ISSN 1600-5767

Received 28 June 2016 Accepted 21 September 2016

Edited by E. P. Gilbert, ANSTO, Kirrawee DC, Australia

Deceased 18 March 2016.

Keywords: small-angle X-ray scattering; SANS; ultra-small-angle X-ray scattering; USANS; rock; CO₂ sequestration; porosity.



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Determination of closed porosity in rocks by smallangle neutron scattering

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Small-angle neutron scattering (SANS) and ultra-small-angle neutron scattering (USANS) have been used to study a carbonate rock from a deep saline aquifer that is a potential candidate as a storage reservoir for CO_2 sequestration. A new methodology is developed for estimating the fraction of accessible and inaccessible pore volume using SANS/USANS measurements. This method does not require the achievement of zero average contrast for the calculation of accessible and inaccessible pore volume fraction. The scattering intensity at high Q increases with increasing CO_2 pressure, in contrast with the low-Q behaviour where the intensity decreases with increasing pressure. Data treatment for high-Q scattering at different pressures of CO_2 is also introduced to explain this anomalous behaviour. The analysis shows that a significant proportion of the pore system consists of micropores (<20 Å) and that the majority (80%) of these micropores remain inaccessible to CO_2 at reservoir pressures.

1. Introduction

The estimation of porosity is quite important in both engineered and natural materials for various applications, such as gas storage (Morris & Wheatley, 2008; Ross & Bustin, 2009) in porous materials. Recently, the sequestration of CO_2 in geological formations has attracted great interest (White et al., 2003; Bachu, 2003). Prediction of the storage capacity of a geological formation demands a thorough characterization of the pore system that includes pore size, shape and connectivity. Clastic and carbonate rocks that host deep saline aquifers offer a suitable target for CO₂ sequestration. These aquifer systems do not have economic or societal benefits for drinking and agricultural water resources because of their depth and high concentration of dissolved solids (Bruant et al., 2002). Also, these aquifers are the largest and most widespread among all the possible targets for CO₂ sequestration (Haszeldine, 2006; Holloway, 2001; Kharaka et al., 2006). These deep aquifers are often located close to the sources of CO₂ emissions (Hovorka et al., 2006), making these deposits potential sites for large-scale CO₂ storage. Determination of porosity is one of the major challenges when quantifying the storage capacity of CO₂ in deep aquifers.

Many experimental techniques have been used to characterize porosity in solids, including gas adsorption (Meyers, 1982), mercury intrusion porosimetry (Liu *et al.*, 2010) and transmission electron microscopy (TEM) (Huxham *et al.*, 1992), as well as small-angle scattering techniques [both smallangle neutron scattering, SANS (Sinha, 1999), and small-angle X-ray scattering, SAXS (Porod, 1982)]. Each of these methods has its limitations, *e.g.* gas adsorption and mercury porosimetry can only provide information regarding accessible porosity, and TEM can only be used to assess porosity inside a very limited sample volume. Many of these analytical techniques are complementary but most have a limited range of pore sizes that can be detected with a given analysis (Clarkson *et al.*, 2012).

SANS/SAXS, in combination with ultra-small-angle neutron and X-ray scattering (USANS/USAXS), are nondestructive techniques that have been used for estimating total porosity; they have a particular capability of differentiating between open and closed pores using contrast variation over the range of pore sizes 4–50 000 Å. The IUPAC classification categorizes pores with diameters >500 Å, 20–500 Å and <20 Å as macropores, mesopores and micropores, respectively (Sing *et al.*, 1985). Often, in natural samples such as coal and shale, the pores possess a power law distribution over a wide length scale. The small-angle scattering profiles for such systems are similar to that of a surface fractal (Bale & Schmidt, 1984). Such pores in coal and shale systems are termed fractal pores (Radlinski *et al.*, 2004; Bahadur *et al.*, 2014; Bahadur, Radlinski *et al.*, 2015).

The volume fraction of inaccessible pores can be quantified by saturating the porous solid with a contrast matching (CM) fluid, *i.e.* a fluid with a scattering length density (SLD) value close to that of the solid matrix. In this case, the scattering from accessible pores does not contribute to the total scattering and the residual scattering comes only from pores that are inaccessible to the fluid. A mixture of H₂O and D₂O is one of the most readily available and widely used fluids (liquids) for contrast matching SANS (CM-SANS) (Brumberger, 1995). CM-SANS results on coal samples were reported in the literature as early as 1986 by Gethner (Gethner, 1986) and other groups (Antxustegi et al., 1998; Hall et al., 1998, 2000). However, the results were affected by a number of problems. To begin with, the diffusion times of liquids into meso- and micropores are long, leading to long equilibration times for H₂O/D₂O mixtures. Furthermore, the CM technique using liquid mixtures depends on the wettability of the pore matrix, and the possibility of dissolution of the components of the porous matrix into the liquid mixture cannot be ignored. Moreover, functional groups in organic media can exchange hydrogen with water on timescales that vary from seconds to weeks. Therefore, isotope exchange may change the composition of a given H₂O/D₂O mixture within the pores and significantly alter the local CM condition, which was not fully acknowledged in previous studies (Antxustegi et al., 1998; Gethner, 1986; Hall et al., 1998, 2000).

