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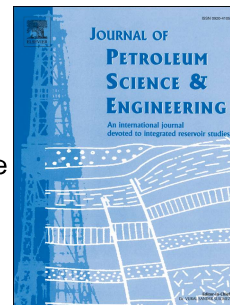
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# Accepted Manuscript

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# Development of a multi-continuum quadruple porosity model to estimate CO<sub>2</sub> storage capacity and CO<sub>2</sub> enhanced shale gas recovery

Minglu Wu<sup>\*a</sup>, Mingcai Ding<sup>b</sup>, Jun Yao<sup>a</sup>, Chenfeng Li<sup>c</sup>, Xuan Li<sup>a</sup>, Jiamin Zhu<sup>a</sup>

<sup>a</sup> School of Petroleum Engineering in China University of Petroleum, Qingdao 266580, China.

<sup>b</sup> School of Mathematics in Dalian University of Technology, Dalian 116024, China.

<sup>c</sup> College of engineering in Swansea University Bay Campus, Swansea SA1 8EN, UK.

## Abstract

Geologic storage of CO<sub>2</sub> in shale formation not only enhances natural gas recovery, but also sequesters CO<sub>2</sub> effectively. According to this technology, a multi-continuum quadruple porosity binary component gas model is developed to investigate carbon dioxide storage capacity and CO<sub>2</sub> enhanced shale gas recovery, which is based on multiple flow mechanisms, including dissolution, adsorption/desorption, viscous flow, diffusion, slip flow and stress sensitivity of hydraulic fractures. This fully coupled model is divided into quadruple media, including organic matters, organic pore system, matrix system and natural fracture system. The matrix-fracture transfer flow is simulated by modified multiple interacting continua (MINC) method. Embedded discrete fracture model (EDFM) is introduced to describe the gas flow in hydraulic fractures and the transfer flow between hydraulic fractures and natural fractures. Finite difference method (FDM) and quasi-Newton iterative method are applied to solve this model. The reliability and practicability of this model is validated by matching the production history of a fractured horizontal well in shale gas reservoir. The effects of relevant parameters on production curves are analyzed, including adsorption parameters, dissolution parameters, well production pressure, injection pressure, volumetric fraction of kerogen and injection opportunity. The result shows that the model in this work is reliable and practicable, and the model presented here can be used to investigate the injectivity of CO<sub>2</sub> and CO<sub>2</sub> enhanced shale gas recovery.

**Keywords:** CO<sub>2</sub> storage; enhanced shale gas recovery; multiple flow mechanisms; quadruple porosity model; fractured horizontal well

## 1. Introduction

Shale gas is one of unconventional resources, its economic and efficient development can effectively meet people's demand for clean energy and solve the current energy shortage problem. Due to ultra-low permeability of shale formation, shale gas is hard to be exploited by conventional technologies, so that horizontal drilling and formation fracturing techniques were used to exploit shale gas. The induced fractures created by the fracturing increase the shale permeability around the horizontal well and improve the final shale gas cumulative production (Wu, Moridis et al. 2009, He, Teng et al. 2016, Wu, Ding et al. 2017).

According to previous studies, shale gas stores at different pores, which include organics or bitumen with dissolved gas (Javadpour, Fisher et al. 2007, Javadpour 2009), the surface of kerogen and clays with adsorbed gas (Liu, Xiao et al. 2015, He, Teng et al. 2016), matrix pores and natural fractures with free gas. Porous kerogen, with huge specific surface area, has been proved to be

ideal storage space for shale gas, and gas in kerogen mainly composed of free gas in organic pores, adsorbed gas on the wall of kerogen bulk and dissolved gas in organic matter. However, the dissolution of kerogen is usually neglected in most models for shale gas reservoir. In fact, the dissolution capacity of bitumen and organics has been proved to be quite considerable (Svrcek and Mehrotra 1982, Swami and Settari 2012). The solubility coefficient of  $\text{CH}_4$  in bitumen of kerogen can reach up to  $1.43 \times 10^{-6} \text{ m}^3/\text{Pa}/\text{m}^3$  and the diffusion coefficient of dissolved gas in organics can arrive at  $10^{-20} \text{ m}^2/\text{s}$  (He, Teng et al. 2016). Therefore, dissolution of gas in shale gas reservoir cannot be ignored. Due to the complex pore structure and unique gas storage mode, the flow of gas in the shale formation follows multiple mechanisms, including adsorption/desorption, dissolution, diffusion, slip flow and viscous flow (He, Teng et al. 2016). During horizontal well production, the free gas in natural fractures and hydraulic fractures comes out first, and follows the slip flow and viscous flow. Then the free gas in matrix pores transfer into natural fractures. And then the adsorbed gas desorbs from the surface of organics and inorganics when the pressure falls below adsorption pressure. Lastly, the dissolved gas in organic matter diffuses into kerogen pores when pressure drops, on the contrary, gas dissolves in organic matter if pressure rises.

In another hand,  $\text{CO}_2$  capture and storage (CCS) is regarded as a promising method to cut down  $\text{CO}_2$  emissions, which can lighten global warming significantly. Geologic storage of  $\text{CO}_2$  in shale formation is one of feasible options to sequester  $\text{CO}_2$ , which can reduce the CCS costs by using the facilities for shale gas exploitation. Moreover, injectivity of  $\text{CO}_2$  into shale formation can enhance shale gas recovery, which is mainly due to the following three reasons. Firstly, the injection of  $\text{CO}_2$  allows the formation to be re-pressurized with the injected gas, which can promote the flow ability of natural gas. In addition,  $\text{CO}_2$  displaces  $\text{CH}_4$  since the shale has a stronger affinity for carbon dioxide than for methane during competitive absorption between  $\text{CO}_2$  and  $\text{CH}_4$  (Kang, Fathi et al. 2011, Sun, Yao et al. 2013, Heller and Zoback 2014, Edwards, Celia et al. 2015, Gallo and Carballo 2016). The experimental results of Kang, Fathi et al. (2011) show that the amount of  $\text{CO}_2$  adsorption was five to ten times greater than the amount of  $\text{CH}_4$  adsorption in the same gas shale. Lastly, carbon dioxide in shale formation not only stored in free and adsorbed state, but also can be dissolved in organic matters (Svrcek and Mehrotra 1982, Swami and Settari 2012), which leads to more dissolved natural gas displaces from organic matter by  $\text{CO}_2$ . Therefore, it is significant to investigate the storage capacity of  $\text{CO}_2$  and  $\text{CO}_2$  enhanced natural gas recovery. However, accurate reservoir simulation of shale gas mining and  $\text{CO}_2$  storage is very difficult due to the ultra-low permeability, complex pore structure, multiple storage mode and multiple flow mechanisms.

In order to investigate the injectivity of  $\text{CO}_2$  and  $\text{CO}_2$  enhanced shale gas recovery, many semi-analytical and numerical models were proposed. The semi-analytical models, based on source function, can solve the pressure and rate solution efficiently. The previous studies (Chen, Liao et al. 2015, Gallo and Carballo 2016, Xiao, Tian et al. 2016) introduced pressure transient analysis (PTA) and rate transient analysis (RTA) to estimate the storage capacity of  $\text{CO}_2$  in depleted shale gas reservoir. However, these semi-analytical models have far more limitations when they are used to simulate geologic storage of  $\text{CO}_2$  in shale formation, the main reasons are as follows. In one hand, numerous simplifications were made in these models to solve the strong nonlinear equations, which enlarges the error between the calculated result and the real data. In another hand, the storage of carbon dioxide in shale reservoirs contains lots of complex mechanisms, including multiple component flow, porous flow, competitive absorption and

dynamic operation of wells. Thus, it is difficult to use these semi-analytical models to investigate the injectivity of CO<sub>2</sub> into shale gas reservoir.

