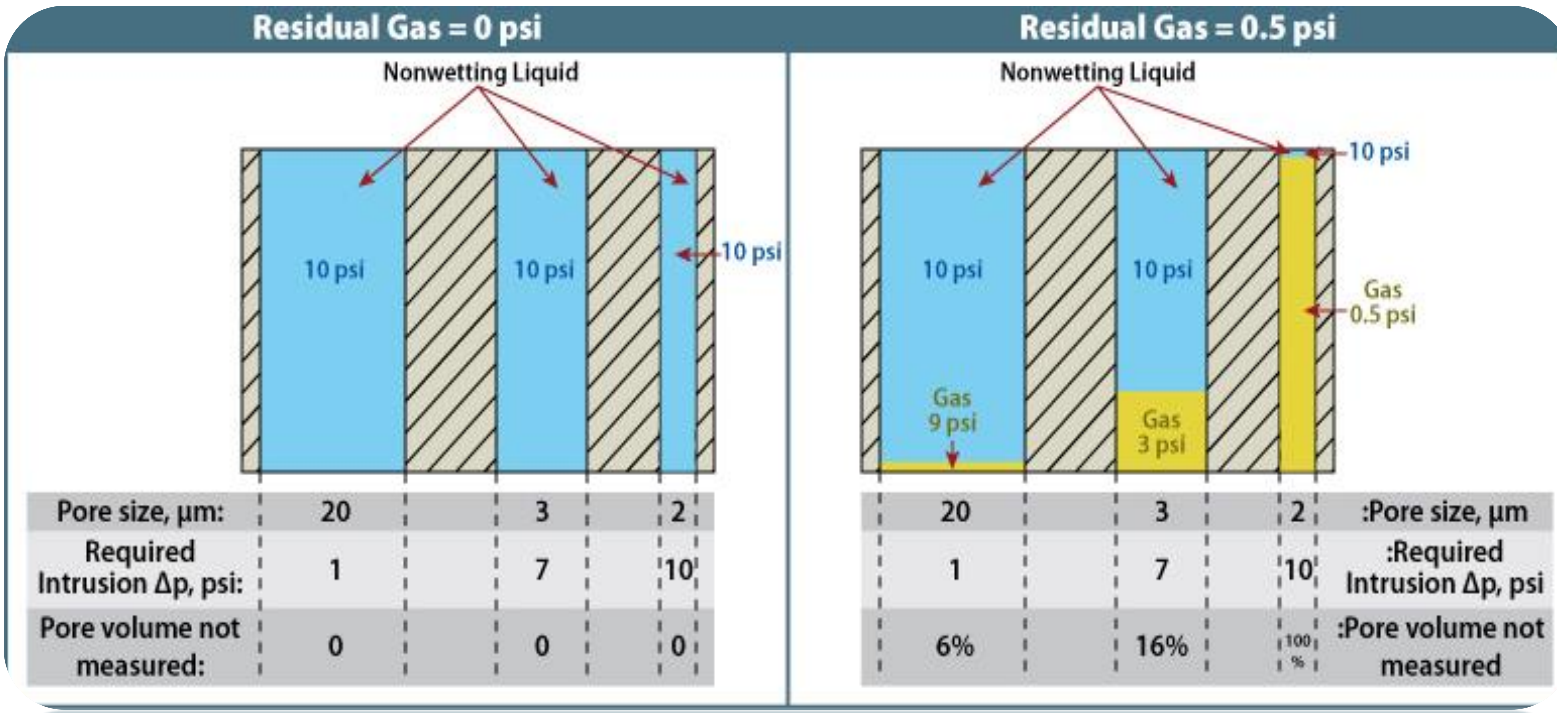




Water Instrusion Porosimetry

INFLUENCE OF RESIDUAL PRESSURE

$$(P - P_g) = -(4\,\gamma_{l/g} \cos\theta) / D,\ P_g = \text{atmospheric pressure}$$



