博士論文（要約）

Molecular Scale Simulation Study on Adsorption and Phase Behavior in Organic Nanopores of Unconventional Resources

(非在来型資源の有機物ナノ孔隙内の吸着と相挙動に関する分子スケールの数値計算研究)

曹　金栄

Unconventional resource development, such as shale gas and coalbed methane (CBM), is expected as a technique for realizing a sustainable society. Shale gas and CBM have some similarities in terms that the gas is stored in organic nanopores (for CBM only in micropores). In these organic nanopores, a substantial amount of hydrocarbon molecules is adsorbed. Previous studies have shown that the adsorbed gas accounts for a large portion (up to 85 %) in shale reservoirs, this may have a significant influence on production behavior.

In the oil and gas industry, the adsorption isotherm is often used to quantify the adsorption potential of a shale sample. Besides, the shape of the isotherm may give us insight into the pore structure of the shale sample. Different types of adsorption isotherms were found in experiments for shale samples from different fields. There is a need to understand factors affecting the gas adsorption behavior in nanopores and consequently the adsorption isotherm, which is difficult to be obtained only from experiments. The knowledge of gas adsorption behavior in organic nanopores is helpful to accurately estimate gas-in-place for shale gas resource assessment.

Despite great success in gas production from US shale gas reservoirs, the recovery factor of shale gas is usually less than 20%, and liquids or condensate less than 5-10% from shale reservoirs. A deeper understanding of the phase behavior of fluid systems in nanopores is required to help to enhance hydrocarbon recovery. The appearance of condensate (i.e. liquid phase) has a significant influence on shale gas production. Moreover, organic nanopores may have different selectivity (i.e. preferable adsorption) for different hydrocarbons for gas and liquid phases. So, better knowledge on the phase behavior of multicomponent hydrocarbon in narrow pore space will be helpful to answer: how condensate blocking develops and affects the shale gas well productivity, and how gas/oil ratio (GOR) and gas-oil (condensate) compositions vary during production for shale gas reservoirs.

CO_2 injection has been proposed to enhance hydrocarbon recovery from both shale and CBM reservoirs. Besides, CO_2 injection does not only enhance recovery but also proves to be a viable option to reduce greenhouse gas emissions. However, in the case of CO_2 enhanced CBM, this may result in the cleat closure of the coal seam due to the coal swelling after CO_2 adsorbed. Consequently, the permeability, CO_2 injectivity, and CH_4 production can be largely reduced.

In these organic nanopores of unconventional resources, such ambiguous phenomena still need to be understood and explained scientifically. The purpose of this study is to understand the adsorption and phase behavior in the nanopores of organic matters such as kerogen or coal matrix by molecular-scale simulation (Molecular Dynamics (MD) and grand canonical Monte Carlo (GCMC)), to obtain knowledge that is useful for assessing the resource amount and enhancing the recovery factor.

For these purposes, the following three items were conducted in this thesis: i) to quantify the adsorption potential of a shale sample, a new method was proposed to obtain CH_4 adsorption

isotherm in shale reservoir; ii) to more properly predict production behavior in shale reservoirs, phase behavior of binary mixture in nanopores was investigated from the molecular-scale by MC simulation; iii) to propose a new approach for enhanced CH_4 recovery from the coal seam, the recovery factor and coal swelling induced by CO_2, N_2, and CO_2–N_2 mixture injection was estimated using MD simulation.

MD simulation is a method to calculate the force acting on all atoms of the system, it is a technique to develop the coordinates of the particles time by solving the Newton equation. In this methodology, the system is described at the atomic scale and simulates the motions of all the atoms in the system to understand and predict the macroscopic properties of the system under desired conditions. Its time and spatial resolutions are about 1 femtosecond and 0.1 Å, respectively. This makes it suitable for analyzing molecular level phenomena, which is difficult to measure by experiments.

The MC simulation is used to sample configurations according to a statistical mechanical ensemble. In the MC simulation scheme, a Markov chain of molecular configurations is produced. The MC simulation method enables the use of certain ensembles specifically designed for computing phase equilibria (e.g. Gibbs ensemble) that are very difficult to simulate using molecular dynamics. For adsorption studies, a natural ensemble to use is the grand-canonical ensemble (or μ, V, T ensemble). In this ensemble, the temperature, volume, and chemical potential are fixed. The pressure is a function of the chemical potential. The temperature and chemical potential are imposed, and the number of particles is allowed to fluctuate during the simulation. This makes these simulations different from the conventional ensembles, where the number of molecules is fixed.

