Review on the kerogen deformation mechanism

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Abstract. Shale gas is unconventional natural gas energy stored in shale, and is one of the important substitutes for conventional oil and gas resources. Since amorphous kerogen is the main component of shale organic matter and has a high degree of deformation ability, it is a key factor to improve shale gas recovery. As an emerging mining technology CS-EGR, the CO_2 injection method replaces the hydraulic pressure method, thereby alleviating the greenhouse effect and energy crisis. The basic understanding of the microscopic mechanism of the multicomponent competitive adsorption and diffusion of the adsorbate in kerogen will provide a theoretical basis and guidance for further understanding of kerogen deformation and further CS-EGR. Starting from the summary of experimental research, this paper systematically summarizes the kerogen model used for kerogen deformation research and discusses the effects of adsorbate, load, moisture, temperature, pressure, and geological depth on different kerogen structures of different maturity. The effect of kerogen deformation.

1 Introduction

With the rapid development of the social economy, the world is facing a shortage of energy, especially clean energy. Shale gas belongs to unconventional natural gas with the characteristics of low emission, large reserves, and high efficiency. The expansion of amorphous kerogen in rock reservoirs has an important impact on shale gas recovery. The composition of shale gas is multi-component alkanes dominated by CH_4, which mainly exist in kerogen and clay in an adsorbed state. As a soft nanoporous material, the coupling deformation leads to changes in pore structure, which in turn affects shale gas. The recovery factor [1]. A fundamental understanding of the microscopic mechanism of the competitive adsorption and diffusion of adsorbates in kerogen is crucial for gaining insight into kerogen deformation and further enhancing CS-EGR recovery.

Cui et al. [2] and Ross and Bustin [3] proposed the potential importance of shale adsorption-induced deformation in gas-bearing shale environments. Previously the traditional test tube expansion was the main experimental research method to study the expansion of kerogen. In recent years, Chen et al.[4] proposed that gas adsorption expansion may affect the gas flow in

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gas-bearing shale, and there is a strain hysteresis phenomenon in and out of CH_4. The results of Lu et al. [5] indicated that the expansion caused by supercritical CO_2 existed in the shale samples. Zhao et al. [6] studied the adsorption hysteresis of CO_2 and light hydrocarbons in shale and kerogen, and the results showed that the adsorption hysteresis of ethane, propane, n-butane, and isobutane was particularly high, reaching 30 Pa, and kerogen The reversible change in structure results in a significant hysteresis. Chen et al. [7] carried out CO_2, CH_4, and N_2 dynamic expansion experiments in organic-rich shale, and found that shale expansion is mainly composed of two parts, the strain caused by pore elasticity and the expansion strain caused by gas adsorption. The rate is positively correlated with the inhalation mass rate. Since shale gas reservoirs are complex heterogeneous geological environmental systems with high production conditions, it is very challenging to obtain accurate experimental data under laboratory conditions [8]. Molecular simulation can be used to study the coupled deformation mechanism of kerogen at the microscopic level and has received more and more attention in the past five years.

2 Models and methods

The kerogen molecular model is the basis for kerogen swelling simulations. In 2015, Ungerer et al. [9] selected 6 kerogen samples from the study by Kelemen et al. [10] A kerogen model was established based on the XPS and 13 C NMR experimental data of the given samples. And quantitatively predict its thermodynamic and bulk properties from quantum mechanics and molecular dynamics (MD). The obtained simulation results are consistent with the experimental data, and the model density is close to 1.2 g/cc. Zhao et al. [6] and Ho. [11] performed repeated experimental validation of the model and obtained a largely consistent density range. In addition, the semi-empirical molecular method MOPAC-PM7 designed by Stewart [12] was used to predict the thermodynamic properties of kerogen units in the ideal gas state and optimize the molecular geometry.

The structural units of kerogen IA, II-A, and III-A consist of $C_{251}H_{385}O_{13}N_7S_3$, $C_{252}H_{294}O_{24}N_6S_3$and $C_{233}H_{204}O_{27}N_4$, respectively. Ogkiongbo et al. [13] and Tomeček and Paluneok [14]. It is obtained from quantum mechanics that the kerogen formation enthalpy changes from low maturity to high maturity negative standard, which strongly proves that the model can be used for simulation experiments.