Water Instrusion Porosimetry

INFLUENCE OF RESIDUAL PRESSURE

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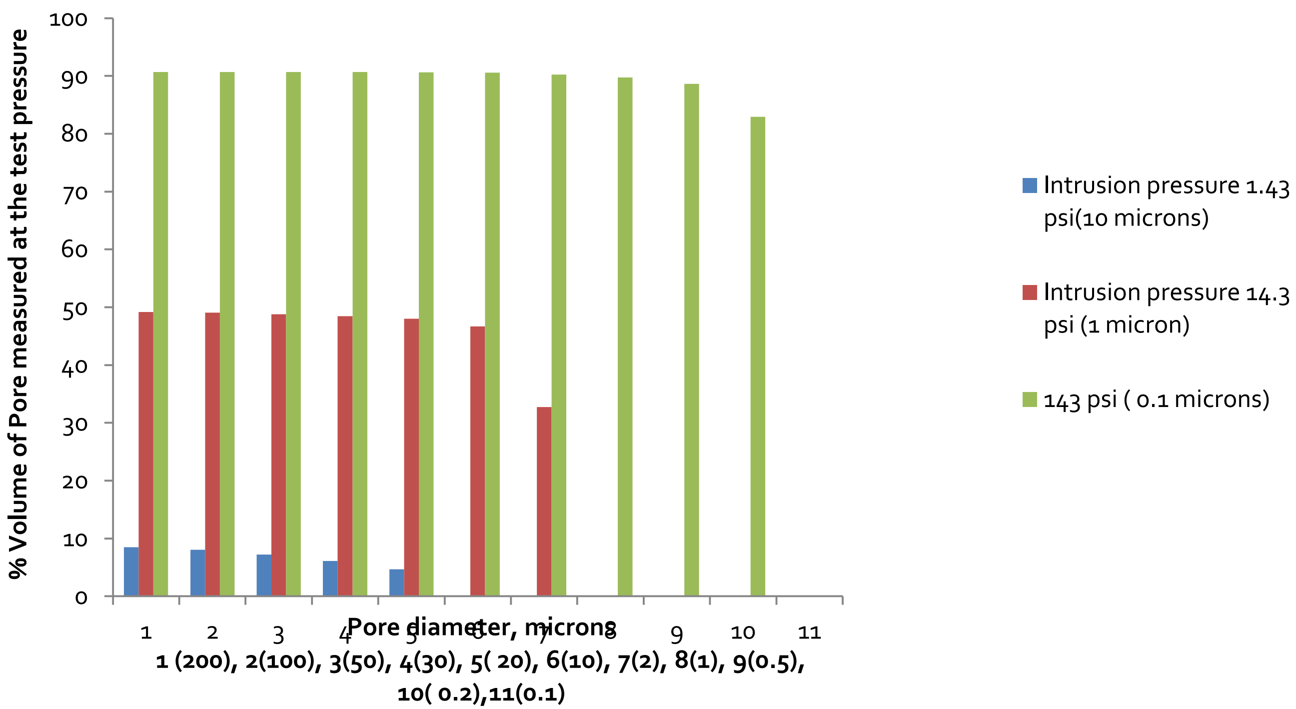
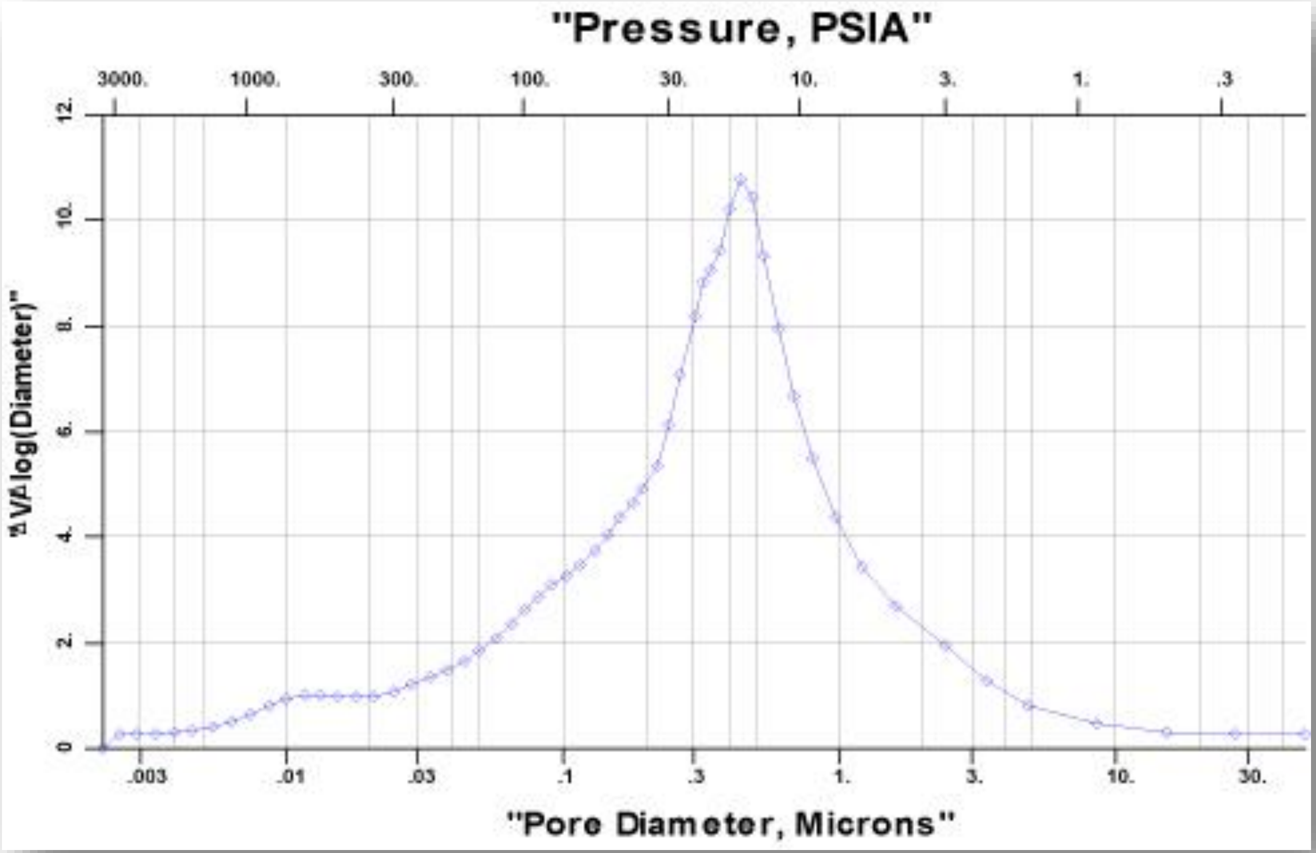


