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Laboratory Simulation of Shale Gas Adsorption under Geological Conditions

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Unconventional energy (e.g. coal bed methane, shale gas) now is playing more important roles in the whole energy system. As Understanding the adsorption capacity and deformation change during adsorption of methane in shales, may help the exploitation and resource evaluation (ROSS and BUSTIN, 2008; SCHMOKER, 1995). Pore structure information of eleven shale samples were measured by N₂ adsorption isotherm method. Isotherms as well as pore size distributions of these samples were obtained (See Fig. 1) by employment of quenched solid density function theory (QSDFT). Based on these experimental data, a systematic simulation work was carried out in this study.

The density functional theory (DFT) with properly chosen parameters of intermolecular interactions bridges scales from molecular simulations to classical thermodynamics (NEIMARK et al., 2003). DFT can approximate the results of Monte Carlo (MC) simulations for pores wider than about 2 nm and, in turn, can be approximated by the macroscopic Derjaguin-Broekhoff-de-Boer (DBdB) equations for pores wider than 7–10 nm. Compared to classical NLDFT (nonlocal density functional theory), the QSDFT model takes into account the carbon surface heterogeneity and significantly improves the way of calculating adsorption isotherms. The details of the QSDFT method are given in earlier literature (NEIMARK et al., 2009; RAVIKOVITCH and NEIMARK, 2006). QSDFT considers the solid as a quenched component of the two-component solid–fluid system and reduces the adsorption interactions to the pairwise interactions between molecules of adsorbate (fluid) and adsorbent (solid). In our calculations, we used the Lennard-Jones (LJ) potential to represent both fluid–fluid and fluid–solid interactions. In addition, we employed the standard WCA scheme to determine the van der Waals attractive potentials as given below,

$$u_{ij}^{att}(r) = \begin{cases} -\varepsilon_{ij} & r \leq 2^{1/6} \sigma_{ij} \\ 4\varepsilon_{ij} \left[(\sigma_{ij}/r)^{12} - (\sigma_{ij}/r)^6 \right] & r \geq 2^{1/6} \sigma_{ij} \end{cases}$$

For methane-methane interaction, the effective LJ parameters for fluid–fluid interactions were chosen as $\epsilon_{ff}/k_B = 148.1$ K, $\sigma_{ff} = d_{HS} = 0.381$ nm. For methane-shale interaction, the effective LJ parameters for solid–fluid interactions were chosen as $\epsilon_{sf}/k_B = 184.62$ K, $\sigma_{sf} = 0.333$ nm (RAVIKOVITCH et al., 2001). In the QSDFT model, the key parameter is the roughness parameter δ , representing an average characteristic scale of the surface corrugations. The roughness parameter δ represents the half-width of the density ramp (2), and is taken as $\delta = 0.04$ nm (RAVIKOVITCH and NEIMARK, 2006)

We calculated adsorption isotherms of methane in shale pores of various sizes, under a range of pressures, at 298K and 360K (see Fig. 2). We applied these results to predict the extent of deformation in a hypothetical shale basin (see Fig. 3).

