SCA2003-52: INTERPRETATION OF MERCURY INJECTION CURVES TO DERIVE PORE SIZE DISTRIBUTION

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ABSTRACT

Mercury porosimetry is often used to characterize the pore (throat) size distribution of porous material and many recent papers show comparison with NMR measurements. However, the way of deriving the pore size distribution is rarely presented and very often, there is no dimension on the Y axis. In fact, most of the authors use the raw data provided by the equipment in terms of incremental saturation vs. incremental pressure. This presentation is misleading since the resulting curve has no physical meaning and depends on the number and spacing of the increments (error also recognized by the American Society for Testing and Materials).

The right procedure consists in fitting and smoothing the experimental data using an analytical function (splines for instance) in order to calculate the derivative. The real pore size distribution (psd), with a dimension of the inverse of a length, is then derived from standard calculation that can be found in any textbook. However, this calculation gives a very high weight for the small pores (presence of the square of the pressure in the formula). This calculation can be useful to derive the fractal dimension of the roughness of the medium but is not very suitable to capture double porosity or determine the average pore size. The logarithmic derivative of saturation versus pressure gives the more useful results concerning pore geometry. This function is also close to the standard increment presentation when increments are equidistant in log scale.

INTRODUCTION

Mercury porosimetry is often used to characterize the pore size distribution of porous materials and many recent papers show comparison with NMR measurements or image Analysis. However, the way of deriving the pore size distribution is rarely presented and, very often, a general term of "amplitude" is used without any precision of dimension [1,2]. In fact, most of the authors use the raw data provided by the equipment in terms of incremental saturation vs. incremental pressure [3,4].

In this paper, I will re-examine the standard definition of pore size distribution in a porous medium (psd) and show how the presentation in terms of incremental saturation may be misleading since the resulting curve has no physical meaning and depends on the number and spacing of the increments.

BACKGROUND

The definition of a pore size distribution $f(r)$ and its calculation from a capillary pressure curve can be found in any textbook [5 for instance]. The pore size distribution is based on an analysis of pore volumes: $f(r)dr$ is the probability to find pores with radius between r and $r+dr$. It is well known that mercury injection does not lead to the true pore volume but to the volume controlled by the thresholds of size r [6]. During a pressure step of mercury invasion, pressure is increased from P to $P+dP$. The corresponding radius of thresholds varies from r to $r+dr$ and radius is related to pressure by the standard Laplace's law, where g is the surface tension and q the contact angle.

$$P = \frac{2\gamma \cos\theta}{r} \tag{1}$$

with the derivative

$$dP = -\frac{2\gamma \cos\theta}{r^2} dr \tag{2}$$

During this step, the injected volume is

$$dV = -V_p f(r) dr \tag{3}$$

where V_p is the total pore volume. The negative sign comes from the relationship between pressure and radius: when the pressure is increased, the corresponding radius decreases. The previous equation is rewritten using the standard definition of saturation S in mercury:

$$dS = -f(r) dr \tag{4}$$

and consequently

$$f(r) = -\frac{dS}{dr} \tag{5}$$

Using the relationship between pressure and radius, equ. (1) and (2), leads to the pore size distribution (psd) as function of the measured parameters, pressure and saturation.

$$f(r) = \frac{P^2}{2\gamma Cos\theta} \frac{dS}{dP} \tag{6}$$

By definition, $f(r)$ is a probability distribution and its integral over all the range of radius (and corresponding pressure) is unity. The dimension of $f(r)$ is the inverse of a length.

$$\int_{\infty}^{0} f(r) dr \quad = \int_{0}^{1} dS = 1 \tag{7}$$

RESULTS

The more accurate way to calculate a derivative is to smooth the experimental data with an analytical function and then analytically calculate the derivative. I used a standard mathematical package of curve fitting by splines functions which are the more suitable for this kind of curves. I recall that splines method fits the curve by a polynomial inside a given interval limited by two knots. Using splines of third degree with about 20 knots leads to a good approximation of the experimental curve but removes the high frequency noise due to experimental uncertainties (Figure 2). The coefficient of the polynomial are adjusted in order to assure continuity and continuity of derivatives at the knots

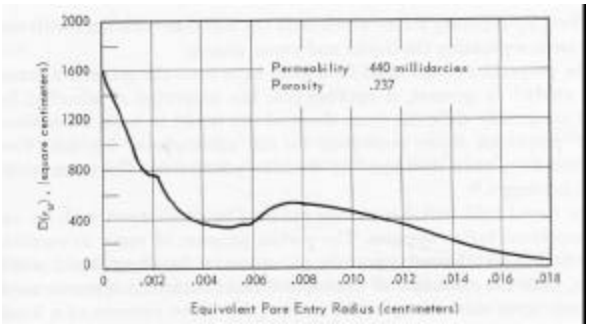

Figure 1 Pore size distribution (after [5]). On this curve, the Y axis is the diameter probability distribution, with the distribution being defined with respect to volume instead of saturation.