In Chapter 3, the CH_4 gas adsorption behavior in the kerogen nanopores of shale rocks was investigated. In previous studies from other researchers, it has been reported that the adsorption isotherm of CH_4 calculated by molecular-scale simulation considering the kerogen nanopores as simplified graphite nanopores, but the result showed that there is a weakness in the high-pressure region that the estimated CH_4 adsorbed amount is lower than the actual adsorbed amount. In this study, a more realistic kerogen nanopore system model was constructed, the CH_4 density distribution in these nanopores was calculated. It is classified into three zones in the nanopores, they are 1) free gas zone (the area where unadsorbed CH_4 exists), 2) CH_4 adsorption zone (the area where CH_4 is adsorbed at high concentration on the rough surface of kerogen), 3) CH_4 absorption zone (the area where CH_4 invades and exists in the micropores inside kerogen). Isotherm for adsorption of CH_4 was calculated based on these. Further, a new method was proposed to obtain the CH_4 adsorption isotherm in the shale reservoir by combining the adsorption isotherm for the kerogen nanopores with the pore size distribution and the total organic carbon of shale rock. By applying this method, the CH_4 adsorption isotherm of

Marcellus shale was appropriately predicted compared with the experimental data reported in the previous study.

Next, in Chapter 4, to understand the characteristics of the phase behavior of multi-component hydrocarbons in the shale reservoirs, the phase behavior of a CH_4/n-C_4H_{10} binary mixture in the nanopores was investigated by GCMC simulation. Here, a method for determining the dew point pressure and bubble point pressure in the nanopores has been constructed. Condensation phenomenon was observed due to the difference in adsorption selectivity of hydrocarbon molecules on nanopore surfaces in the molecular simulation, hence, the dew point pressure and bubble point pressure of hydrocarbon mixtures in the nanopores were shifted significantly. Both higher and lower bubble point pressures of CH_4/n-C_4H_{10} mixtures in nanopores than the bulk bubble point pressure were observed. The results also showed the retrograde condensation phenomenon (a phenomenon in which liquefaction progresses with the pressure drops). Due to the strong selectivity of n-C_4H_{10} in the vapor phase of the binary mixture, a narrower phase envelope is obtained. It is expected that these new findings will be valuable for interpreting the relationship between the adsorption selectivity of hydrocarbon molecules in nanopores and the production behavior of gas condensates in the shale field.

Finally, in Chapter 5, for the enhanced CH_4 recovery process by injecting CO_2, N_2, or CO_2-N_2 mixture into the coal matrix, the relationship between the swelling of coal matrix due to CO_2 adsorption, and permeability and CH_4 recovery factor decline due to swelling, were investigated by MD simulation. Here, it was shown that the injection of the CO_2-N_2 mixture is the best way to enhance the CH_4 recovery factor without causing a permeability decline due to the swelling of the coal matrix. A model of a coal matrix filled with CH_4 was constructed, and the CO_2 (N_2 or CO_2–N_2) molecules were added to a large-size fracture of the coal system. This system was equilibrated to investigate coal swelling and the CO_2 (N_2 or CO_2–N_2) – CH_4 replacement process. The number of CO_2 (N_2 or CO_2–N_2) molecules loaded in the coal matrix was used to determine the system was equilibrated. A long enough simulation was performed, to allow CO_2 (N_2 or CO_2–N_2) molecules enough time to enter the coal matrix and displace the CH_4 molecules. The calculated recovery factors were 79.9, 54.3, and 70.5% for CO_2, N_2, and CO_2–N_2 mixture injection, respectively. After equilibration, the specific volume (i.e. volume per unit mass) and thickness of the coal matrix were estimated and compared to those at the initial stage for estimation of the coal swelling. There is a swell of 12–17% in the pure liquid CO_2 injection. There are no swell in the pure N_2 case and CO_2–N_2 mixture case, shrinkage may be observed during N_2 injection and negligible during the CO_2–N_2 mixture injection. The permeability change was also estimated by using the coal matrix swell data. The swelling estimated by the specific volume for the pure CO_2 case is about 17%. Therefore, the estimated permeability will

drop to 0.4% of the original one. The reported porosity of the Yubari field has some uncertainty, but, if the natural fracture porosity of 0.4% was used, the cleat will be fully closed then. Apart from the micropores, the formation becomes almost impermeable. In conclusion, in the case of pure liquid CO_2, the permeability will reduce dramatically. In the case of pure N_2, it can be helpful to enhance the permeability. If carefully choose the CO_2–N_2 mixture, the permeability reduction may be avoided, while keeping enough high CH_4 recovery factor.

The feature of this thesis is that molecular-scale simulation techniques were applied to the evaluation of unconventional resources in which the phenomena in the nanopores greatly influence gas/liquid production behavior and recovery factor. In summary, a new method for predicting CH_4 adsorption isotherms for shale samples was proposed based on the MD simulation results, and they can be used in a table form in the history matching and production forecasting simulations in the future. For the phase behavior study, the selectivity of nanopores was evaluated and its influence on the phase behavior in nanopores was observed. This provides us an opportunity to explain the abnormal production data in shale reservoirs. The underlying mechanism of the swelling phenomenon and permeability decline during the CO_2 displacement was understood and a mixture of CO_2–N_2 mixture was suggested.