The PMI Aquapore

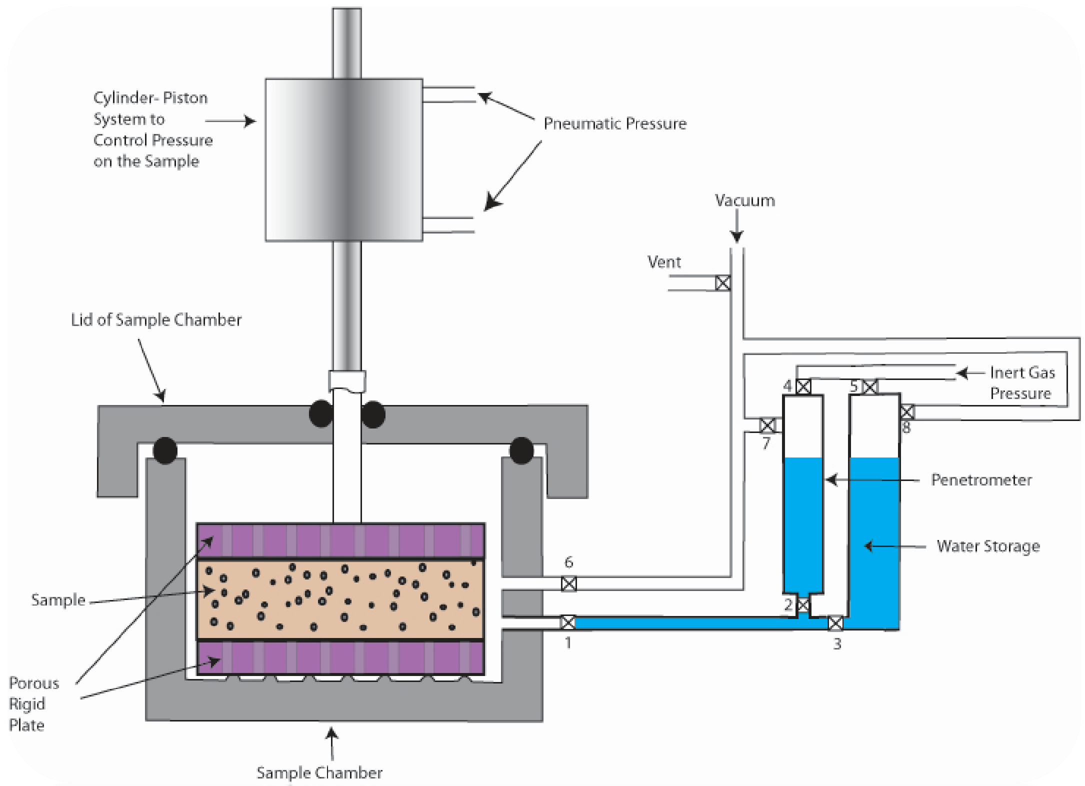
Through and Blind Pore Volume Distribution



Advanced Water Intrusion Compression Porosimeter

THE PMI VACUAPORE

- Evacuation of Sample, Sample Chamber, Water
- Sample under compressive stress
- Option for In-Plane intrusion



The PMI Vacuapore

INTRUSION PRESSURE

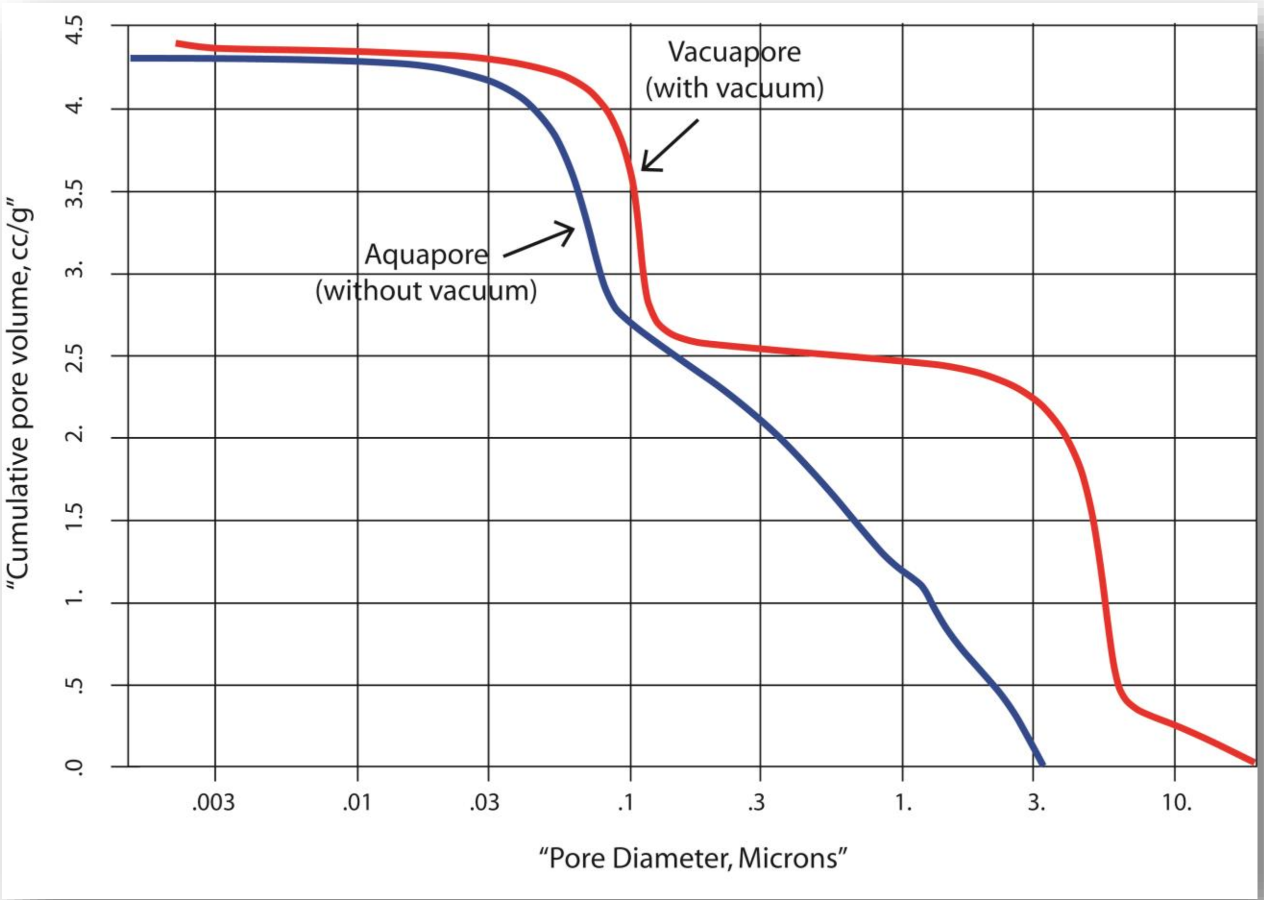
Intrusion Pressure on Water, psi	Gas Pressure (0.3 psi) in Pore(P_g) relative to intrusion pressure, psi	Pore diameter Computed neglecting P_g, µm
20,000	Negligible	0.001
10,000	Negligible	0.002
5,000	Negligible	0.004
2,000	Negligible	0.010
1,000	Negligible	0.021
100	Negligible	0.209
10	Negligible	2.088
5	Negligible	4.1276
1	< 30 % *	20.877