In recent years, numerous multiple component numerical models (Sun, Yao et al. 2013, Jiang, Shao et al. 2014, Boosari, Aybar et al. 2015, Edwards, Celia et al. 2015, Merey and Sinayuc 2016, Kim, Cho et al. 2017, Xu, Zeng et al. 2017) were established to simulate the storage of CO<sub>2</sub> in shale gas reservoirs. Sun, Yao et al. (2013) proposed a dual-porosity model to investigate the CO<sub>2</sub> sequestration in shale gas reservoirs, in which, multiple binary gas transport mechanisms, including viscous flow, Knudsen diffusion and ordinary diffusion, were considered. However, the multiple fractured horizontal well, as the only effective exploration way can be used now in most ultra-low permeability shale gas reservoirs, has not been used to study enhancement of natural gas recovery or injectivity of CO<sub>2</sub> in their model. Jiang, Shao et al. (2014) developed a multi-continuum multi-component simulator to investigate CO<sub>2</sub> storage in shale gas reservoirs, which incorporates multiple mechanisms and considers the complex fracture network around the fractured horizontal well in shale reservoirs. Multiple interacting continua (MINC) method was applied to simulate the fluid migration between matrix and natural fractures, in addition, embedded discrete fracture model (EDFM) was used to describe the flow in hydraulic fractures the transfer flow between hydraulic fractures and MINC elements. However, the dissolution of CO<sub>2</sub> and CH<sub>4</sub> in organic matter was ignored in their model, which is one of important storage modes in shale gas reservoirs as discussed above. Moreover, they haven't considered the fluid flow in stimulated reservoir volume (SRV) around fractured horizontal well, which has been proved to be very important to improve final cumulative gas production and recovery of fractured shale gas reservoirs. Edwards, Celia et al. (2015) established a one-dimension linear flow model to estimate CO<sub>2</sub> injection and storage capacity for geological sequestration in shale gas reservoirs, and excess adsorption of CO<sub>2</sub> and CH<sub>4</sub> was considered. Obviously, it's difficult to use one-dimension linear flow model to describe the fluid migration in shale formation with complex pore structure. Xu, Zeng et al. (2017) proposed a triple-porosity dual permeability model to assess the feasibility of CO<sub>2</sub> enhanced shale gas recovery and CO<sub>2</sub> storage capacity, which considering binary component and multiple flow mechanism. However, dissolution of organic matter and SRV were also ignored in their study.

In light of the questions discussed above, this paper presented a fully coupled multi-continuum quadruple porosity binary component gas model to investigate CO<sub>2</sub> enhanced shale gas recovery and CO<sub>2</sub> storage capacity in shale formation. The structure of this paper is as follows. In first section, according to the multiple storage mode and multiple pore structure of shale gas reservoir with multiple fractured horizontal well (MFHW), the physical model of multi-continuum quadruple porosity shale gas reservoir was developed. In second section, On the basis of the physical model, the mathematical model was established, and which was solved by difference method (FDM) and quasi-Newton iterative method. In third section, the calculated result of this model was validated by field data. In the last section, the sensitivity of several main parameters was analyzed.

## 2. Physical model

According to previous study (He, Teng et al. 2016), the gas shale contains organic matters, organic pores, matrix pores and natural fractures. The gas stored in shale formation composed by three states gas, including dissolved gas in organic matters (Javadpour, Fisher et al. 2007,

Javadpour 2009). adsorbed gas on the surface of organics and clays and free gas stored in organic pores, matrix pores and natural fractures. Horizontal drilling and formation fracturing techniques are used to exploit shale gas, and several main fractures and fracture networks are created after hydraulic fracturing. The region interconnected by moderate conductivity fracture networks is defined as stimulated reservoir volume (SRV), which is marked in blue in Fig. 1. The zone that has not been influenced by fracturing is defined as un-stimulated reservoir volume (USRV), which is marked in black in Fig. 1.

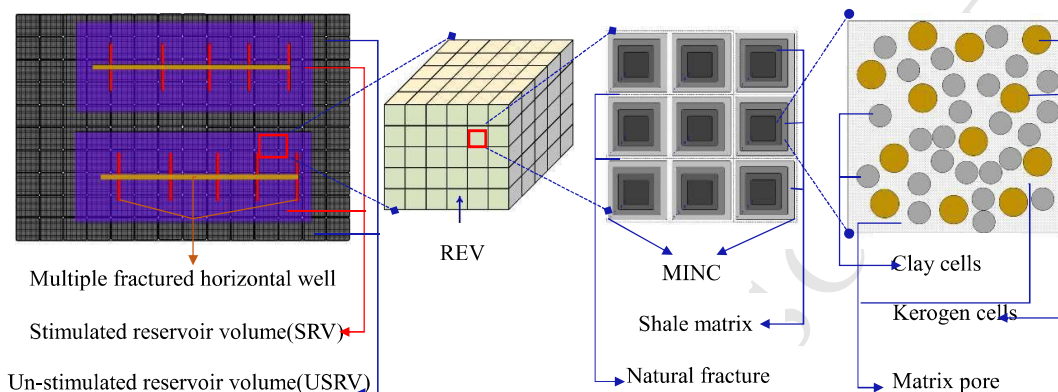


Fig. 1. Schematic diagram of a multi-continuum quadruple-porosity model for shale gas reservoirs.

As is shown in Fig. 1, a coupled multi-continuum quadruple porosity model is presented. The region marked in blue is the SRV, which can be simulated by quadruple-medium model, including natural fractures, matrix system, clay cells and kerogen cells. Because of the ultra-low permeability of shale matrix, the conventional dual-continuum model cannot be applicable to simulate the transfer flow between natural fracture and shale matrix any more, fortunately, multiple interacting continua (MINC) method can effectively be used to investigate the matrix-fracture transfer flow. Thus, a coupled multi-continuum quadruple porosity model is used to study the storage and transport mechanisms. In SRV, each representative elementary volume (REV) is divided into finite MINC elements, and each MINC element is divided into a series of nested sub-elements; each sub-element denotes different calculation element; the outer nested cell is natural fracture and the inner nested cell is matrix cells; clay cells and kerogen cells are contained in every nested cell. The region marked in black is the USRV, which can be simulated by triple porosity model, including matrix system, clay cells and kerogen cells.

The other assumptions of this proposed model are listed as follows:

(1) The dissolution of dissolved gas in organic matters obeys the Henry's law (Svrcek and Mehrotra 1982, Swami and Settari 2012), and the dissolved gas transport in organics can be driven by pressure difference diffusion, Knudsen diffusion and surface diffusion.

(2) The adsorption/desorption of each component gas on the surface of kerogen and clays follows Langmuir isothermal adsorption law, and different adsorption constant are considered for kerogen and clays, respectively.

(3) CO<sub>2</sub> is mixed with CH<sub>4</sub> immediately, and the miscible time can be neglected.

(4) All hydraulic fractures fully penetrate the shale formation. Shale gas and carbon dioxide enter the horizontal wellbore only through hydraulic fractures from perforation location. Gas in matrix system and natural fracture system consists of compressed gas and adsorbed gas. The flow of gas in natural fracture system in SRV and the gas in matrix system in USRV obeys Darcy's law.

The effects of gravity and capillary pressure are neglected.

### 3. Mathematical model

#### 3.1. Formulation of gas diffusion in kerogen cells

As discussed in model assumption, gas in kerogen cells consists of the free gas stored in kerogen pores, the adsorbed gas on the surface of organic pores and the dissolved gas in organic matters. Thus, the mass conservation equation of kerogen can be expressed as

$$\frac{\partial}{\partial t} \left[ f_k \phi_k \rho_{gki} + f_k (1 - \phi_k) q_{\text{adk},i}^c + f_k (1 - \phi_k) q_{\text{d},i} \right] - q_i^{\text{m-k}} = -\nabla \cdot (\rho_{gki} v_{gki}), i = 1, 2 \quad (1)$$

In which,  $\rho_{gki}$  is the gas density of component  $i$  in kerogen cells,  $\text{kg/m}^3$ ;  $v_{gki}$  denotes the gas flow velocity of component  $i$  in kerogen cells,  $\text{m/s}$ ;  $\phi_k$  is porosity of kerogen, fraction;  $q_{\text{adk},i}^c$  denotes the amount of component  $i$  remaining adsorbed on the surface of kerogen,  $\text{kg/m}^3$ ;  $q_{\text{d},i}$  denotes the amount of component  $i$  remaining dissolved in organic matters,  $\text{kg/m}^3$ ;  $q_i^{\text{m-k}}$  denotes mass rate of kerogen-matrix transfer flow,  $\text{kg/m}^3$ ; Subscript  $i$  refers to the gas species, with  $i=1$  for methane and  $i=2$  for carbon dioxide.

