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Estimation and modeling of coal pore accessibility using small angle neutron scattering

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HIGHLIGHTS

- Apply small-angle neutron scattering (SANS) to quantify pore accessibility in coal matrix.
- Propose and validate a pore accessibility model using SANS results.
- Estimate pore accessibility for two different rank coals.
- Pore accessibility and pore radius has a power-law relationship.

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ABSTRACT

Gas diffusion in coal is controlled by nano-structure of the pores. The interconnectivity of pores not only determines the dynamics of gas transport in the coal matrix but also influences the mechanical strength. In this study, small angle neutron scattering (SANS) was employed to quantify pore accessibility for two coal samples, one of sub-bituminous rank and the other of anthracite rank. A theoretical pore accessibility model was proposed based on scattering intensities under both vacuum and zero average contrast (ZAC) conditions. The results show that scattering intensity decreases with increasing gas pressure using deuterated methane (CD_4) at low Q values for both coals. Pores smaller than 40 nm in radius are less accessible for anthracite than sub-bituminous coal. On the contrary, when the pore radius is larger than 40 nm, the pore accessibility of anthracite becomes larger than that of sub-bituminous coal. Only 20% of pores are accessible to CD_4 for anthracite and 37% for sub-bituminous coal, where the pore radius is 16 nm. For these two coals, pore accessibility and pore radius follows a power-law relationship.

1. Introduction

Natural gas has a relatively lower CO_2-to-energy content than coal and oil and therefore has some advantages as a substitute fuel to reduce the carbon intensity of energy production. For this reason, as well as their newfound abundance, unconventional natural gas resources are progressively displacing coal and oil in static combustion [1]. Among all the unconventional gas reservoirs, coalbed methane (CBM) is one of the most important resources with a relatively low risk of development and its utilization has grown rapidly in the last few decades. Coal permeability and gas content are two of the most important parameters in the successful recovery of CBM and both are closely related to coal pore structure [2–4].

As an organic-rich material, coal has a complex pore architecture which is not fully understood [5]. The pore structure of coal is heterogeneous and anisotropic and includes macropores (>50 nm), mesopores (2–50 nm), and micropores (<2 nm) [6]. Microporosity dominates in high rank coals, while most of the porosity present in low rank coals is distributed in the macropore range [7]. Within the same rank, high-vitrinite bituminous coals have more micropores than low-vitrinite bituminous coals, which affect gas adsorption capacity [8]. The connectivity of micropores exerts a significant contribution to gas diffusion in micropores and to overall permeability [9]. The fraction of accessible pores becomes increasingly important in various areas, such as, the estimation of original gas-in-place (GIP), and in the prediction of gas production, permeability evolution, recovery of enhanced coalbed methane (ECBM) and in estimate of mass of carbon potentially sequestered [10].

Many techniques have been applied to investigate pore accessibility in porous media – each method with advantages and limitations. Optical microscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) can only give qualitative

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Nomenclature

Q	scattering vector or momentum transfer
λ	neutron wavelength
θ	scattering angle
$I(Q)$	scattering intensity at a certain scattering vector
$\varnothing$	volume fraction of a phase
$\gamma_0(r)$	correlation function
ρ_s^*	scattering length density of solid matrix
ρ_f^*	scattering length density of fluid in pores
N_A	Avogadro's constant
d	bulk density (solid matrix or fluid in the pores)
M	pseudo-molar mass of a phase
p_j	proportion of compound j in a mixture
s_i	proportion of nucleus i in compound j
b_i	coherent scattering amplitude of nucleus i
$I(Q, ZAC)$	scattering intensity at zero average contrast condition
$I(Q, VAC)$	scattering intensity at vacuum condition
$C_{AC}(Q)$	fraction of accessible pores (pore accessibility)
C_p	power law constant (contrast factor)
α	power law exponent
B	incoherent background
$I_{subtracted}(Q)$	background-subtracted scattering intensity
$I_{subtracted,VAC}(Q)$	background-subtracted scattering intensity at vacuum condition
$I_{subtracted,ZAC}(Q)$	background-subtracted scattering intensity at zero average contrast condition
$C_{p,VAC}$	contrast factor at vacuum condition
$C_{p,ZAC}$	contrast factor at zero average contrast condition
α_{VAC}	power law exponent at vacuum condition
α_{ZAC}	power law exponent at zero average contrast condition
a	ratio of contrast factor between zero average contrast and vacuum conditions
b	difference of power law exponent between vacuum and zero average contrast conditions
R	pore radius
a'	equals to $a \times (0.25)^b$
b'	equals to $-b$