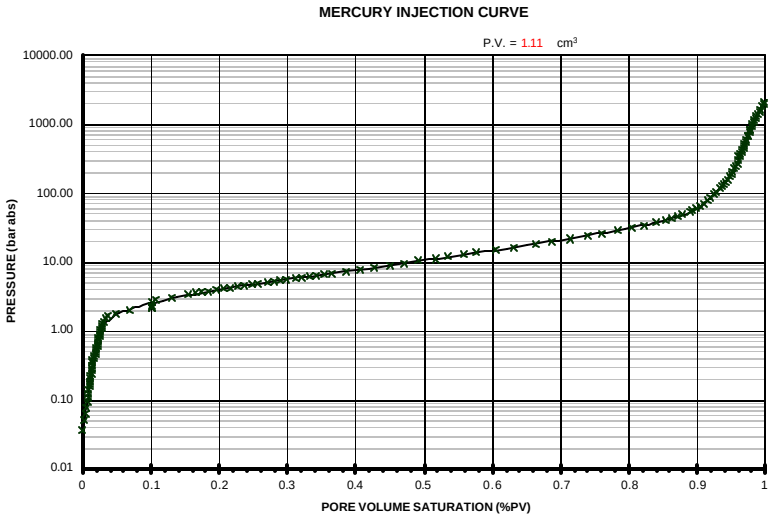

Figure 2 Experimental pressure (points) and fit by a spline (solid line).

The pore size distribution is calculated using equation (6) and the result (Figure 3) is in agreement with the curve presented by Collins (Figure 1).

DISCUSSION

The probability distribution function shows a very large contribution for low values of radius corresponding to high pressures. That is due to the factor P^2 in the formula. This curves can be useful to characterize the structure of the roughness of the solid walls of the medium. For instance, this curve can be used to derive a fractal dimension by fitting with a power law. However, this function is not adequate for estimating a mean pore radius or to found a double porosity. This is why a display of saturation increments is generally used to present the results.

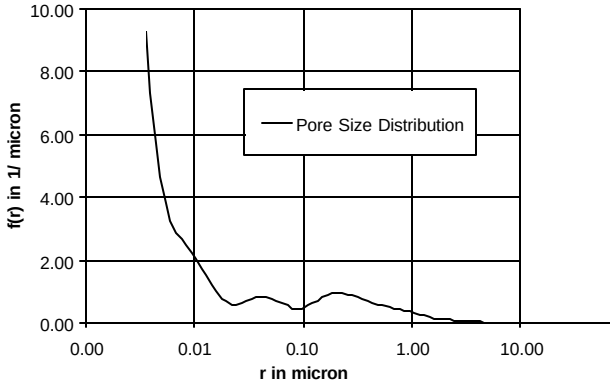

Figure 3 Pore size distribution calculated with the standard definition

Shafer and Neasham [4], in their documented study about the methodology for mercury injection have displayed their results in terms of "incremental saturation", but they note that they use "logarithmically-spaced pressure steps". If this condition is not verified, the results have no meaning and since the curve is a histogram and not a function, a maximum can appear where large steps are taken (when you group two classes in a histogram, you add the value of the two classes for the resulting one). This point is recognized in the recommendation of the American Association for Testing and Material [7]: *"a differential plot can lead to a distorted image of the pore size distribution, unless care is exercised in the selection of the diameter points at which the slope or change in intrusion is calculated. It is recommended that pore diameters be selected that are equally spaced on the logarithmic diameter axis,*".

For logarithmically-spaced pressure, the incremental saturation ΔS is proportional to a dimensionless function $g(r)$

$$g(r) = \frac{dS}{d(LnP)} = P\frac{dS}{dP} \tag{8}$$

If we call $e = \Delta(\ln P)$ the constant spacing in log scale, the incremental saturation is equal to $\Delta S = e\ g(r)$. However, $g(r)$ is not a probability distribution and its integral over all the values

of the radius is not equal to unity. This point must be considered when comparing the results to other sources of information, such as NMR relaxation or image analysis.

Compared to the standard psd, both functions have in common the derivative dS/dP but multiplied only by P for the logarithmic derivative instead of P^2 for the standard psd. That explains why there is more information contained in the intermediate values of pressure.
Another possibility is to plot only the derivative dS/dP, that corresponds to saturation increments with equally-spaced pressure. Compared to the two other functions, this simple derivative leads to more weight for small values of pressure (large radius).
I have analytically calculated the distribution $g(r)$ using the splines approximation and compared it to the plot of saturation increments (Figure 4, with two different scales). In the example, pressure steps are not logarithmically spaced and the plot of increments differs from the logarithmic derivative. In addition this figure shows the "noise" in the experimental data.