An alternative method of obtaining CM in porous media using non-adsorbing or weakly adsorbing gases, such as CO_2 or deuterated methane (CD₄), was pioneered by Melnichenko and co-workers (Melnichenko, 2016; Melnichenko *et al.*, 2012; Mastalerz *et al.*, 2012; Ruppert *et al.*, 2013; Zhang *et al.*, 2015; He *et al.*, 2012). Dr Yuri Melnichenko contributed immensely to the field of high-pressure gas experiments using SANS on both natural and engineered porous materials such as rocks, coal, shale, porous silica, activated carbon *etc.* The structure and phase behaviour of confined fluids in nanopores are strikingly different compared with their bulk counterparts. Dr Melnichenko's work provides a direct insight into the density of adsorbed fluid using the modelling of SANS data. Over the past decade, he was instrumental in developing various generations of high-pressure cells at Oak Ridge National Laboratory which are used by many diverse user groups for high gas pressure SANS experiments.

Contrast variation using CO_2 and CD_4 is superior owing to their high permeability and high diffusion rate in materials. This method has been used extensively to determine the fraction of closed and open pores in various materials, including geological materials such as coal and shale. The SLD of deuterated methane and carbon dioxide can be varied by achieving the desired physical density as a function of pressure and temperature. The relationship between the SLD of CO_2 and CD_4 and their physical density can be written as

$$\begin{split} \rho_{\rm CO_2} &= 2.49\,d_{\rm CO_2} \times 10^{10}\,{\rm cm}^{-2}, \\ \rho_{\rm CD_4} &= 10\,d_{\rm CD_4} \times 10^{10}\,{\rm cm}^{-2}, \end{split} \tag{1}$$

where ρ_{CO_2} and ρ_{CD_4} represent the SLDs of CO₂ and CD₄, respectively, corresponding to their physical densities d_{CO_2} and d_{CD_4} . The critical temperature for carbon dioxide is 304.25 K and that for methane is 190.6 K. Thus, at room temperature CO₂ is subcritical and it undergoes a vapour to liquid transition at 73.84 bar (1 bar = 100 kPa). The SLD of subcritical CO_2 can only cover a limited range as a function of pressure owing to forbidden density space, and therefore it is not possible to obtain the zero average contrast (ZAC) value for several materials such as coal and shale. Thus, to achieve a high SLD, supercritical CO_2 at high pressure is required (e.g. the SLD of CO₂ at 1 kbar and 310 K is 2.7×10^{10} cm⁻²), but this is not sufficient to contrast-match the many inorganic porous media, including sandstones, carbonates, mudstones and shale, for which a typical SLD larger than $3.0 \times 10^{10} \text{ cm}^{-2}$ is required (Bahadur et al., 2014; Bahadur, Radlinski et al., 2015). Because CD₄ is supercritical at room temperature, it can be used to yield a wide range of SLDs as a function of pressure and can be used to obtain ZAC values for several porous media. At 300 K and 1 kbar, the SLD of CD_4 is 3.4×10^{10} cm⁻² and this is sufficient to contrast-match many inorganic porous media such as sandstones and carbonates.

The determination of accessible and inaccessible porosity using CM requires high pressures of the order of kilobars. It is possible that CM at high gas pressure might affect the pore morphology that is being measured, and hence it could be useful to work at a lower pressure without CM. To overcome this need, we report a methodology for estimating the fraction of closed porosity using SANS/USANS data at lower pressures of CO₂ without reaching contrast-matched conditions. The method used here is similar to that of anomalous SAXS (ASAXS) in which different wavelengths are used to obtain differences in scattering power (Goerigk *et al.*, 2003).

2. Experimental

2.1. Sample

The sample (M1) chosen for this study is a porous carbonate pack stone (Knox supergroup) from a borehole located in Knox County, Indiana, USA. The core was taken from a depth of 1611.26 m. A thin section of this rock sample suggests that it exhibits complexity in both its matrix texture and pore structure. The matrix displays two distinctive textures, one characterized by a microcrystalline fabric and the other dominated by larger rounded clasts. Fig. 1 depicts the visible porosity in the sample with pores that range from less than 1 mm to larger than 10 mm in diameter. The chemical composition of the sample is shown in Table 1.

The neutron SLD was estimated for components of the sample using the formula used in earlier work (Bahadur et al., 2014; Bahadur, Radlinski et al., 2015). Finally, the SLD value was calculated for the sample as a volume average over all component minerals according to the chemical formula of the sample. The results are listed in Table 1. The SLD variation between two constituents of the sample remains less than 5%. Hence, the two-phase approximation is valid in the present case. The first phase is the matrix of the sample with an approximately uniform SLD ($\sim 5.15 \times 10^{10} \text{ cm}^{-2}$) and the pores with zero SLD are considered as the second phase. Rocks and other natural materials can be heterogeneous as far as neutron scattering is concerned if the SLDs of the constituent phases are quite different. In this case, the two-phase approximation no longer remains valid. The analysis of SANS data becomes quite complicated for systems with more than two phases. The scattering intensity from pores in different constituent phases of the sample should be weighted by their contrast factor, i.e. the square of the SLD difference. Moreover, there can be scattering contributions from cross terms arising from different phases.