Abbreviations

SANS	small angle neutron scattering
ZAC	zero average contrast
CBM	coalbed methane
GIP	gas-in-place
ECBM	enhanced coalbed methane
SEM	scanning electron microscopy
TEM	transmission electron microscopy
Micro-XCT	micro X-ray computed tomography
MIP	mercury intrusion porosimetry
LPGA	low-pressure gas (N_2/CO_2) adsorption
PSD	pore size distribution
SSA	specific surface area
1D	one dimensional
2D	two dimensional
SLD	scattering length density
SAXS	small angle X-ray scattering
ORNL	Oak Ridge National Laboratory
GP-SANS	general-purpose small angle neutron scattering diffractometer
XRD	X-ray diffraction
EOS	equation of state

information within a very limited window of observation [11]. Micro X-ray computed tomography (Micro-XCT) cannot provide details at nano-scale resolution required for characterization [12]. Mercury intrusion porosimetry (MIP) and low-pressure gas (N_2/CO_2) adsorption (LPGA) are invasive methods, which can only detect the accessible pore structures but also may destroy the samples [8]. Fortunately, small angle neutron scattering (SANS), as an emerging technique for investigating pore structure in porous media, has recently been applied in quantitatively characterizing pore accessibility in geomaterials [10,13–20]. Historically, SANS has been employed in the micropore characterization of coal [21,22], but has recently been applied to quantify coal pore accessibility [10,13,14].

MIP, LPGA and SANS techniques have been used to obtain the pore size distribution (PSD) of six coals of varying rank [23]. The porosity estimated from SANS data is larger than that of both MIP and LPGA for all six samples. This is because SANS detects both open and closed pores while MIP and LPGA only probe open pores [23]. Similarly, specific surface area (SSA) estimated by SANS is larger than that obtained by LPGA technique for both coal and shale samples, which is also due to capability of SANS in detecting both open and closed pores [24].

A new methodology was recently developed for determining pores accessible to deuterated methane (CD_4) and CO_2 for three coals and one porous silica [10], which found that pore accessibility in coals may have a positive correlation with total porosity and that pore accessibility may not only depend on pore size but also on fluid type, temperature, pressure, and experiment duration. Wettability and capillary pressure of coal matrix are two additional important parameters affecting the fraction of accessible pores [25,26]. Pores that are inaccessible to CD_4 and CO_2 have been examined for four different bituminous coals [13]. Evident from this work is that closed porosity has a negative correlation with total porosity and SSA. But no correlation was observed between closed porosity and coal rank or maceral composition. The relationship between pore accessibility and physical properties of coal has been further investigated by studying 24 bituminous coals [14] with the observation that the fraction of inaccessible mesopores (pore size range 8–25 nm) exhibits a positive correlation with both hydrogen and vitrinite contents in vitrinite-rich coals. While the relationship between closed porosity and coal properties shows obvious region dependent. Similarly, the fraction of inaccessible pores is independent of coal rank were found. Thus, these findings of Sakurovs et al. [14] are in good agreement with those of Clarkson et al. who noted that pore accessibility is both pore size and sample dependent for shale samples [18]. Most recently observed is that the fraction of nanopores (<30 nm) accessible to heavy water (D_2O) is larger than that of CD_4 for shale [19]. Bahadur et al. suggested that there are strong correlation between mineral matter contents and the closed porosity in shale samples [20].

In this study, we refine a pore accessibility model based on the fundamental theory of SANS and test its applicability. Subsequently, two coal samples with different ranks are characterized to quantify pore accessibility and compared with this new model.

2. Fundamental theory of SANS and pore accessibility estimation

2.1. Fundamental theory

Fig. 1 shows a schematic of typical SANS experimental system [27]. The incident neutron beam of a fixed wavelength is elastically