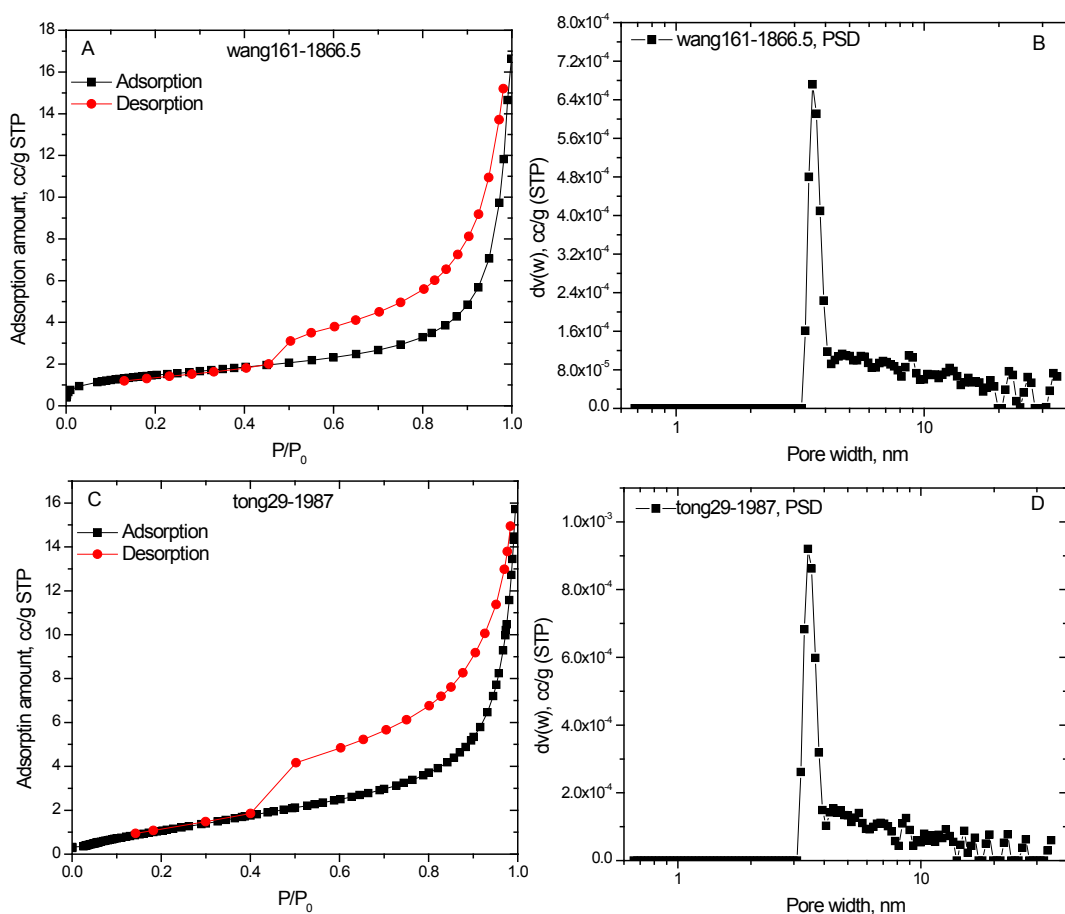


Figure 1: N₂ adsorption isotherms and pore size distribution of shales sampled from the Shahejie Formation, Dongying Depression, Shengli Oilfield

A) and C) Adsorption and desorption isotherms of N₂; B) and D) Corresponding PSD obtained from QSDFT method.