3 CH_4/CO_2 Adsorption and Kerogen deformation

In 2018, Tesson et al. [15] used MD-GCMC simulation to obtain that the adsorption capacity of methane in the flexible matrix was about 57% higher than that in the rigid matrix at different temperatures and pressures. Suggest a possible coupling between gas adsorption and structural deformation of the kerogen matrix, which also hints at the importance of considering matrix flexibility in molecular simulation studies.

To study the effect of pressure on kerogen deformation and adsorption properties, 2020 Zhang et al. [16] used GCMC simulation to study the pore deformation strain isotherm induced by the adsorption of CO in deformable carbon slit pores. The pressure reaches around 1000Pa but becomes apparent as the pressure increases further. When the pressure reaches 20 MPa, the deformation has a nonlinear relationship with the pressure. The deformation strain under the corresponding CO adsorption density was also investigated, the morphology was similar to the pressure deformation, and the deformation was nonlinearly related to the adsorption density.

4 Competitive adsorption of CO_2/N_2 and CH_4 in kerogen

In 2016, Sui et al. [8] showed that the volumetric strain expansion caused by CO_2 adsorption is larger than that caused by CH_4 adsorption. Both the adsorption expansion effect and the mechanical compression effect affect the volumetric strain and the two act in opposite directions. In 2018, Pathak et al. [17] further stated that kerogen that adsorbed the same number of CO_2 and methane molecules would expand more than methane. And Wu et al. [18] pointed out that under high-pressure conditions similar to subsurface conditions, the use of traditional models to calculate the absolute amount of adsorption for excess adsorption is flawed. It is suggested that the swelling effect may not be the only mechanism leading to the decreasing trend of pore volume, and the accessible pore volume effect needs to be considered. During kerogen separation, the pore structure may change, which may also lead to small deviations. To reduce experimental error, Zhang et al. [19] used GCMC simulations to study the effects of CO_2 and N_2 compositions in deformable organic micropores on CH_4 recovery. The results show that the CH recovery, CO_2 adsorption, and deformation all decrease with the increase in pore size. Huang et al. [20] further analyzed the contribution of the compression effect and adsorption effect. Compared with the induced deformation, IA < IIA < IIIA, the pressure compression effect is IA>IIA>IIIA, which is closely related to the flexibility of the kerogen unit. And simulating the geological depth shows that the geological depth effect includes pressure effect and temperature effect. Among them, the temperature effect leads to the reduction of volume strain, which plays a major role.

5 H_2O adsorption and kerogen deformation

2019 Huang et al. [1] compared the volume expansion with the molecular simulation results of Ho et al. [21] through the distribution of water molecules in different mature kerogen models. It was concluded that the adsorption capacity increased with increasing kerogen maturity and decreased with increasing moisture content. Afterward, a shale clay-kerogen nanocomposite with a heterogeneous pore structure was established, and the dynamic properties of pressure loss and fluid state during CO_2 storage were investigated using molecular simulation methods. The experimental results of [22] showed that the structural flexibility of kerogen has little effect on the free and adsorbed states of CH_4 and CO_2. And the flexibility of the kerogen structure greatly increases the dissolved state of CH_4 and CO_2, thereby improving the recovery rate of dissolved CH_4.

6 Conclusion

In recent years, natural gas production from shale formations has changed the world energy landscape, and CS-EGR has been proposed as a potential strategy for shale gas reservoirs to increase shale gas production while reducing CO_2 emissions. However, previous studies are based on the assumption that the kerogen structure is fixed, thus ignoring the dynamic properties of kerogen. According to the results of recent related articles, the volume deformation of kerogen is caused by a variety of factors, and it hurts shale gas. Mining and underground storage of CO_2 has had an impact. At the same time, it is known that the research of kerogen coupling deformation at the micro level is not a small challenge, and it is still in the preliminary stage.

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