***Expected to be much less than 30 % because of evacuation & small test duration**

The PMI Vacuapore

MEASURABLE CHARACTERISTICS

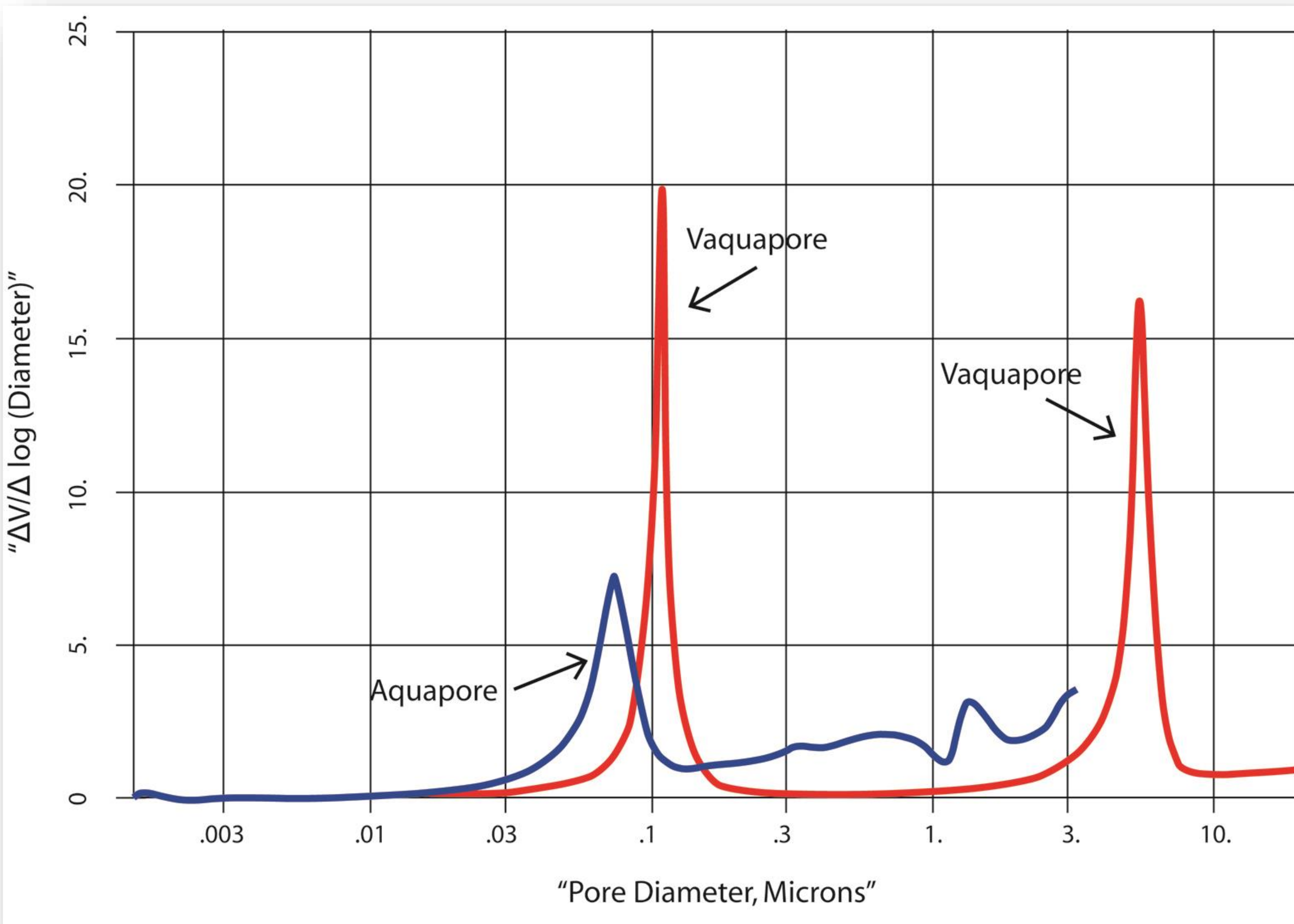
Through & blind pore volume & diameter



The PMI Vacuapore

MEASURABLE CHARACTERISTICS

Through & blind pore volume distribution



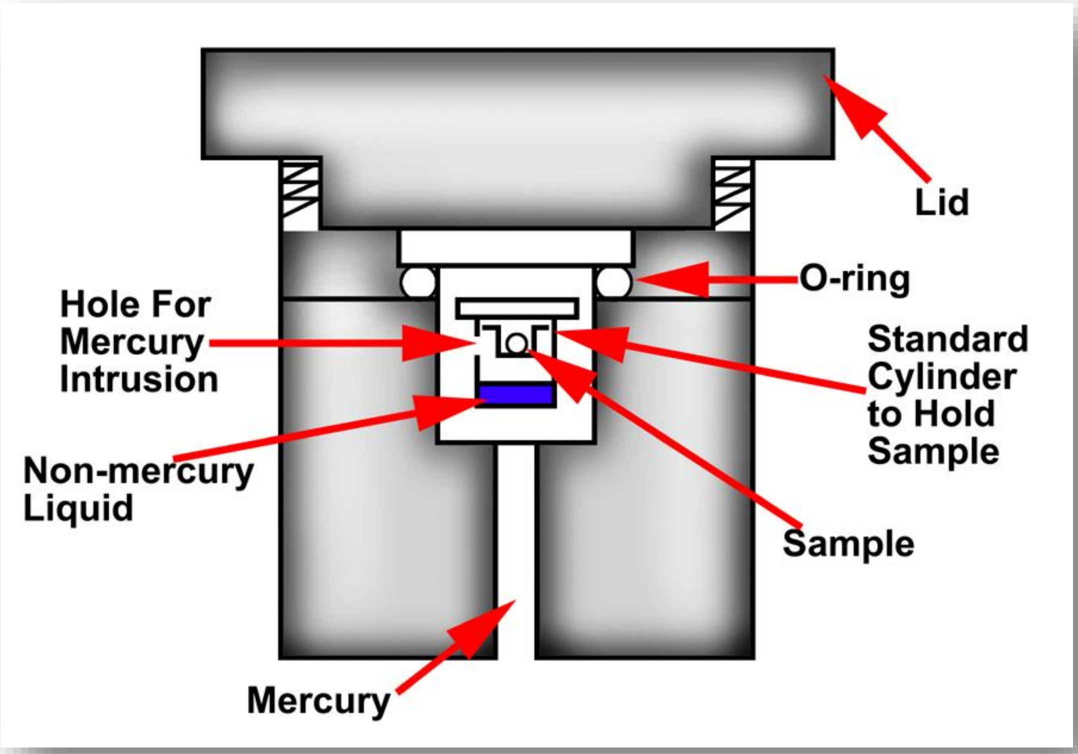
Nonmercury Intrusion Porosimetry

PMI Nonmercury Intrusion Porosimeter can perform Mercury intrusion & nonmercury intrusion

- **Mercury pressurizes the nonwetting liquid**