Figure 1

The sample used in the SANS/USANS experiments. The left-hand image is a photograph of a thin section, whereas the right-hand image is a core sample. The sample is from a depth of 1611.26 m.

Table 1

The	chemical	composition	of	the	sample,	with	the	scattering	length
dens	ities of the	e constituents	an	d sai	nple.				

Chemical constituent	Chemical formula	Molecular weight	Mass%	Vol.%	$\frac{\rm SLD}{(10^{10}{\rm cm}^{-2})}$	Density (g cm ⁻³)
Limestone Dolomite Sample	CaCO ₃ CaMg(CO ₃) ₂	100 184	38.7 61.3	40 60	4.69 5.45 5.15	2.71 2.87 2.81

2.2. SANS and USANS experiments

The SANS measurements were taken using the generalpurpose SANS instrument (Wignall et al., 2012) at Oak Ridge National Laboratory (ORNL). The sample-to-detector distances (13 and 1.0 m) were chosen to cover a wide range of scattering vector magnitudes Q of $0.006 < Q < 1.0 \text{ Å}^{-1}$, where $Q = 4\pi\lambda^{-1}\sin(\theta)$ and 2θ is the scattering angle. The neutron wavelength λ was chosen as 4.72 Å with a wavelength spread $\Delta\lambda/\lambda = 0.13$ for each sample-to-detector distance. Scattered neutrons were detected using a 1×1 m helium-filled twodimensional position-sensitive detector with 192×192 pixels. The SANS measurements were performed on a powder sample with grain size ~ 0.5 mm. A high-pressure dome cell rated for 1 kbar pressure and 573 K temperature was used for the high-CO₂-pressure experiment (Bahadur, Melnichenko et al., 2015). First, a granulated sample of about 1 g, with an average particle size of 1 mm³, was placed in a cylindrical aluminium capsule of 1.0 mm internal thickness to confine it. The filled Al capsule was inserted into the dome cell, which was then sealed for the introduction of high-pressure gas for SANS measurements. The effective thickness of the sample was calculated to be ~ 0.42 mm. The raw two-dimensional data were corrected for the detector pixel sensitivity, dome cell scattering and dark current. The corrected data were then azimuthally averaged to produce a one-dimensional intensity profile I(Q). The first SANS experiment was performed with the sample under vacuum at 355.65 K, and then CO₂ was injected into the high-pressure cell. In order to explore the possibility of a hysteresis effect on the SANS data, the SANS profiles were recorded in both pressure-up and pressure-down cycles up to 686 bar. These data indicate no evidence of hysteresis over the time frame of the measurement with changes in pressure over the entire range of measured values of Q.

The USANS measurements were carried out at NIST using the BT-5 perfect-crystal SANS instrument with a wavelength $\lambda = 2.38$ Å and a wavelength spread $\Delta\lambda/\lambda$ of 0.06 (Barker *et al.*, 2005). The *Q* range for the USANS measurements was 4×10^{-5} to 0.0025 Å⁻¹. The USANS measurements were carried out using the ORNL-2 high-pressure cell (Melnichenko, 2016). The temperature of the cell was controlled by a water-bath arrangement. The scattering curves were measured at ~348 K (the maximum temperature realized at the sample position). The combined SANS and USANS data for the sample under vacuum are shown in Fig. 2, indicating that there is no overlapping *Q* range between the SANS and USANS data. Moreover, achieving exactly the same pressure and temperature

conditions for both SANS and USANS experiments was not practical. Hence, the SANS and USANS data have been analysed separately, thus avoiding any amplification of the errors in the USANS data caused by the desmearing of the data to make them compatible with the SANS pinhole geometry. It is well known that the slit smearing of USANS measurements affects the pinhole SANS profile by reducing the exponent of the power law by 1 (Schaefer & Martin, 1984), provided that the slit height may be considered as infinite.

3. Results and discussion

3.1. Data interpretation of the sample under vacuum

Fig. 2 shows the combined experimental SANS and USANS profiles for the sample under vacuum. It is evident that the USANS profile deviates from a simple power law at the lowest values of Q, with the separation of the profiles becoming less obvious. This may be an artifact of measurements close to the incident beam, or it may be caused by the onset of multiple scattering. We observe power-law-type scattering below $Q < 0.1 \text{ Å}^{-1}$, whereas the high-Q scattering beyond $Q > 0.1 \text{ Å}^{-1}$ deviates significantly from linearity and shows relatively flat scattering. The slopes of the linear regions of the SANS and USANS profiles are 3.7 and 3.1, respectively. This gradual flattening of the scattering curves at lower values of Q with a lower power law exponent is not unknown. Gu et al. (2015) found that Marcellus shale samples have an exponent of 3.0 in the SANS regime which decreases to around 2.6 in the USANS regime.