The migration of gas in kerogen cells can be driven by pressure difference diffusion, Knudsen diffusion and surface diffusion(Cao, Liu et al. 2017), and the total diffusivity related to pressure in kerogen system can be defined as

$$D_i = D_{\text{p},i} + D_{\text{kn},i} + D_{\text{surf},i}, i = 1, 2 \quad (2)$$

where  $D_{\text{p},i}$  represents pressure driven diffusivity of component  $i$ ,  $\text{m}^2/\text{s}$ ;  $D_{\text{kn},i}$  denotes the effective Knudsen diffusivity of component  $i$  in kerogen cells,  $\text{m}^2/\text{s}$ ;  $D_{\text{surf},i}$  is the surface diffusion coefficient of adsorbed gas in kerogen cells,  $\text{m}^2/\text{s}$ .

According to previous study(Cao, Liu et al. 2017), the apparent permeability for kerogen cells can be obtained by total diffusion coefficient, expressed as

$$k_{\text{ka},i} = \frac{D_i \mu_g}{p_k}, i = 1, 2 \quad (3)$$

In which,  $k_{\text{ka},i}$  denotes the apparent permeability for kerogen cells,  $\mu\text{m}^2$ ;  $\mu_g$  represents gas viscosity,  $\text{mPa}\cdot\text{s}$ ;  $p_k$  is the pressure in kerogens cells,  $\text{MPa}$ .

The motion equation can be derived from Darcy's law, given as

$$v_{gki} = -\frac{k_{\text{ka},i}}{\mu_g} \nabla p_k, i = 1, 2 \quad (4)$$

Given the mole fraction of  $\text{CH}_4$  in the bulk gas, the mole fraction of  $\text{CO}_2$  is easily calculated since the two components satisfy the following equation, shown as

$$\omega_1 + \omega_2 = 1 \quad (5)$$

where  $\omega_1$  and  $\omega_2$  are the mole fraction of  $\text{CH}_4$  and  $\text{CO}_2$ , respectively.

The mole fraction of component  $i$  can be expressed by the concentration of each component gas, given as

$$\omega_i = \frac{C_i}{C_1 + C_2}, i = 1, 2 \quad (6)$$

where  $C_1$  and  $C_2$  are the molarity of  $\text{CH}_4$  and  $\text{CO}_2$ , respectively.

According to the state equation, the partial pressure of each component gas can be obtained(Sun, Yao et al. 2013, Xu, Zeng et al. 2017), expressed as

$$p_i = p\omega_i = C_i Z_g RT, i = 1, 2 \quad (7)$$

In which,  $Z_g$  denotes the compressibility factors of mixture gas, the details is presented in previous studies(Jiang, Shao et al. 2014, Kim, Cho et al. 2017).

As is shown in Fig.1, the kerogen cells are embedded in matrix system, so, we need to simulate the transfer flow between matrix and kerogen cells. In this study, kerogen cells act as mass source in the multi-continuum quadruple porosity model. the transfer flow between matrix and kerogen can be simulated by the dual porosity model(Warren and Root 1963).The mass rate of kerogen-matrix transfer flow  $q_i^{\text{m-k}}$ ,  $\text{kg/m}^3$ , can be expressed as

$$q_i^{\text{m-k}} = C_{k,i} M_i \frac{\alpha k_{ka,i}}{\mu_g} (p_m - p_k), i = 1, 2 \quad (8)$$

$C_{k,i}$  denotes molarity of component  $i$  in the kerogen,  $\text{mol/m}^3$ ;  $M_i$  is molar mass of component  $i$ , fraction; According to previous studies(Sun, Yao et al. 2013, Jiang, Shao et al. 2014), competitive absorption between  $\text{CO}_2$  and  $\text{CH}_4$  exists in two gas components system, and the binary component Langmuir model can be used to estimate adsorption of each component, given as

$$q_{\text{adk},i} = \frac{\rho_k M_i}{V_{\text{std}}} \frac{V_{\text{Lk},i} p_i B_{ki}}{1 + \sum_j^2 p_j B_{kj}} = \frac{\rho_k M_i}{V_{\text{std}}} \frac{V_{\text{Lk},i} B_{ki} C_{k,i} Z_g RT}{1 + \sum_{j=1}^2 C_{k,j} B_{kj} Z_g RT}, i = 1, 2 \quad (9)$$

In which,  $B_{ki}$  represents the inverse of Langmuir pressure of component  $i$  ( $B_{ki} = p_{L,i}$ ),  $\text{MPa}^{-1}$ .  $V_{\text{std}}$  is the molar volume at standard condition,  $\text{sm}^3/\text{mol}$ ;  $\rho_k$  denotes the density of kerogen,  $\text{kg/m}^3$ ;  $V_{\text{Lk},i}$  denotes the Langmuir volume constant of component  $i$  for kerogen system,  $\text{sm}^3/\text{kg}$ ;  $p_1$  and  $p_2$  are the partial pressures of  $\text{CH}_4$  and  $\text{CO}_2$ , respectively.

In fact, the concept of “excess adsorption” is usually used in adsorption measurements. Excess adsorption is the mass of gases stored in porous medium with adsorption in excess of the mass that would be stored if there were no adsorption at a given gas density (Edwards, Celia et al. 2015). Thus, the excess adsorption of component  $i$  can be formulated as

$$q_{\text{adk},i}^e = q_{\text{adk},i} \left( 1 - \frac{\rho_{gi}}{\omega_i^a \rho_a} \right), i = 1, 2 \quad (10)$$

where  $\rho_a$  denotes density of adsorption,  $\text{kg/m}^3$ , which is assumed to be constant and estimated from experimental excess adsorption data(Weniger, Kalkreuth et al. 2010);  $\omega_i^a$  is adsorbed mass fraction of component  $i$ , given as

$$\omega_i^a = \frac{q_{\text{ad},i}}{q_{\text{ad},1} + q_{\text{ad},2}}, i = 1, 2 \quad (11)$$

Thus, the competitive excess absorption between  $\text{CO}_2$  and  $\text{CH}_4$  can be expressed as



$$q_{\text{adk},i}^e = \frac{\rho_k M_i}{V_{\text{std}}} \frac{V_{\text{Lk},i} B_{ki} C_{k,i} Z_g RT}{1 + \sum_{j=1}^2 C_{k,j} B_{kj} Z_g RT} \left[ 1 - \frac{C_{k,i} M_i}{\rho_a} \left( 1 + \frac{M_j C_{k,j} V_{\text{Lk},j} B_{kj}}{M_i C_{k,i} V_{\text{Lk},i} B_{ki}} \right) \right], i, j = 1, 2 (i \neq j) \quad (12)$$

The amount of component  $i$  remaining dissolved in organic matters in kerogen can be obtained by Henry's law (Swami and Settari 2012, He, Teng et al. 2016), expressed as

$$q_{\text{d},i} = k_{\text{H},i} p_{k,i} = k_{\text{H},i} C_{k,i} Z_g RT, i = 1, 2 \quad (13)$$

In which,  $k_{\text{H},i}$  denotes solubility coefficient,  $\text{m}^3/(\text{Pa} \cdot \text{m}^3)$ .

Combining Eq. (6) ~ Eq. (9), the governing equation of component  $i$  in kerogen cells can be obtained, expressed as

$$\begin{aligned} & \frac{\partial}{\partial t} \left\{ f_k (1 - \phi_k) \frac{\rho_k M_i}{V_{\text{std}}} \frac{V_{\text{Lk},i} B_{ki} C_{k,i} Z_g RT}{1 + \sum_{j=1}^2 C_{k,j} B_{kj} Z_g RT} \left[ 1 - \frac{C_{k,i} M_i}{\rho_a} \left( 1 + \frac{M_j C_{k,j} V_{\text{Lk},j} B_{kj}}{M_i C_{k,i} V_{\text{Lk},i} B_{ki}} \right) \right] \right\} \\ & + \frac{\partial}{\partial t} \left[ f_k \phi_k M_i C_{k,i} + f_k (1 - \phi_k) k_{\text{H},i} C_{k,i} Z_g RT \right] \\ & = \nabla \cdot \left( C_{k,i} M_i \frac{k_{\text{ka},i}}{\mu_g} \nabla p_k \right) + q_i^{\text{m-k}}, i, j = 1, 2 (i \neq j) \end{aligned} \quad (14)$$

According to previous studies (Wilke 1950, Wu, Moridis et al. 2009), the viscosity values of mixture gas can be calculated by mole fraction and molar mass of each component gas, shown as

$$\mu_g = \sum_{i=1}^2 \frac{\mu_i}{1 + \frac{1}{\omega_i} \sum_{j=1, j \neq i}^2 \omega_j \varphi_{i,j}} \quad (15)$$

where  $\varphi_{i,j}$  can be expressed as

$$\varphi_{i,j} = \frac{\left[ 1 + (\mu_i / \mu_j)^{0.5} (M_j / M_i)^{0.25} \right]^2}{(4 / \sqrt{2}) \left[ 1 + (M_i / M_j) \right]^{0.5}} \quad (16)$$