- **Nonwetting liquids like water and mineral oil have been used**
- **Application liquid is used in the test**
- **Chamber is evacuated**
- **Pressures are usually very low**

Nonmercury Intrusion Porosimetry

Any nonwetting liquid lighter than mercury can be used

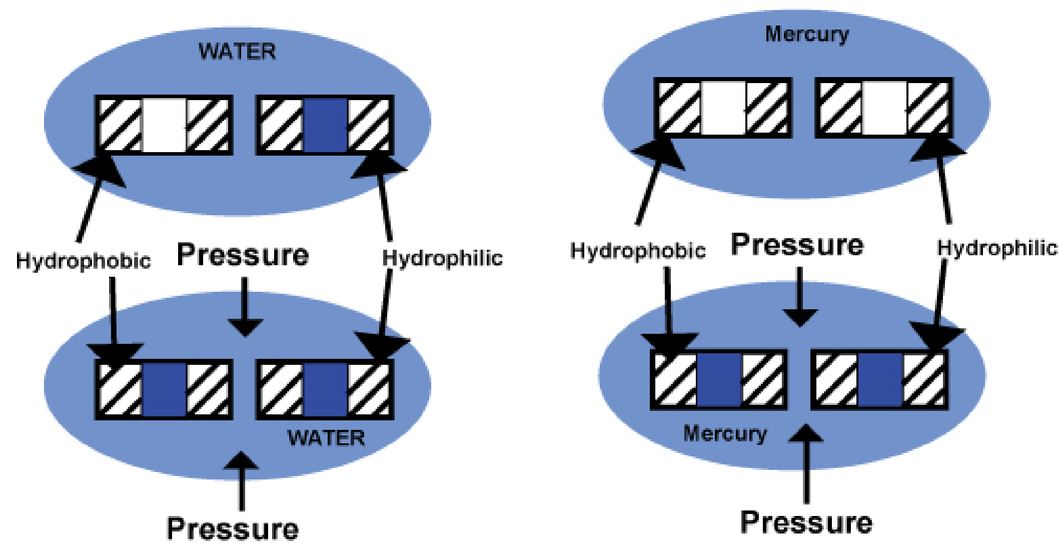


Sample chamber with cell and wetting liquid for nonmercury intrusion porosimetry

Application

Pore Structure of Hydrophobic Pores in a Mixture of Hydrophobic and Hydrophilic Pores