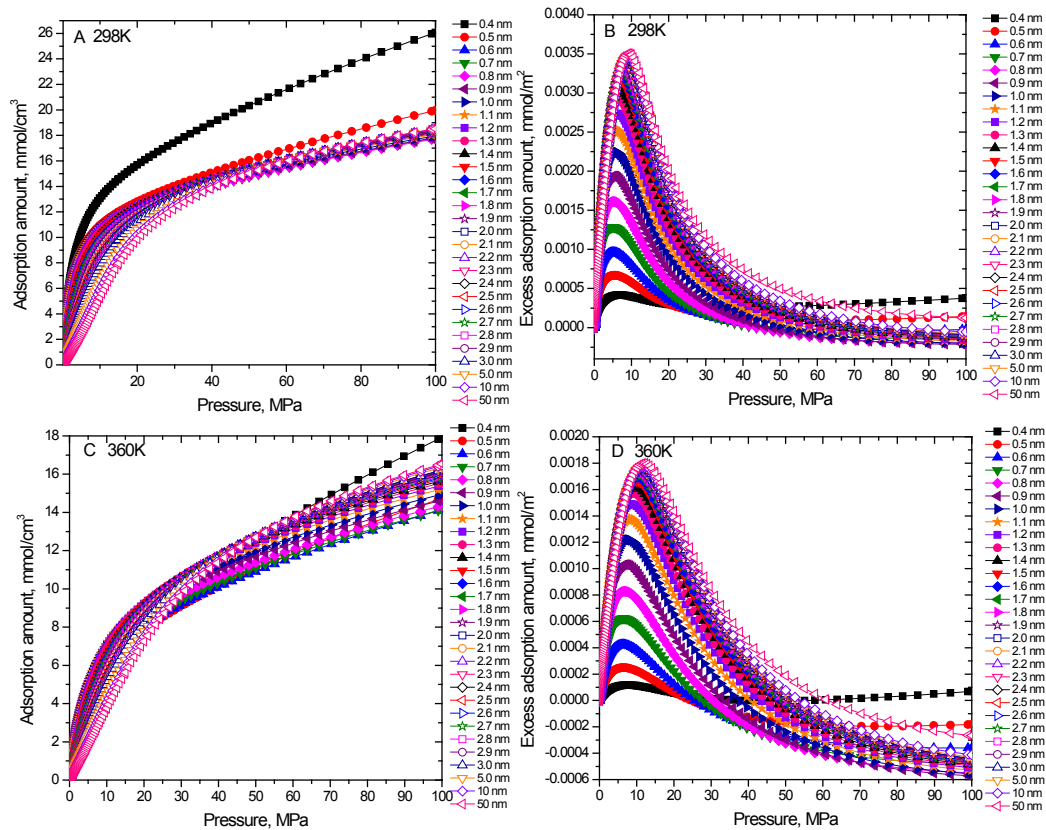


Figure 2 Adsorption isotherms of methane in pores of width from 0.5 to 50 nm.

A) and B) Isotherms of total adsorption and excess adsorption at 298 K, respectively; C) and D) Isotherms of total adsorption and excess adsorption at 360 K, respectively.

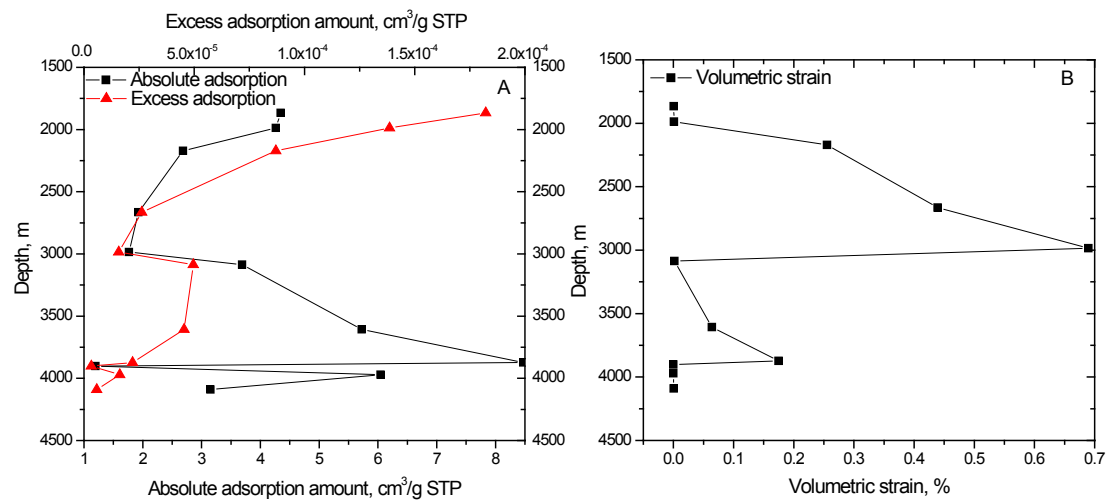


Figure 3 Adsorption amount and deformation of different shale samples at in-situ conditions

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