### 3.2. Formulation of gas flow in matrix system

In USRV, gas in matrix system exists as adsorbed gas and free gas. The matrix pores are much larger than the organic pores, therefore, the surface diffusion of adsorbed gas on the surface of the clays can be ignored. Similar with the derivation in kerogen cell, the governing equation for gas flow in matrix system can be expressed as

$$\frac{\partial}{\partial t} \left[ (1 - f_k) \phi_m M_i C_{m,i} + (1 - f_k) (1 - \phi_m) q_{\text{adc},i}^e \right] = \nabla \cdot \left( \frac{k_m}{\mu_g} M_i C_{m,i} \nabla p_m \right) + q_i^{\text{m-k}}, i = 1, 2 \quad (17)$$

where  $C_{m,i}$  denotes molarity of component  $i$  in the matrix system,  $\text{mol}/\text{m}^3$ ;  $\phi_m$  is porosity of matrix system, fraction;  $p_m$  represents the gas pressure in matrix system, MPa;  $M_i$  is molar mass of component  $i$ ;  $q_{\text{adc},i}^e$  denotes the amount of component  $i$  remaining absorbed on the surface of clays;

For clays in matrix system, the dual-component excess adsorption model can be used to

estimate the content of adsorption for each component gas, given as

$$q_{\text{adc},i}^e = \frac{\rho_c M_i}{V_{\text{std}}} \frac{V_{\text{Lc},i} B_{ci} C_{m,i} Z_g RT}{1 + \sum_{j=1}^2 C_{m,j} B_{cj} Z_g RT} \left[ 1 - \frac{C_{m,i} M_i}{\rho_a} \left( 1 + \frac{M_j C_{m,j} V_{\text{Lc},j} B_{cj}}{M_i C_{m,i} V_{\text{Lc},i} B_{ci}} \right) \right], i, j = 1, 2 (i \neq j) \quad (18)$$

Thus, the governing equation of component  $i$  in matrix in USRV can be obtained, expressed as

$$\begin{aligned} & \frac{\partial}{\partial t} \left\{ \frac{\rho_c M_i}{V_{\text{std}}} \frac{V_{\text{Lc},i} B_{ci} C_{m,i} Z_g RT}{1 + \sum_{j=1}^2 C_{m,j} B_{cj} Z_g RT} \left[ 1 - \frac{C_{m,i} M_i}{\rho_a} \left( 1 + \frac{M_j C_{m,j} V_{\text{Lc},j} B_{cj}}{M_i C_{m,i} V_{\text{Lc},i} B_{ci}} \right) \right] \right\} \\ & + \frac{\partial}{\partial t} [(1 - f_k) \phi_m M_i C_{m,i}] - q_i^{\text{m-k}} = \nabla \cdot \left( \frac{k_m}{\mu_g} M_i C_{m,i} \nabla \cdot p_m \right), i = 1, 2 (i \neq j) \end{aligned} \quad (19)$$

In SRV, matrix system was taken as source to apply liquid to natural fracture. As discussed in assumption above, the multiple interacting continua (MINC) method was used to simulate the transfer flow between matrix and natural fracture. As shown in Fig. 1, MINC element is divided into a series of nested sub-elements, and transfer flow exists between two adjacent sub-elements. The transfer flow rate can be calculated by following equation (Pruess and Narasimhan 1982, Pruess 2010), given as

$$q_{m,i}^{l,l+1} = \sigma A_{l,l+1} \left( \frac{k_m}{\mu_g} M_i C_{m,i,l}^{n+1} \frac{p_{m,i,l+1}^{n+1} - p_{m,i,l}^{n+1}}{d_{l,l+1}} \right) \quad (20)$$

$$q_{m,i}^{l,l-1} = \sigma A_{l,l-1} \left( \frac{k_m}{\mu_g} C_{m,i,l}^{n+1} M_i \frac{p_{m,i,l-1}^{n+1} - p_{m,i,l}^{n+1}}{d_{l,l-1}} \right) \quad (21)$$

In which,  $V_l$  is the volume of MINC sub-element  $l$ ,  $\text{m}^3$ ;  $A_{l,l+1}$  donates the area of interface between element  $l$  and  $l+1$ ,  $\text{m}^2$ ;  $d_{l,l+1}$  donates the distance from element  $l$  to element  $l+1$ ,  $\text{m}$ ; the details can be found in previous study (Pruess and Narasimhan 1982, Pruess 2010, Jiang, Shao et al. 2014).  $\sigma$  is the number of elements contained in  $V_m$ , which is

$$\sigma = \frac{V_m}{L^3} \quad (22)$$

where  $V_m$  is the volume of arbitrary a representative elementary volume (REV),  $\text{m}^3$ ;  $L$  is the scale of MINC element,  $\text{m}$ .

Then the discretized governing equation of component  $i$  of sub-element  $l$  can be expressed as

$$\begin{aligned} & \frac{V_l}{\Delta t} \left\{ \frac{\rho_c M_i}{V_{\text{std}}} \frac{V_{\text{Lc},i} B_{ci} C_{m,i} Z_g RT}{1 + \sum_{j=1}^2 C_{m,j} B_{cj} Z_g RT} \left[ 1 - \frac{C_{m,i} M_i}{\rho_a} \left( 1 + \frac{M_j C_{m,j} V_{\text{Lc},j} B_{cj}}{C_{m,i} M_i V_{\text{Lc},i} B_{ci}} \right) \right] \right\}^{n+1} \\ & - \frac{V_l}{\Delta t} \left\{ \frac{\rho_c M_i}{V_{\text{std}}} \frac{V_{\text{Lc},i} B_{ci} C_{m,i} Z_g RT}{1 + \sum_{j=1}^2 C_{m,j} B_{cj} Z_g RT} \left[ 1 - \frac{C_{m,i} M_i}{\rho_a} \left( 1 + \frac{M_j C_{m,j} V_{\text{Lc},j} B_{cj}}{C_{m,i} M_i V_{\text{Lc},i} B_{ci}} \right) \right] \right\}^n \\ & + \frac{V_l}{\Delta t} [(1 - f_k) \phi_m M_i C_{m,i}]_l^{n+1} - \frac{V_l}{\Delta t} [(1 - f_k) \phi_m M_i C_{m,i}]_l^n \\ & = q_{m,i}^{l,l+1} + q_{m,i}^{l,l-1}, i = 1, 2 (i \neq j) \end{aligned} \quad (23)$$

### 3.3. Formulation of gas flow in natural fractures

The permeability of natural fractures is much larger than the matrix system and kerogen system, the main migration mechanism in natural fractures is viscous flow, so the diffusion can be neglected. Then, the governing equation for the dual component mixture gas flow in natural fractures can be obtained, expressed as

$$\frac{\partial}{\partial t}(\phi_f C_{f,i} M_i) = \nabla \cdot \left( \frac{k_f}{\mu_g} C_{f,i} M_i \nabla p_f \right) + q_i^{\text{conn}}, i = 1, 2 \quad (24)$$

where  $q_i^{\text{conn}}$  denotes gas flow rate between matrix and natural fractures, m<sup>3</sup>/s, which can be calculated by Eq. (20) because natural fractures are located at the outer of nested cell of MINC element.

According to previous study(Zhu, Yao et al. 2016), permeability sensitivity should be considered in natural fracture because they are un-propped, and the natural fracture permeability can be expressed as a function of initial fracture permeability  $k_f^0$ , the permeability modulus of natural fracture  $\gamma$  and the pressure in natural fracture  $p_h$ , which is

$$k_f = k_f^0 e^{-\gamma(p_f - p_0)} \quad (25)$$

In which,  $k_f^0$  is the absolutely permeability,  $\mu\text{m}^2$ ;  $b_k$  is the Klingenberg factor, MPa.