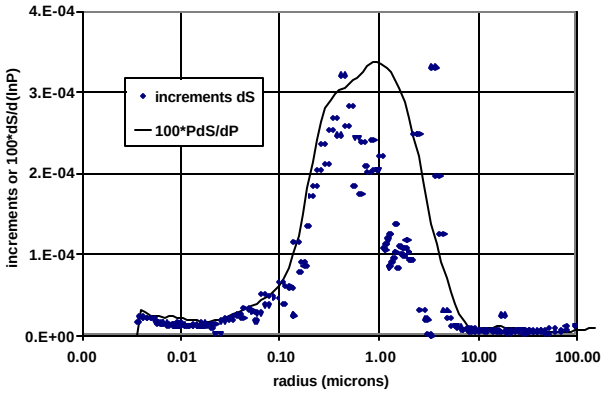

Figure 4 Comparison between the analytical curve $dS/d(\ln P)$ and the saturation increments (not at the same scale).

CONCLUSION

Instead of just plotting the measured incremental saturation, the simple procedure of curve fitting presents two main advantages:

- to remove the experimental dispersion
- to allow the calculation of true functions that have physical meanings and not depend on the spacing on pressure steps.

Several functions can be calculated, depending on the purpose of the study

- the pore size distribution (psd), suitable for the characterization of the distribution of the smallest pores and roughness of the walls (fractal dimension),

- the logarithmic derivative $dS/d(\ln P)$ which gives a good representation of pore topology, mean diameter and presence of a double porosity.
- the derivative dS/dP which gives information for large radius and low capillary pressures.

However, we must be aware that any function derived from mercury porosimetry gives a "theshold" distribution and not a "true" pore distribution.

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REFERENCES

1 Ausbrooks, R., Hurley, N.F., May, A., Neese, D.G., Pore-size distributions in vuggy carbonates from core images, NMR, and capillary pressure, SPE 56506, Annual Technical Conference and Exhibition of the Society of Petroleum Engineers, Houston USA, 1999.

2 Agut, R., Levallois, B., Klopf, W., Integrating core measurements and NMR logs in complex lithology, SPE 63211, Annual Technical Conference and Exhibition of the Society of Petroleum Engineers, Dallas, USA, 2000.

3 Leal, L., Barbato, R., Qualia, A., Porras, J.C., Lazarde, H., Bimodal behavior of mercury-injection capillary pressure curve and its relationship to pore geometry, rock-quality and production performance in a laminated and heterogeneous reservoir, SPE 69457, Latin American and Caribbean Petroleum Engineering Conference, Buenos Aires, Argentina, 2001.

4 Shafer, J., Neashman, J., , Mercury porosimetry protocol for rapid determination of petrophysical and reservoir quality properties, proceedings of the Society of Core Analysts, 2000.

5 Collins, R.E., Flow of fluids through porous material, New York, 1961.

6 Dullien, F.A.L.,*Porous media. Porous structure and fluid transport,* , San Diego, 1992.

7 ASTM, Standard test method for determination of pore volume and pore volume distribution of soil and rock by mercury intrusion porosimetrydetermination of, ASTM (American society for Testing and Materials), D 4404 – 84, 1984 (reapproved 1998).

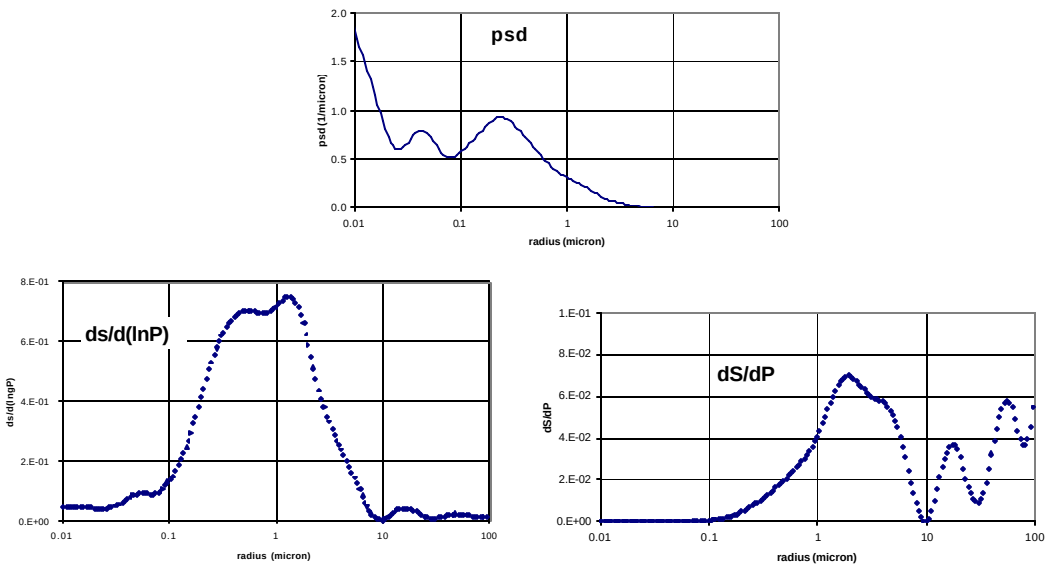

Figure 5 Comparison between the three functions that can be used to display the pore size distribution from thecapillary pressure curve: the true pore size distribution, the logarithmique derivative $dS / d(\ln P)$ and the derivative dS / dP .