Both Water and Mercury intrusion used



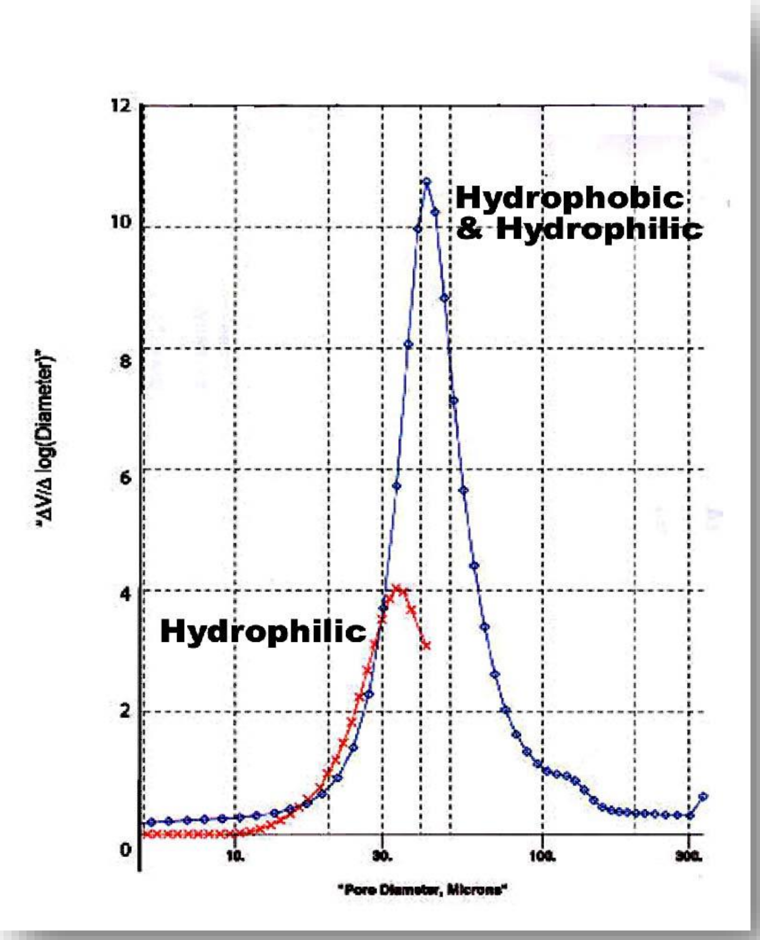
Application

Pore Structure of Hydrophobic Pores in a Mixture of Hydrophobic and Hydrophilic Pores

Characteristics	Hydrophobic Pores	Hydrophilic Pores
Volume cm^3/g	1.05	2.61
% by Volume	28.7	71.3
Distribution peak, µm	33	40
Diameter, µm	20-40	30-100

Application

Pore Structure of Hydrophobic Pores in a Mixture of Hydrophobic and Hydrophilic Pores