Then the governing equation of component  $i$  in natural fractures can be presented as Eq. (26).

$$\frac{\partial}{\partial t}(\phi_f M_i C_{f,i}) = \nabla \cdot \left[ \frac{M_i k_f^0}{\mu_g} e^{-\gamma(p_f - p_0)} C_{f,i} \nabla p_f \right] + q_i^{\text{conn}}, i = 1, 2 \quad (26)$$

### 3.4. Formulation of gas flow in hydraulic fracture

The hydraulic fracture created by fracturing, enlarged the contact area of horizontal well and shale formation, is the ideal gas channel around horizontal well. Combing gas motion equation, gas state equation and continuity equation, the governing equation of hydraulic fractures can be derived, presented as

$$\frac{\partial}{\partial t}(\phi_h C_{h,i} M_i) = \nabla \cdot \left( \frac{k_h}{\mu_g} C_{h,i} M_i \nabla p_h \right), i = 1, 2 \quad (27)$$

where  $C_{h,i}$  denotes molarity of component  $i$  in hydraulic fracture, mol/m<sup>3</sup>;  $\phi_h$  is porosity of hydraulic fracture, fraction;  $p_h$  denotes the gas pressure in hydraulic fracture, MPa;  $k_h$  is permeability of hydraulic fracture,  $\mu\text{m}^2$ ;

The Knudsen number for the gas flow in hydraulic fractures is in the high Knudsen number regime(Xu, Zeng et al. 2017), so the slip flow for gas in hydraulic fractures should be considered, which also is called Klingenberg effect, given as

$$k_h = k_\infty \left( 1 + \frac{b_k}{p_h} \right) \quad (28)$$

where  $p_0$  is the initial pressure of shale reservoir, MPa. Then the governing equation of hydraulic fracture can be presented as

$$\frac{\partial}{\partial t}(\phi_h M_i C_{h,i}) = \nabla \cdot \left[ \frac{M_i k_\infty}{\mu_g} \left( 1 + \frac{b_k}{p_h} \right) C_{h,i} \nabla p_h \right], i = 1, 2 \quad (29)$$

### 3.5. Numerical solution

Finite difference method (FDM) was used to solve this fully coupled multi-continuum quadruple porosity binary component gas model. The governing equations of the kerogen system, the matrix system in the USRV, the natural fractures and the hydraulic fractures were discretized by fully implicit scheme. Time discretization is carried out using forward difference scheme.

The embedded discrete fracture model (EDFM), established by (Li and Lee (2008), Moïnfar, Varavei et al. (2014)), was used to simulate the flow of hydraulic fractures and the transfer flow between natural fractures and hydraulic fractures, and the transfer flow rate can be expressed by

$$q_i^{h-f} = \frac{k_{h-f} A_{h-f} M_i C_{i,h-f}^{n+1} (p_{i,h}^{n+1} - p_{i,f}^{n+1})}{\mu_g d_{h-f}} \quad (30)$$

where  $k_{h-f}$  denotes the transfer flow permeability between natural fracture and hydraulic fracture,  $\mu\text{m}^2$ ;  $A_{h-f}$  is the transfer area,  $\text{m}^2$ ;  $d_{h-f}$  is the transfer distance, m.  $C_{i,h-f}^{n+1}$  denotes the molarity of component  $i$  transfer flow between hydraulic fractures and natural fractures. The more details can be found in previous studies (Li and Lee 2008, Moïnfar, Varavei et al. 2014).

According to the method proposed by Moïnfar, Varavei et al. (2014), the flow rate of component  $i$  between hydraulic fractures and horizontal well can be expressed as

$$q_{h-w} = WI\_h \cdot M_i C_{i,h-w}^{n+1} (p_h^{n+1} - p_w^{n+1}) \quad (31)$$

where  $C_{i,h-w}^{n+1}$  denotes the molarity of component  $i$  transfer flow between hydraulic fractures and horizontal wellbore,  $\text{mol}/\text{m}^3$ ;  $WI\_h$  is the well index, expressed as

$$WI\_h = \frac{2\pi\omega_h}{\ln\left(0.14\sqrt{h^2 + \Delta l_h^2}\right) + S_h} \quad (32)$$

where  $\omega_h$  is the width of hydraulic fracture, m;  $S_h$  is the skin factor of hydraulic fracture around horizontal well, dimensionless;  $h$  is the gas reservoir thickness, m;  $\Delta l_h$  is the fracture length bounded in the hydraulic fracture element, m;

The finite difference method was used to solve this model, the governing equations of each media were discretized into differential form. The full implicit central difference in space and forward difference in time term were employed to discretize the equations. Then, these differential equations of each media were coupled, and the embedded discrete fracture model (EDFM) was used to simulate the flow between hydraulic fracture and natural fracture in SRV. The model proposed in this paper is fully coupled and strongly nonlinear due to the multiple flow mechanisms of binary component gas in shale formation. Due to the strongly nonlinear of the numerical equations for this model, conventional linear numerical method is helpless. In order to solve this model successfully, the quasi-Newton iterative method was used to solve the solution of numerical equations, the numerical solution is implemented in MATLAB.

As all we known, the numerical convergence and stability are quite important for numerical simulations. The governing equations are discretized by implicit method, which is unconditionally

stable(Jiang, Shao et al. 2014). Moreover, the Jacobi matrix of the nonlinear differential equations derived above paragraph is symmetric positive definite, so the quasi-Newton iterative method is convergent in second order.

#### 4. Discussion

The basic parameters for injection CO<sub>2</sub> into shale gas reservoir was presented in table 1, Based on which, a shale gas mining simulation with carbon dioxide injection was performed to investigate the injectivity of CO<sub>2</sub> in shale gas reservoirs and CO<sub>2</sub> enhanced natural gas recovery. The total production period is 6000 days, and CO<sub>2</sub> was injected in shale formation through well-2 after 2000 days. Then, the pressure distribution and mole fraction distribution of mixture gas can be solved by this proposed model, which were shown in Fig. 2 and Fig. 3, respectively.

Table 1 Basic reservoir parameters for the calculation based on this proposed model.

Parameters	Value	Parameters	Value
Initial pressure, $p_i$ (MPa)	12	Herry's constant of CH <sub>4</sub> , $k_{H1}$ (m <sup>3</sup> /Pa/m <sup>3</sup> )	$5.9 \times 10^{-7}$
Wellbore pressure, $p_{wf}$ (MPa)	3.6	Herry's constant of CO <sub>2</sub> , $k_{H2}$ (m <sup>3</sup> /Pa/m <sup>3</sup> )	$2.5 \times 10^{-6}$
Injection pressure, $p_{inj}$ (MPa)	8.6	Sensitivity coefficient, $\gamma$ , (MPa <sup>-1</sup> )	$1 \times 10^{-10}$
Reservoir temperature, T(K)	353	Slipping coefficient, $b_k$ , (MPa)	$7.6 \times 10^5$
Fracture skin factor, $S_f$	-1	Hydraulic fracture number, $N_f$	7
Production period, time (day)	6000	Hydraulic fracture spacing, (m)	80
Porosity of matrix, $\phi_m$	0.1	CH <sub>4</sub> Langmuir volume in kerogen, $V_{L1k}$ (m <sup>3</sup> /kg)	0.0023
Porosity of kerogen, $\phi_k$	0.3	CO <sub>2</sub> Langmuir volume in kerogen, $V_{L2k}$ (m <sup>3</sup> /kg)	0.0086
Porosity of hydraulic fracture, $\phi_h$	0.5	CH <sub>4</sub> Langmuir volume in matrix, $V_{L1c}$ (m <sup>3</sup> /kg)	0.0015
Volumetric fraction of kerogen, $f_k$	0.3	CO <sub>2</sub> Langmuir volume in matrix, $V_{L2c}$ (m <sup>3</sup> /kg)	0.0053
Density of rock, $\rho_{sc}$ (kg/m <sup>3</sup> )	2600	CH <sub>4</sub> Langmuir pressure in kerogen, $P_{L1k}$ (MPa)	6.54
Density of kerogen $k_h$ (kg/m <sup>3</sup> )	1500	CO <sub>2</sub> Langmuir pressure in kerogen, $P_{L2k}$ (MPa)	2.05
Diffusivity of CH <sub>4</sub> , $D_1$ (m <sup>2</sup> /s)	$2.5 \times 10^{-16}$	CH <sub>4</sub> Langmuir pressure in matrix, $P_{L1c}$ (MPa)	7.86
Diffusivity of CO <sub>2</sub> , $D_2$ (m <sup>2</sup> /s)	$4.5 \times 10^{-16}$	CO <sub>2</sub> Langmuir pressure in matrix, $P_{L2c}$ (MPa)	1.52
Gas viscosity of CH <sub>4</sub> , $\mu_{g1}$ (Pa·s)	$1.61 \times 10^{-5}$	Matrix permeability, $k_m$ ( $\mu\text{m}^2$ )	$1 \times 10^{-5}$
Gas viscosity of CO <sub>2</sub> , $\mu_{g2}$ (Pa·s)	$3.24 \times 10^{-5}$	Natural fracture permeability, $k_m$ ( $\mu\text{m}^2$ )	$1 \times 10^{-3}$
Reservoir thickness, h (m)	50	Hydraulic-fracture permeability $k_h$ ( $\mu\text{m}^2$ )	$1 \times 10^3$