The flat scattering of the high-Q SANS data is due to incoherent scattering from the organic content on the atomic length scale (a few ångströms), giving rise to density fluctuations that give Q-independent scattering in the small-angle scattering window. We estimate the constant background from the experimental SANS profile in order to observe the Porod scattering at high Q (Ruland, 1971; Vonk, 1973; Koberstein *et al.*, 1980). The estimated high-Q background for the sample under vacuum is ~0.035 cm⁻¹. Fig. 3 shows the SANS data



Figure 2

Experimental SANS and USANS profiles of the sample under vacuum, on a double logarithmic scale.

after the background has been subtracted. Both Figs. 2 and 3 indicate that the form of the high-Q region of the scattering modifies significantly after background subtraction.

The power law scattering in both USANS and SANS data arises because of the surface fractal nature of the pores. It is well known that the scattering intensity from a surface fractal follows a power law, *i.e.* $I(Q) \simeq Q^{-(6-D_s)}$ where D_s is the surface fractal dimension. For a smooth surface, $D_s \simeq 2.0$, whereas for an extremely rough surface, $D_s \simeq 3.0$ (Bale & Schmidt, 1984). The surface fractal dimensions of the pores in the SANS and USANS regimes are 2.3 and 2.9, respectively. These results suggest that the nature of the surface on the large length scale (1000–16 000 Å) is different from that on the smaller length scale (25–450 Å): the pore–rock interface is smoother on the length scale of 25–450 Å, whereas it is rougher on the larger length scale of 1000–16 000 Å.

Scattering from a polydisperse pore system having a power law distribution also gives power law scattering similar to a surface fractal (Schmidt, 1991; Radlinski *et al.*, 2004). Pores that follow a power law size distribution have been termed 'fractal pores'. The polydisperse spherical pore (PDSP) model (Radlinski *et al.*, 2004) is therefore assumed to fit the linear portion of the scattering profile.

In order to fit the high-Q scattering data, we have taken into account the spherical polydisperse micropores. By combining the two contributions the scattering intensity can be written as

$$I(Q) = I_{\text{fractal}}(Q) + I_{\text{micropore}}(Q), \qquad (2)$$

$$I_{\text{fractal}}(Q) = (\rho_{\text{fm}} - \rho_{\text{f}})^2 \frac{\varphi_{\text{f}}}{\overline{V}} \int_{R_{\text{min}}}^{R_{\text{max}}} V_r^2 f(r) F_{\text{sph}}(Qr) \, \mathrm{d}r, \quad (3)$$

where $(\rho_{\rm fm} - \rho_{\rm f})^2$ is the contrast factor for fractal pores, $\rho_{\rm fm}$ and $\rho_{\rm f}$ are the SLDs of the fractal pore matrix and fractal pores, respectively, $\overline{V} = \int_0^\infty V_r f(r) dr$ is the average pore



Figure 3

Background-subtracted SANS profiles of the sample. The solid lines show the fitting of the SANS profile using a power law pore-size distribution and polydisperse micropores. volume, V_r is the volume of pores having radius r, φ_f is the porosity of the specimen due to fractal pores, and

$$f(r) = \frac{r^{-(1+D_{\rm s})}}{\left(R_{\rm min}^{-D_{\rm s}} - R_{\rm max}^{-D_{\rm s}}\right)/D_{\rm s}}.$$
 (4)

The SLD of the fractal pores ρ_f is zero for the sample under vacuum. Therefore, the contrast factor is simply the square of the SLD of the matrix for the sample under vacuum.

The scattering contribution due to micropores can be written as

$$I_{\rm micro}(Q) = (\rho_{\rm sm} - \rho_{\rm m})^2 \frac{\varphi_{\rm m}}{\overline{V}} \int V_r^2 D(r) F_{\rm sph}(Qr) \,\mathrm{d}r, \quad (5)$$

where D(r) is the lognormal distribution of the micropores. $F_{\rm sph}(Qr)$ is the form factor for spherical pores. $(\rho_{\rm sm} - \rho_{\rm m})^2$ is the contrast factor for micropores, where $\rho_{\rm m}$ and $\rho_{\rm sm}$ are the SLDs of the micropores and the surrounding matrix, respectively. $\varphi_{\rm m}$ is the volume fraction of the micropores. The SLD of the micropores is zero for the sample under vacuum. Owing to the greatly different length scales of fractal pores and micropores, the SLD of the matrix corresponding to fractal pores $\rho_{\rm fm}$ and that for micropores $\rho_{\rm sm}$ are modified by the volume fraction $\varphi_{\rm m}$ of micropores, *i.e.*

$$\rho_{\rm fm} = (1 - \varphi_{\rm m})\rho_{\rm sm}.\tag{6}$$

The SANS profile of the sample under vacuum is fitted using equation (2) under the constraint of equation (6). The



Figure 4 (*a*) Estimated size distribution of fractal pores and (*b*) micropore size distribution.

SLD of the micropore matrix $\rho_{\rm sm}$ was taken as ~5.15 × 10^{10} cm⁻², as shown in Table 1. Fig. 3 shows the fitting of the scattering profile for the sample under vacuum. The fractal dimension $D_{\rm s}$ of the fractal pores is 2.3. The average SLD of the fractal pore matrix $\rho_{\rm fm}$ is estimated using equation (3) as ~4.89 × 10^{10} cm⁻². Fig. 4 shows the estimated pore-size distributions for fractal and micropores. It is evident from the fitting of the SANS data that the rock, in the present case, possesses both fractal and spherical micropores.