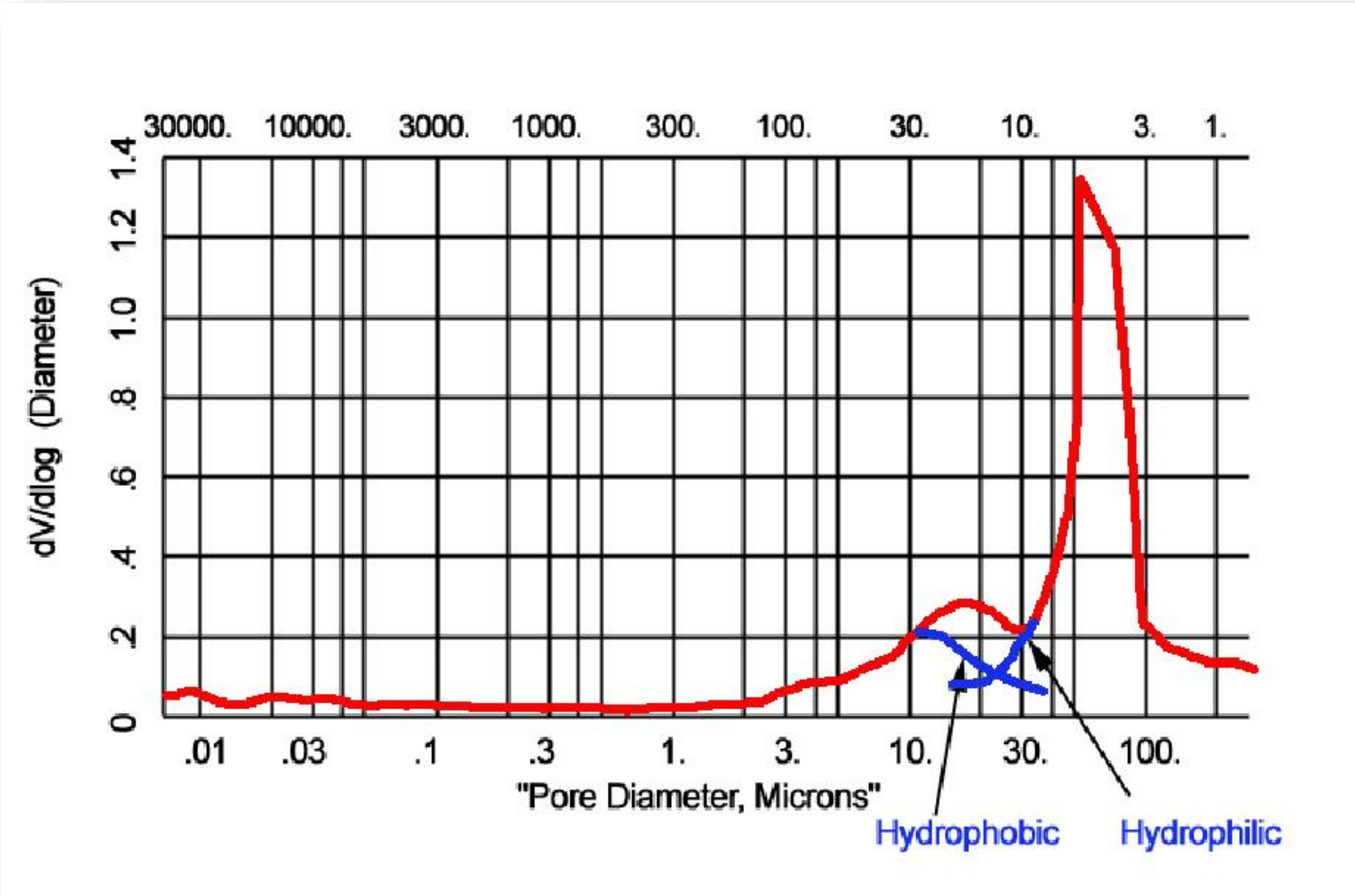
Application

Pore Structure of Hydrophobic Pores in another Mixture of Hydrophobic and Hydrophilic Pores

Pore Structure Characteristics	Hydrophobic	Hydrophilic
Volume, cc/g	0.116 (17.8%)	0.536 (82.2%)
Pore size with maximum contribution to volume, µm	9.175	60
Range of pore volume distribution peak, µm	3-20	20-150

Application

Pore Structure of Hydrophobic Pores in another Mixture of Hydrophobic and Hydrophilic Pores



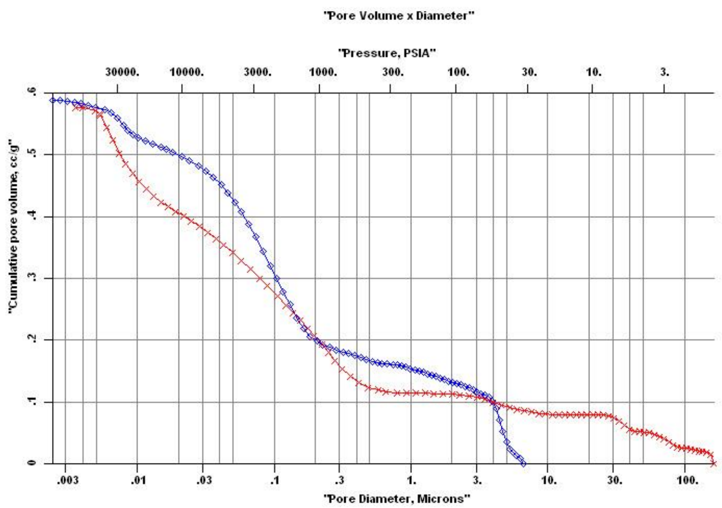
Comparison of Nonwetting Liquid Intrusion Techniques

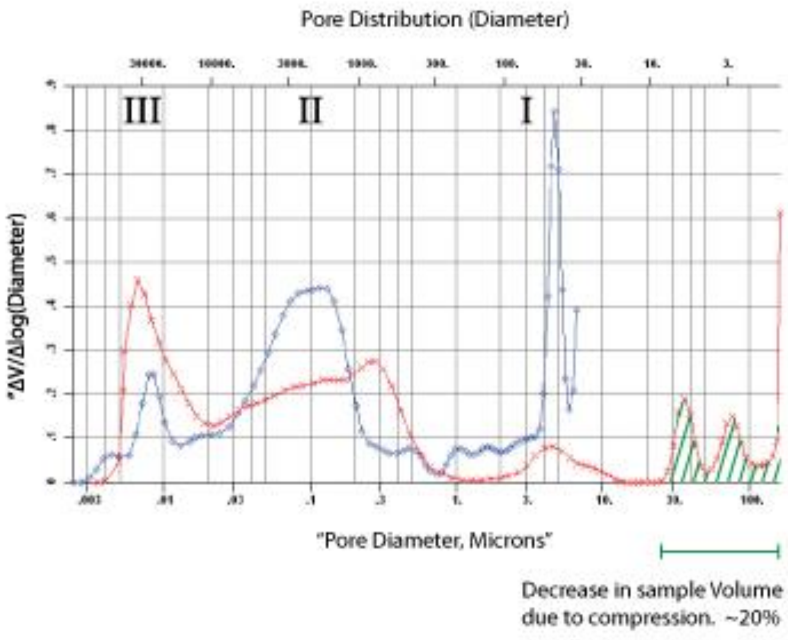
Features	Vaquapore	Aquapore	Nonmercury Porosimetry	Mercury Porosimetry
		STRENGTHS		
Sample under Compression	√	×	×	×
Only Hydrophobic Pores	√	√	√	×
Use of Application Liquid	√	√	√	×
Simple Inexpensive Instrument	×	√	×	×
Suitable for a Wide Variety of Materials	×	×	×	√
Accurately Measurable Pore Diameter	20 – 0.001	0.2 – 0.001	50 – 0.001	200 – 0.0035
		LIMITATIONS		
High Intrusion Pressure	×	×	×	√
Use of Toxic Material	×	×	×	√
Involved Instrument	√	×	√	√
Sample Not Reusable	×	×	×	√