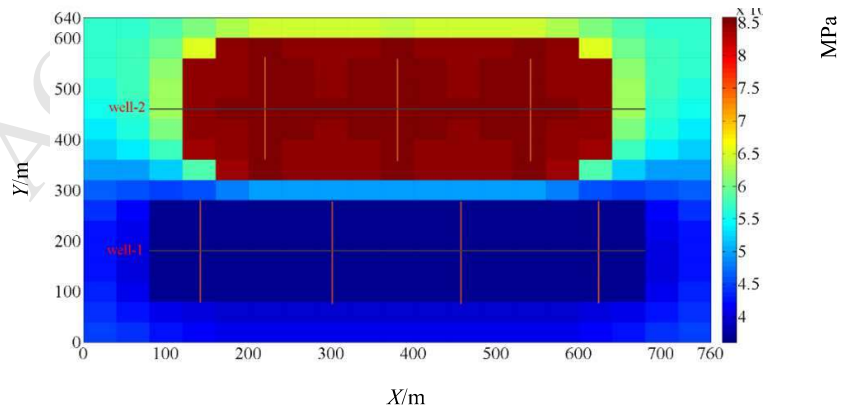


Fig. 2. Pressure distribution of gas reservoir on 2200<sup>th</sup> day.

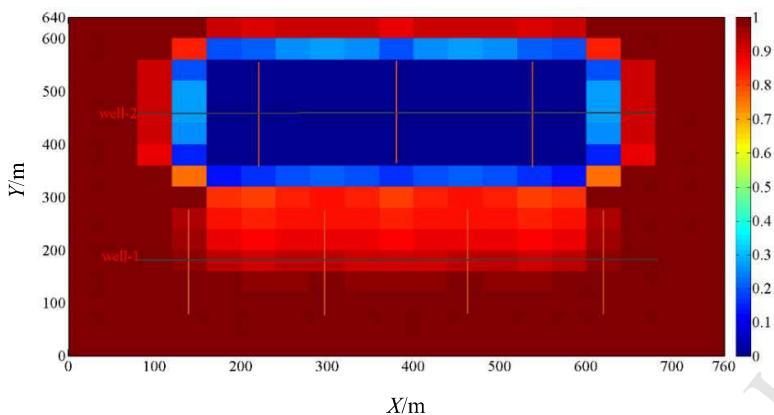


Fig. 3. Mole fraction distribution of gas reservoir on 2200<sup>th</sup> day.

Fig. 2 and Fig. 3 shows the pressure distribution and mole fraction distribution for outer nested-cell of natural fracture continuum in SRV and matrix system in USRV on 2200<sup>th</sup> days. The pressure in SRV around well-2 is higher than that around well-1, which means that injectivity of CO<sub>2</sub> can make shale formation re-pressurized, and SRV is beneficial to CO<sub>2</sub> injection and CO<sub>2</sub> enhanced natural gas recovery. The CH<sub>4</sub> mole fraction distribution can indicate the location of CO<sub>2</sub> injected from well-2, a smaller CH<sub>4</sub> mole fraction means that the more CO<sub>2</sub> was stored here. As is shown in Fig. 3, the CH<sub>4</sub> mole fraction in SRV around well-2 is close to zero, and the CH<sub>4</sub> mole fraction in the zone between well-1 and well-2 is also lower than that in remaining zone around well-1, the reason is that the SRV has high conductivity due to the interconnected natural fracture network, so CO<sub>2</sub> can migrate through the SRV easily.

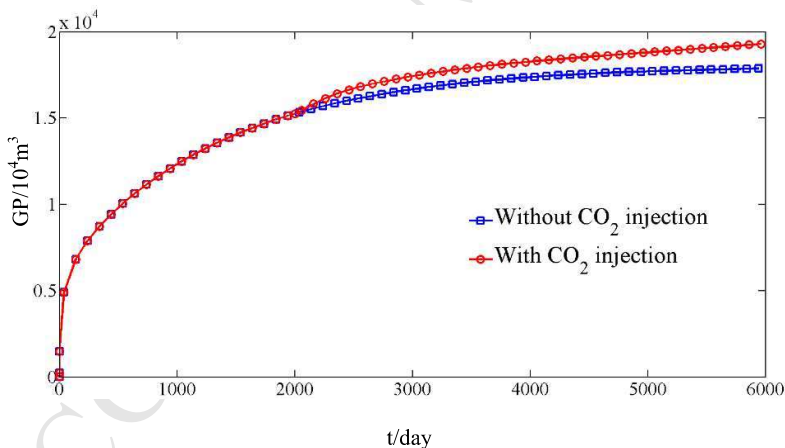


Fig. 4. Effect of CO<sub>2</sub> injection on CH<sub>4</sub> cumulative production curves.

Fig. 4 shows effect of CO<sub>2</sub> injection on CH<sub>4</sub> cumulative production curves, the slope of CH<sub>4</sub> cumulative production curve increased shortly after carbon dioxide injection. CO<sub>2</sub> from injection well drives CH<sub>4</sub> from stagnant zone into production well, so that CH<sub>4</sub> cumulative production increases faster. As discussed in assumption, CO<sub>2</sub> is mixed with CH<sub>4</sub> immediately, moreover, the distance between the SRV around injection and that around production well is very short (as shown in Fig. 3), so that CO<sub>2</sub> injection can soon influence the CH<sub>4</sub> cumulative production. As is shown in Fig. 4, injecting CO<sub>2</sub> into shale gas reservoir can significantly increase natural gas cumulative production. The reason is that CO<sub>2</sub> injection improves the production rate of CH<sub>4</sub> by reservoir re-pressurization and CH<sub>4</sub> replacement by CO<sub>2</sub>. Therefore, injectivity of CO<sub>2</sub> into shale

gas reservoir is feasible technology to sequestrate CO<sub>2</sub> and enhanced CH<sub>4</sub> recovery in shale gas reservoir.

#### 4.1. Validation

Due to few samples of CO<sub>2</sub> injection into shale gas reservoir are implemented successfully around the world, it is difficult to find field data to verify this proposed model. In order to validate the reliability and practicality of the model in this paper, published shale gas reservoir production data of a well from (He, Teng et al. (2016)) was used. This shale gas reservoir with fractured horizontal well have long production period, so this proposed model is appropriate to match the production history of this reservoir. Combining parameter search method, this proposed model was used to obtain fitting parameters along the given reservoir parameters and production history data. We first adjust the physical model as a boxed shale gas reservoir with a fractured horizontal well. The 12 hydraulic fractures are symmetrical and vertical to the horizontal well. The more detailed input parameters for matching production history of well-3 is listed in Table 2.

Table 2 Input parameters for matching production history of well-3.

Parameters	Value	Parameters	Value
Initial pressure, $p_i$ (MPa)	20.34	Hydraulic-fracture half length, $x_f$ (m)	75
Wellbore pressure, $p_{wf}$ (MPa)	3.45	Length of horizontal well: $L_H$ (m)	1006
Reservoir temperature, $T$ (K)	335	Hydraulic fracture number, $N_f$	12
Thickness of formation: $h$ (m)	46	Gas viscosity, $\mu_g$ ( $\mu\text{m}^2$ )	0.022
Porosity of fracture, $\phi_f$	0.0045	Fracture skin factor, $S_f$	0.2
Grid size, (m)	50×50	Sensitivity coefficient, $\gamma$ , (MPa <sup>-1</sup> )	1×10 <sup>-9</sup>
Slipping coefficient, $b_k$ , (MPa)	6×10 <sup>5</sup>	Production period, time (day)	800

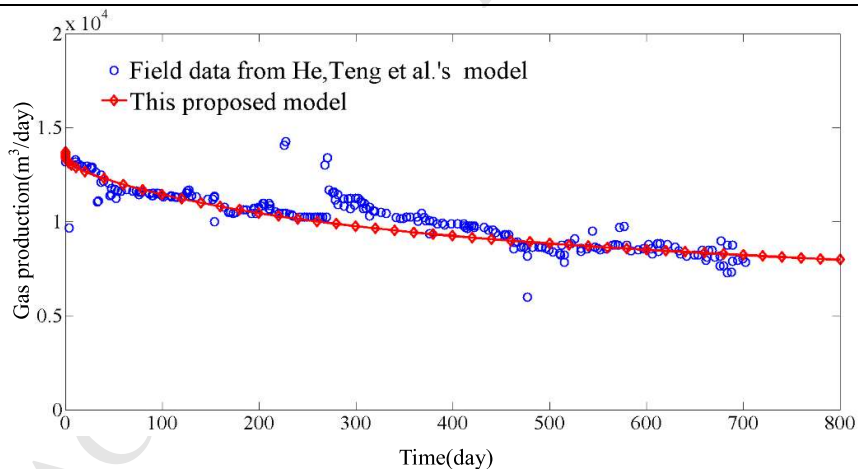


Fig.5. Comparison of the field data to this proposed model.