Clearly, the average size (diameter) of the micropores is about 6 Å. The volume fractions of micropores and fractal pores are 0.05 and 0.001 (5 and 0.1%), respectively. Thus, the total porosity in the sample determined by the SANS/USANS measurement is ~5.1%. We employed helium pycnometry to provide information regarding the volume fraction of accessible pores, which was found to be ~1%. Thus, the majority of micropores (~80%) are inaccessible to helium.

The specific surface area for a probe size *r* is calculated from the pore-size distribution as the sum of the surface areas of all pores of radius larger than *r*, divided by the sample volume, *i.e.*

$$\frac{S(r)}{V} = n_v \int_r^{R_{\text{max}}} A_r f(r') \,\mathrm{d}r'. \tag{7}$$

Here, n_v is the average number of pores per unit volume, $n_v = \varphi_f/\overline{V_r}$. S(r)/V is the specific surface area of pores of radius larger than r, and $A_r = 4\pi r^2$. Fig. 5 shows the estimated surface area due to fractal pores.

The scattering contribution due to micropores is estimated by subtracting the power law contribution from the total scattering intensity. The scattering invariant γ_{inv} due to micropores is defined as

$$\gamma_{\rm inv} = \int I_{\rm micropore} \left(Q\right) Q^2 \,\mathrm{d}Q. \tag{8}$$

The specific surface area due to micropores was also determined using the following expression:



Figure 5 The specific surface area $(m^2 g^{-1})$ due to fractal pores as a function of the pore size.

$$\frac{S}{V} = \frac{\pi \,\varphi_{\rm m}(1-\varphi_{\rm m})}{Q_{\rm inv}} \lim_{Q \to \infty} \left[I(Q)Q^4 \right]. \tag{9}$$

The specific surface area due to micropores is $\sim 246 \pm 25 \text{ m}^2 \text{ g}^{-1}$. It is important to note that, although the specific micropore surface area is quite large, the accessible surface area will be less as the majority of the micropores are inaccessible.

3.2. Data interpretation of the sample under supercritical CO_2

Fig. 6 presents the SANS profiles for the sample at various pressures of supercritical CO_2 , clearly showing that the scattering intensity at low Q decreases with pressure, whereas the scattering intensity increases at high Q.

Fig. 7 shows that the form of the slit-smeared USANS profiles at different pressures has the same power law with an exponent of 2.1 over the range of 1.5×10^{-4} to 2.5×10^{-4} Å⁻¹. As CO₂ is injected into the sample, the decrease in scattered intensity is similar to that of the SANS measurements, with the greatest decrease corresponding to the highest pressure, indicating the reduction in contrast. Note also that the scattered intensity returns to its initial profile at the vacuum condition after increasing and decreasing the gas pressure, again indicating a lack of hysteresis. This also indicates that there is no significant damage to the pore morphology during the experiment at high gas pressure.

As CO₂ is injected into the sample, the SLD of the fractal pores attains that of bulk CO₂, *i.e.* $\rho_f(P) = \rho_{CO2}(P)$, where P is the CO₂ pressure. The form of the scattering profile at low Q remains the same, with an unchanged power law exponent. (Note that the scattering profiles at high Q, however, do not vary in a parallel fashion as a function of CO₂ pressure.) The reduction in low-Q intensity with pressure is related to the decrease in the contrast factor $(\rho_{fm} - \rho_f)^2$ caused by the increase in density of bulk CO₂ with pressure. The SLD of the



Figure 6

Experimental SANS profiles at different pressures of CO_2 at 355.65 K. The inset shows the low-Q behaviour on a magnified scale.

matrix surrounding the fractal pores now also depends on the SLD of the CO_2 confined in the micropores, by

$$\rho_{\rm fm} = (1 - \varphi_{\rm m})\rho_{\rm sm} + \varphi_{\rm am}\rho_{\rm am}, \qquad (10)$$

where φ_m is the total volume fraction of micropores, φ_{am} is the fraction of accessible micropores and ρ_{am} is the SLD of the confined fluid in the accessible micropores. Since the majority (~80%) of micropores are inaccessible to the fluid, as shown by SANS analysis and helium pycnometry, the SLD of the fractal pore matrix ρ_{fm} does not vary significantly with pressure. Thus, the contrast factor at low Q is reduced owing to the increase in the SLD of the CO₂ in the fractal pores. The scattered intensity as a function of CO₂ pressure is therefore a parabola, with $\rho_{fm} = \rho_f$ the minimum scattered intensity at the ZAC condition, if such a pressure could be attained.

We now outline a method to determine the fraction of accessible and inaccessible fractal pores using the pressure dependence of the low-Q data, without the necessity of determining the pressure at which we have ZAC.