COMPARISON BETWEEN MERCURY INTRUSION AND WATER INTRUSION

Fuel Cell Component Tested by WIP & MIP

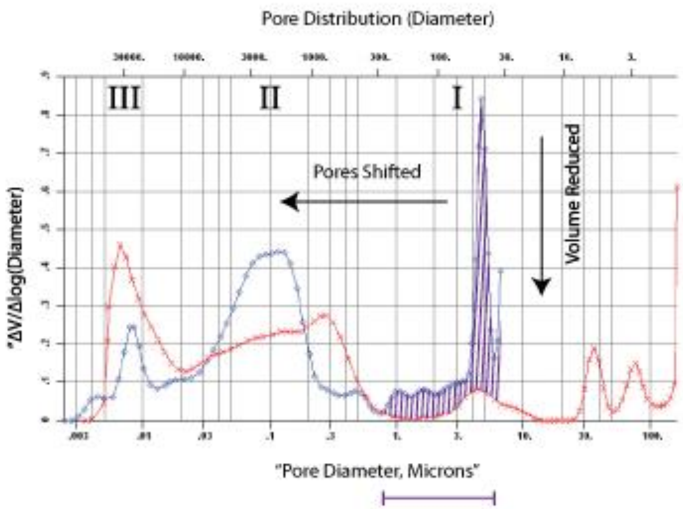
- The same pore volume by both methods indicates 100% hydrophobic pores
- Greater pressure in MIP compresses the sample, reduces the pore sizes & volume, shifts peaks
- Decrease in sample volume appears as pore volume at lower pressures (larger pore sizes)

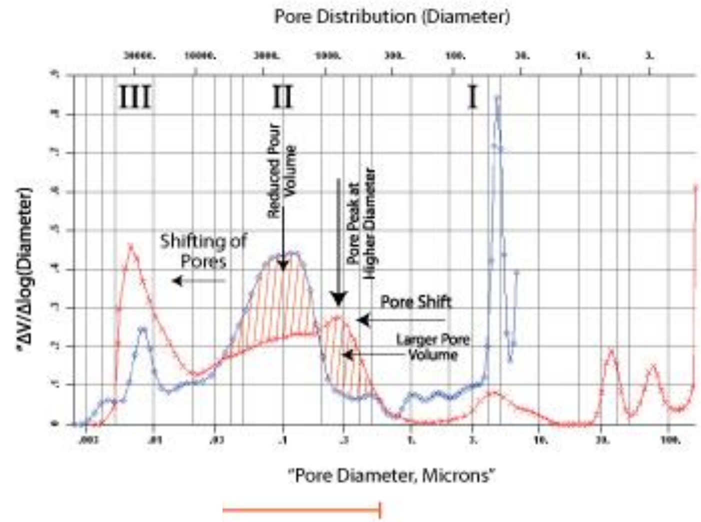


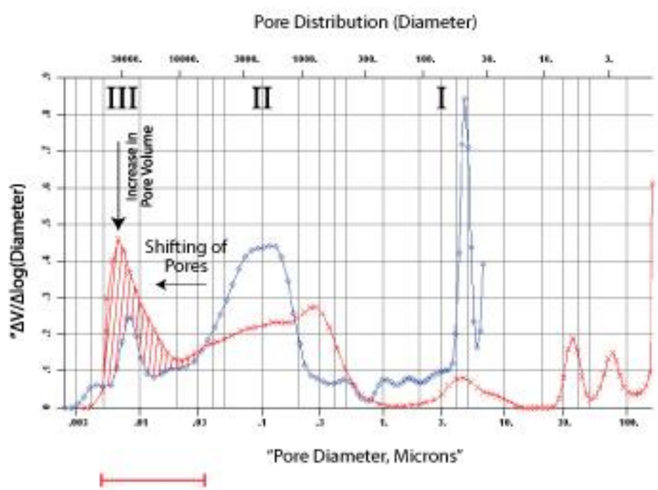


COMPARISON BETWEEN MERCURY INTRUSION AND WATER INTRUSION

- Distribution peaks volume reduced & peak position shifted to lower pore sizes







Summary and Conclusion

We Have Discussed:

- Principles of nonwetting liquid intrusion techniques
- The mercury intrusion technique and its applications
- Unique applications of Aquapore
- The novel technique Vacuapore
- The strengths and limitations of the techniques

Thank You!

PMI

POROSITY & PERMEABILITY TESTING