With the given parameters fixed, when we changed the fitting parameters, the shale gas production curve changed as well. So, we performed amount of simulation test to find the most appropriate parameters, with which the result of this model matches the production history best. As is shown in Fig. 5, the line data marked in red is the results derived from this proposed model, and the point data marked in blue represents field data from well-3. The matching results calculated by this proposed model is listed in Table 3, which is close to the result derived by (He, Teng et al. (2016)). It indicates that this proposed model can match well with the production history, moreover, this model can be used to predict the production of the fractured horizontal well

in this reservoir. Therefore, our model is reasonable and practical.

Table 3 Matching results calculated by this proposed model.

Parameters	Value
Natural fracture permeability, $k_f$ ( $\mu\text{m}^2$ )	0.001
Solubility coefficient, $k_{HI}$ ( $\text{m}^3/\text{Pa}/\text{m}^3$ )	$1.9 \times 10^{-6}$
$\text{CH}_4$ diffusion coefficient, $D_1$ ( $\text{m}^2/\text{s}$ )	$5 \times 10^{-17}$
Hydraulic fracture permeability $k_h$ ( $\mu\text{m}^2$ )	800
Matrix permeability, $k_m$ ( $\mu\text{m}^2$ )	$9 \times 10^{-5}$

## 4.2. Sensitivity analysis

### 4.2.1. Adsorption parameters

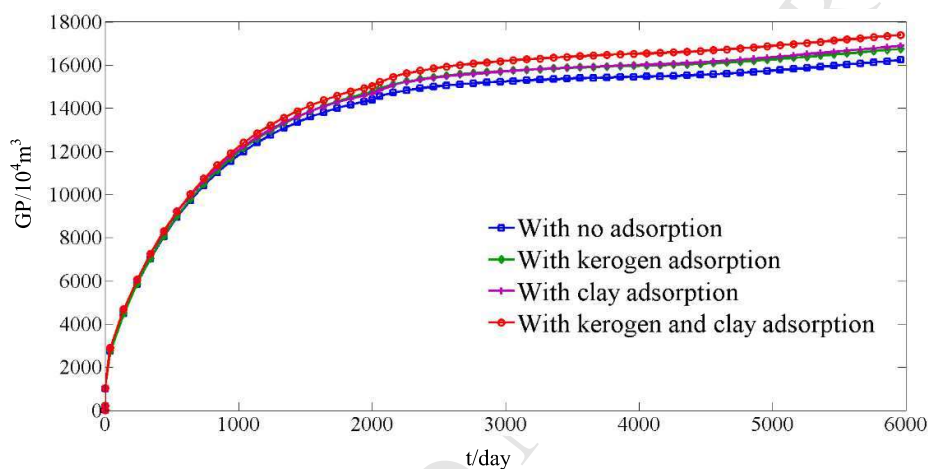


Fig. 6. The effect of adsorption on  $\text{CH}_4$  cumulative production curves.

Fig. 6 and Fig. 7 show the effect of adsorption on  $\text{CH}_4$  cumulative production curves and  $\text{CO}_2$  storage capacity curves, respectively. When this model come to four different adsorption cases, including the model with no adsorption, with clay adsorption only, with kerogen adsorption only and with both two adsorptions. The  $\text{CH}_4$  cumulative production and  $\text{CO}_2$  storage capacity increase as the model varies from case 1 to case 4. The reason is that the stronger the adsorption ability of shale formation, the more adsorbed natural gas was exploited during producing, and the more  $\text{CO}_2$  adsorbed on the surface of porous media during competitive absorption between  $\text{CO}_2$  and  $\text{CH}_4$ .

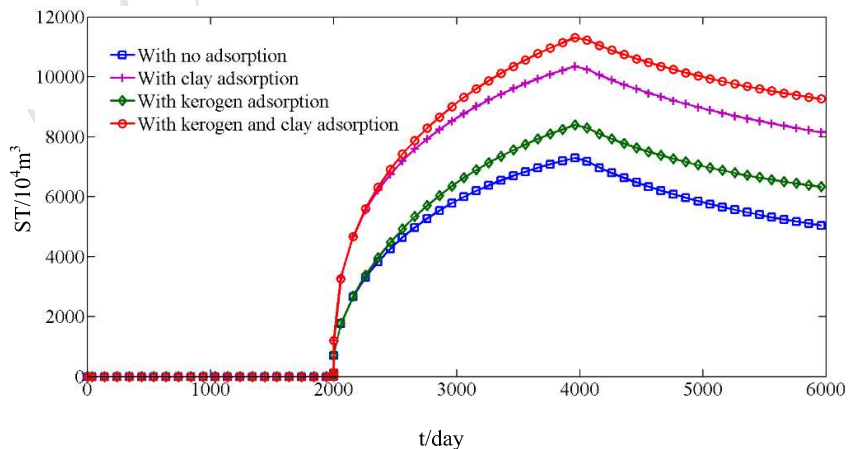


Fig. 7. The effect of adsorption on  $\text{CO}_2$  storage capacity.



As is shown in Fig 7, CO<sub>2</sub> storage capacity is increased about 60% when the kerogen and clay adsorption was considered in this proposed model. The reasons are as follows. After carbon dioxide is injected into shale gas reservoirs, some of CO<sub>2</sub> is stored in natural fracture and matrix pore, some of CO<sub>2</sub> is adsorbed on the surface of kerogen and clay, and the other part of CO<sub>2</sub> is dissolved into organic matter. At the same time, the production well is mining, when CO<sub>2</sub> arrives the production wellbore, it will be exploited. So, most of the CO<sub>2</sub> stored in natural fracture and matrix pores will be mined out, while the adsorption CO<sub>2</sub> and dissolved CO<sub>2</sub> are difficult to be exploited, so they are sequestered in shale formation forever. Therefore, the CO<sub>2</sub> storage capacity mainly depends on the adsorption and dissolution of shale formation for CO<sub>2</sub>.

#### 4.2.2. Dissolution parameters

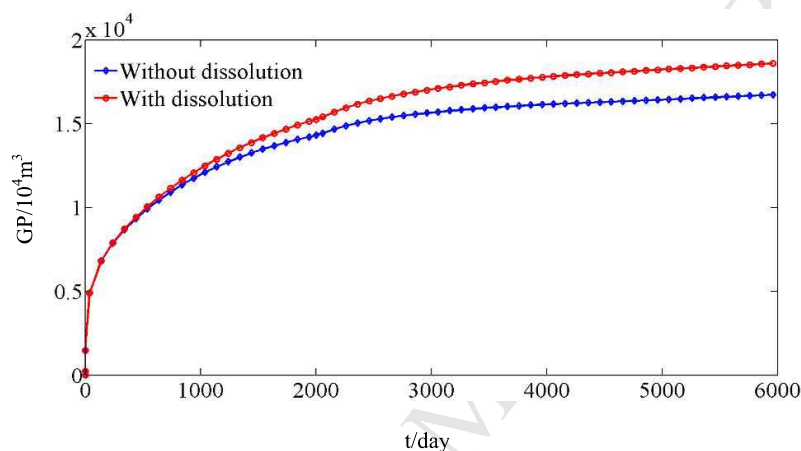
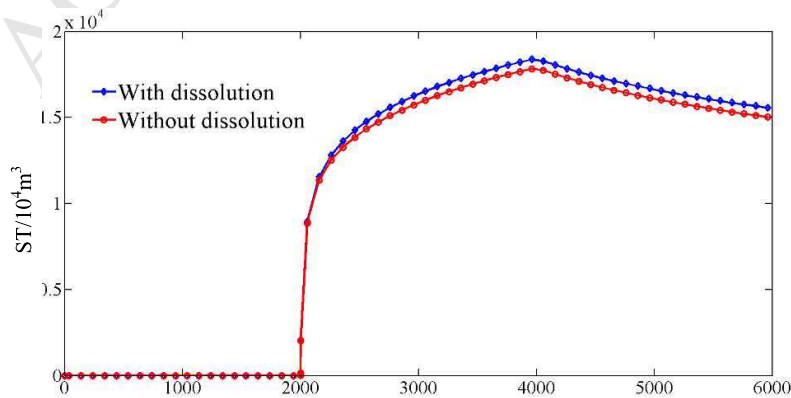


Fig. 8. The effect of dissolution on CH<sub>4</sub> cumulative production curves.