3.2.1. Calculation of accessibility of fractal pores. The expression for the scattered intensity from the fractal pores is given by equation (3), which may be simplified as

$$I(Q) = (\rho_{\rm fm} - \rho_{\rm f})^2 \varphi_{\rm f} F(Q), \qquad (11)$$

where F(Q) contains all parameters other than the SLD contrast and the fraction of fractal pores. The total fractal porosity $\varphi_{\rm f}$ consists of both accessible and inaccessible pores, *i.e.* $\varphi_{\rm f} = \varphi_{\rm ac} + \varphi_{\rm in}$. As fluid is injected into the sample, it occupies the pore volume. Here, we are assuming that there is no significant confinement of the fluid in the fractal pores, *i.e.* the density of the fluid in the pore remains equal to that of the bulk fluid density. The scattering intensity can be written as a function of pressure P by modifying equation (11) as follows:

$$I(Q, P) = \left[\rho_{\rm fm} - \rho_{\rm f}(P)\right]^2 \varphi_{\rm ac} F_{\rm ac}(Q) + \left(\rho_{\rm fm}\right)^2 \varphi_{\rm in} F_{\rm in}(Q), \quad (12)$$

where $\rho_{\rm f}(P)$ is the bulk fluid density at pressure *P*, and $F_{\rm ac}(Q)$ and $F_{\rm in}(Q)$ are the form factors of the accessible and inaccessible pores, respectively.



Figure 7 Slit-smeared USANS data at different pressures of supercritical CO₂.

At zero pressure (P = 0), this reduces to

$$I(Q,0) = (\rho_{\rm fm})^2 \varphi_{\rm f} F(Q), \qquad (13)$$

where $F(Q) = \varphi_{ac}F_{ac}(Q) + \varphi_{in}F_{in}(Q)$. The ratio of the intensity at pressure *P* to that at zero pressure is given by the expression

$$\frac{I(Q, P)}{I(Q, 0)} = \frac{\left[\rho_{\rm fm} - \rho_{\rm f}(P)\right]^2 \varphi_{\rm ac} F_{\rm ac}(Q) + (\rho_{\rm fm})^2 \varphi_{\rm in} F_{\rm in}(Q)}{(\rho_{\rm fm})^2 \varphi_{\rm f} F(Q)}.$$
 (14)

This equation has three independent parameters: $F_{in}(Q)$, $F_{ac}(Q)$, and φ_{in} or φ_{ac} . Thus, it is not possible to obtain information about accessible or inaccessible pore volume fraction using equation (14); that is, unless we reach ZAC pressure, so that the first term of the numerator of equation (14) becomes zero. However, equation (14) can be used to determine the volume fraction of accessible and inaccessible pores if the pore morphology of the accessible and inaccessible pores is identical; this may be true in natural samples such as rock, coal and shale, *i.e.* $F_{ac}(Q) \simeq F_{in}(Q) \simeq F(Q)$. In this case, equation (14) can be written as

$$\frac{I(P)}{I(0)} = \frac{\left[\rho_{\rm fm} - \rho_{\rm f}(P)\right]^2 \varphi_{\rm ac} + (\rho_{\rm fm})^2 \varphi_{\rm in}}{(\rho_{\rm fm})^2 \varphi_{\rm f}}.$$
 (15)

Furthermore, this may be rearranged to give

$$\frac{I(P)}{I(0)} = \left[1 - \frac{\rho_{\rm f}(P)}{\rho_{\rm fm}}\right]^2 \frac{\varphi_{\rm ac}}{\varphi_{\rm f}} + \frac{\varphi_{\rm in}}{\varphi_{\rm f}} = S(P) \frac{\varphi_{\rm ac}}{\varphi_{\rm f}} + \frac{\varphi_{\rm in}}{\varphi_{\rm f}}.$$
 (16)

Here we define

$$S(P) = \left[1 - \frac{\rho_{\rm f}(P)}{\rho_{\rm fm}}\right]^2,\tag{17}$$

which is related to the relative difference between the SLD of the CO₂ inside the fractal pores and the SLD of the matrix of the fractal pores. It is evident that the intensity ratio I(P)/I(0)is linear with $\{1 - [\rho_f(P)/\rho_{fm}]\}^2$. The gradient and intercept of the line described by equation (16) give the accessible and inaccessible pore fractions.

The assumption that the accessible and inaccessible pore morphologies, *i.e.* the shapes and sizes of the pores, are

identical can be validated if the intensity ratio I(P)/I(0) is linear in S(P). It is important to note that equation (16) is valid for any shape of pore, including fractal pores, if the morphologies of the accessible and inaccessible pores are identical and there is no confinement of fluid in the pores. We have measured the intensity ratio I(P)/I(0) as a function of pressure and the values of S(P) are calculated using the equation of state (Span & Wagner, 1996) for bulk CO₂, whereas the SLD of the matrix $\rho_{\rm fm}$ is known. Fig. 8 shows a plot of I(P)/I(0) versus S(P) for $Q \simeq 0.006 \text{ Å}^{-1}$. The linear function of I(P)/I(0) validates the approximation that the pore morphologies of the accessible and inaccessible pores are identical in the present case, and also that there are no confinement effects in the fractal pores. Since at P = 0, $\rho_f(P) =$ 0, it is necessary that the fit to equation (16) of the line in Fig. 8 must pass through the point (1, 1). The linear fit at Q =0.006 Å⁻¹ to equation (16) is given by I(P)/I(0) = 0.55S(P) +0.45. The fractions of inaccessible and accessible fractal pores are therefore estimated to be 0.45 ± 0.11 and 0.55 ± 0.15 , respectively, for $Q = 0.006 \text{ Å}^{-1}$. The I(P)/I(0) versus S(P) plots for other Q values in the linear region $(0.006 < Q < 0.03 \text{ Å}^{-1})$ of the scattering profile give results similar to Fig. 8. Thus, 55 (±15)% of the fractal pores in the Q range of 0.006 < Q < 0.03 Å^{-1} are accessible to CO₂.

This methodology to obtain the accessibility of the pores was also applied to the USANS data. Fig. 9 shows a plot of I(P)/I(0) versus S(P) in the USANS range. The linear fit at Q = 0.002 Å^{-1} to equation (16) is I(P)/I(0) = 0.70S(P) + 0.30. Hence, the fractions of accessible and inaccessible pores in the range 1000–16 000 Å are 0.70 ± 0.25 and 0.30 ± 0.16 , respectively. Table 2 shows the pore volume fractions of accessible and inaccessible fractal pores at different values of Q. For the lower values of Q, the scattered intensity is more sensitive to the larger pores, so that the accessibility of the larger pores is higher than that of the smaller pores. We did not choose values in the very low Q range ($Q < 0.001 \text{ Å}^{-1}$) owing to the possible effect of multiple scattering on the estimation of the fraction of accessible pores. The above methodology cannot be applied for high-Q scattering ($Q > 0.01 \text{ Å}^{-1}$) in the present case



Figure 8

The ratio I(P)/I(0) versus S(P) at $Q = 0.006 \text{ Å}^{-1}$. The straight line shows the linear fit to the data.



The ratio I(P)/I(0) versus S(P) at Q = 0.002 Å⁻¹. The straight line shows the linear fit to the data.

Table 2						
The pore volume	fraction o	f accessible	and ina	ccessible	fractal	pores.

Q (Å ⁻¹)	$arphi_{ m ac} / arphi_{ m f}$	$arphi_{ m in}/arphi_{ m f}$
0.001	0.78 ± 0.20	0.22 ± 0.15
0.002	0.70 ± 0.25	0.30 ± 0.16
0.006	0.55 ± 0.15	0.45 ± 0.11
0.01	0.48 ± 0.12	0.52 ± 0.13

because there is significant scattering from the fluid (highpressure supercritical CO_2).

3.2.2. Interpretation of high-Q scattering. We observe from Fig. 6 that the scattering intensity in the linear region decreases with increasing pressure owing to the increase in the bulk CO_2 density in the fractal pores. On the other hand, the scattering profile in the high-Q regime shows a dramatic increase with increasing pressure. It is important to note that supercritical CO₂ at high pressure was injected into the samples. At this pressure, the density of bulk CO_2 is quite high (Table 3). The scattering from supercritical bulk CO_2 due to density fluctuations causes additional scattering at high Q. The scattering from fluids, for example water (H₂O and D₂O) or CCl₄, has been studied in the past (Bosio et al., 1981; Huang et al., 2009; Clark et al., 2010). It is assumed that the fluid possesses a homogenous structure as far as small-angle scattering is concerned. However, it is well established (Bosio et al., 1981; Huang et al., 2009; Clark et al., 2010) that there are thermal density fluctuations in the liquid. The length scale of these fluctuations beyond the critical point of the fluids is of the order of ångströms. The fluid scattering at low Q normally depends on its isothermal compressibility. However, thermally induced density fluctuations may cause additional scattering in the high-Q regime. We have adopted the model used by Clark et al. (2010) to account for the high-Q scattering arising from the supercritical CO_2 .

The scattering from dense CO₂ consists of two factors. The first is the molecular form factor and the other is the structure factor due to local density fluctuations in CO₂ at high pressure. The molecular form factor for SANS can be assumed constant in the range 0.1–1.0 Å⁻¹, whereas the structure factor dominates in this Q range. Thus, the structure factor S(Q) and the scattering intensity $I_{\text{fluid}}(Q)$ due to supercritical CO₂ in the present Q range are related by

$$I_{\text{fluid}}(Q) = f_{\text{m}} S(Q), \qquad (18)$$

where f_m is a *Q*-independent molecular form factor. The structure factor S(Q) from a liquid can be expressed as the sum of two components, namely a normal and an anomalous component:

$$S(Q) = S_{\rm N}(Q) + S_{\rm A}(Q).$$
 (19)

The normal component of S(Q) can be assumed Q independent in a typical Q range of 0.1–1.0 Å⁻¹, and it depends on the fluid isothermal compressibility χ_T through

$$S_{\rm N}(Q) = S_{\rm N}(0) = n \, k_{\rm B} \, T \, \chi_T,$$
 (20)

The physical density and scattering length density (SLD) of CO_2 at each pressure used in these measurements.

The Ornstein–Zernike correlation length ξ , obtained by fitting, is also given at each pressure.

Drogguro	Pulk CO	Pulk CO		
(bar)	density (g cm ^{-3})	SLD $(10^{10} \text{ cm}^{-2})$	ξ (Å)	
173	0.491	1.226	5.0 ± 1.0	
260	0.686	1.713	4.0 ± 1.0	
434	0.835	2.085	3.3 ± 1.0	
523	0.878	2.193	2.8 ± 1.0	
609	0.912	2.278	3.7 ± 1.0	
686	0.938	2.343	4.2 ± 1.0	

where $n = N_A d/M_w$ is the molecular number density, k_B is the Boltzmann constant, T is the temperature, N_A is Avogadro's number and d is the density of bulk CO₂. χ_T is the normal component of the isothermal compressibility and M_w is the molecular weight of CO₂.

The anomalous component is given by the Lorentzian function

$$S_{\rm A}(Q) = \frac{I_0}{\xi^{-2} + Q^2},$$
 (21)

where I_0 is a temperature-dependent constant, and ξ is the Ornstein–Zernike (OZ) correlation length and a measure of the characteristic length scale of the density fluctuations. Using equations (19)–(21), equation (18) can be rewritten as

$$I_{\rm fluid}(Q) = f_{\rm m} \bigg[n \, k_{\rm B} \, T \, \chi_T + \frac{I_0}{\xi^{-2} + Q^2} \bigg].$$
(22)

In order to observe the scattering from the dense supercritical fluid, the scattering profile for the sample under vacuum is subtracted from the scattering profiles of the sample under CO_2 .

Fig. 10 shows the subtracted scattering profiles $I_{\text{fluid}}(Q)$, which are directly proportional to the dimensionless structure



Figure 10

The scattering intensity $I_{\text{fluid}}(Q)$ obtained by subtracting the scattering profile of the sample under vacuum from the high-pressure SANS profiles at the various measured pressures. The lines represent the fits of the experimental data to equation (22).



Figure 11

The normal component of the structure factor $S_N(0)$ in arbitrary units for supercritical CO₂ as a function of its bulk density.

factor from the supercritical CO₂ at different pressures. Fig. 10 also shows the fit of the experimental data to equation (22). The fitting is carried out by taking a constant value of temperature and thus of I_0 for all measured pressures. The fit of the model to the data is quite good. It is evident that equation (22) contains several unknown parameters (f_m , χ_T , I_0 , ξ). Hence, it is not possible to obtain the absolute value of χ_T at different pressures. Fig. 11 shows the O-independent normal component $S_{N}(0)$ of the fluid scattering in arbitrary units at different densities of bulk CO2. As is evident from equation (20), $S_{\rm N}(0)$ is proportional to the density of the fluid, indicating a constant value of the isothermal compressibility in the present pressure range. The OZ correlation length ξ may be viewed as the length scale over which the density fluctuations in the fluid can be observed, and the results shown in Table 3 are found to be \sim 3–5 Å, which are quite realistic.

4. Conclusions

The pore structure of deep saline aquifer carbonate rock has been investigated by SANS over a wide Q range. The total porosity in the sample is 5.1%. The porosity due to micropores (<10 Å) is 5% and the remaining porosity comes from fractal pores. Comparison of the porosity values obtained by pycnometry and by SANS measurement indicates that the majority of micropores (~80%) are inaccessible to helium. Owing to this lower accessibility of the micropores in the rock, the effective available surface area for CO2 adsorption decreases. A method has been developed to extract the accessibility of the fractal pores using SANS data at different pressures. We take the ratio of intensities collected at specific values of Q and, knowing the ratio of their contrasts, we can obtain the ratio of the fractions of closed and open pores. This method does not require finding the zero average contrast pressure, which is usually very high, and can be used to determine the fraction of accessible and inaccessible pores using different fluids such as CO₂ or CD₄ at lower pressures. In this method the possibility of pore disruption at high pressure is negligible. The accessibility of the fractal pores varies in the range of 48–78% for this rock specimen.

The anomalously large scattering at high Q after injection of high-pressure supercritical CO₂ into the sample has been understood by invoking the fundamentals of liquid scattering. It has been observed that density fluctuations on the 5 Å length scale give Q-dependent scattering of the Lorentzian kind. On the other hand, a Q-independent term is related to the isothermal compressibility of the fluid, which increases with the density of the bulk CO₂. Scattering from bulk CO₂ in the high-Q regime can be avoided by choosing a lower pressure or subtracting the scattering from bulk CO₂.

Acknowledgements

The research at Oak Ridge National Laboratory's High Flux Isotope Reactor was sponsored by the Laboratory Directed Research and Development Program and the Scientific User Facilities Division, Office of Basic Energy Sciences, US Department of Energy (DOE). The USANS measurements at the National Institute of Standards and Technology were supported in part by the National Science Foundation under agreement No. DMR-0944772. This work was partially supported by a subcontract to the Indiana Geological Survey from Battelle Memorial Institute under a DOE contract for the Midwest Regional Carbon Sequestration Partnership (MRCSP). TPB thanks the Central Analytical Research Facility and the Science and Engineering Faculty of the Queensland University of Technology for funding travel to ORNL and NIST. We dedicate this paper to the memory of Yuri Melnichenko, recognizing his achievements in the development of SANS techniques for investigating the petrophysical characteristics of earth materials.

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