Fig. 8 and Fig. 9 show the effect of dissolution on CH<sub>4</sub> cumulative production curves and CO<sub>2</sub> storage capacity curves, respectively. The CH<sub>4</sub> cumulative production and CO<sub>2</sub> storage capacity increase significantly when considering the gas dissolved in organics. This is because both CH<sub>4</sub> and CO<sub>2</sub> can be dissolved in organic matters, dissolved methane diffuses into matrix pores during depressurization producing and improve the final natural gas production; Carbon dioxide will be dissolved in organics during injection process, which can increase the CO<sub>2</sub> storage capacity greatly. Therefore, the dissolution of CH<sub>4</sub>/CO<sub>2</sub> for organic matters so important for CO<sub>2</sub> storage and CO<sub>2</sub> enhanced shale gas recovery that it cannot be neglected. Moreover, the dissolution of CH<sub>4</sub>/CO<sub>2</sub> can effectively increase the CO<sub>2</sub> storage capacity and CH<sub>4</sub> final cumulative production.

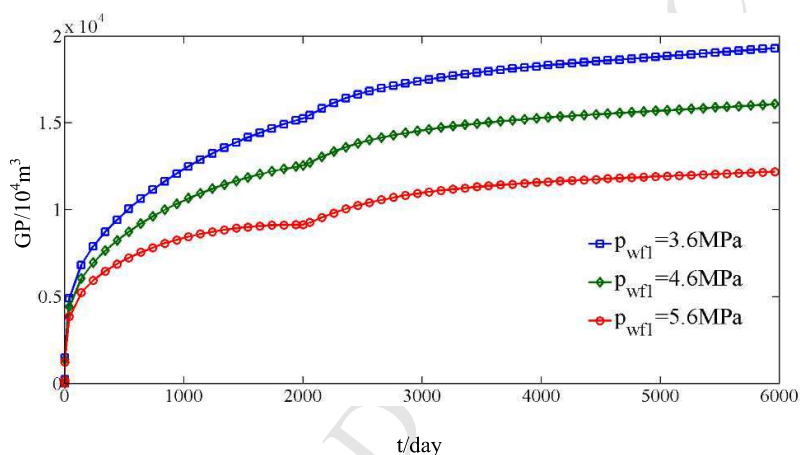


t/day

Fig. 9. The effect of dissolution on CO<sub>2</sub> storage capacity.

### 4.2.3. Production pressure

Fig. 10 and Fig. 11 show the effect of production pressure of well-1  $p_{wfl}$  on CH<sub>4</sub> cumulative production curves and CO<sub>2</sub> storage capacity curves, respectively. It is very obvious that  $p_{wfl}$  has significant impact, with all other parameters kept fixed, on CH<sub>4</sub> cumulative production and CO<sub>2</sub> storage capacity. The larger the value of  $p_{wfl}$  is, the less shale gas will be obtained, and the less carbon dioxide will be injected in shale formation. The main reason is that a larger value of  $p_{wfl}$  leads to less energy loss in shale gas reservoir, which means that more CH<sub>4</sub> will be still stored, and less CO<sub>2</sub> can be injected in shale formation. However, the lower pressure of production well  $p_{wfl}$  is, the more CO<sub>2</sub> will be exploited, so that less CO<sub>2</sub> will be sequestered in shale formation, which is shown in Fig. 11.

Fig. 10. The effect of production pressure on CH<sub>4</sub> cumulative production curves.

The CO<sub>2</sub> injection has been performed from 2000<sup>th</sup> day to 4000<sup>th</sup> day, after 4000<sup>th</sup> day, the CO<sub>2</sub> injection was stopped, while the production well continued to produce and part of CO<sub>2</sub> was mined out. So, the amount of CO<sub>2</sub> storage increases from 2000<sup>th</sup> day to 4000<sup>th</sup> day, then it decreases after 4000<sup>th</sup> day, which is shown in Fig. 11.

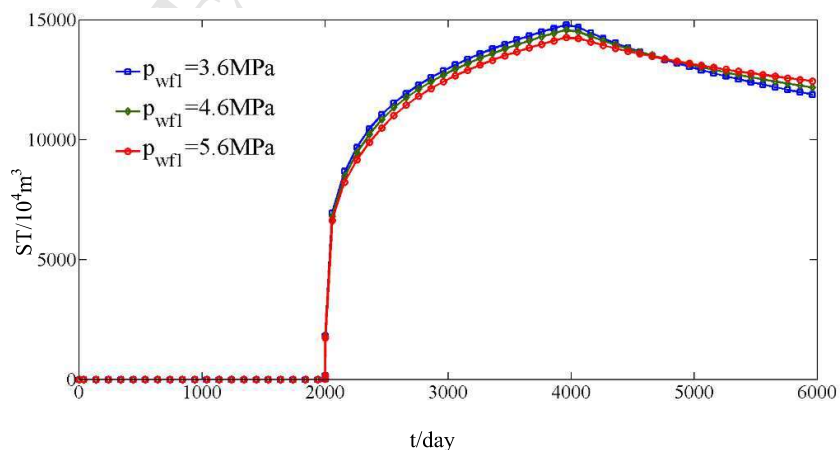
Fig. 11. The effect of production pressure on CO<sub>2</sub> storage capacity.

Fig. 12 shows the effect of production pressure of well-1  $p_{wfl}$  on CO<sub>2</sub> cumulative production

curves. The higher the production pressure is, the lower CO<sub>2</sub> cumulative production curve is. This is because that the higher production pressure leads to less energy loss, so the less CO<sub>2</sub> can be exploited from the production well.

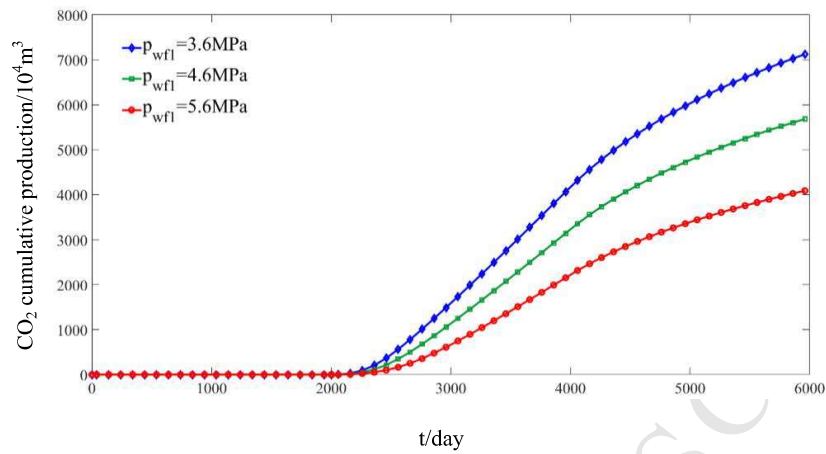


Fig. 12. The effect of production pressure on CO<sub>2</sub> cumulative production curve.

#### 4.2.4. Injection pressure

Fig. 13 shows the effect of injection pressure of well-2  $p_{wf2}$  on CO<sub>2</sub> storage capacity curves.  $p_{wf2}$  has significant effect on CO<sub>2</sub> storage capacity curves, and the larger the value of  $p_{wf2}$  is, the more carbon dioxide is sequestrated in shale formation. The reason is that a larger value of  $p_{wf2}$  means that more CO<sub>2</sub> can be injected and stored in shale formation, so the CO<sub>2</sub> storage capacity curves are higher.

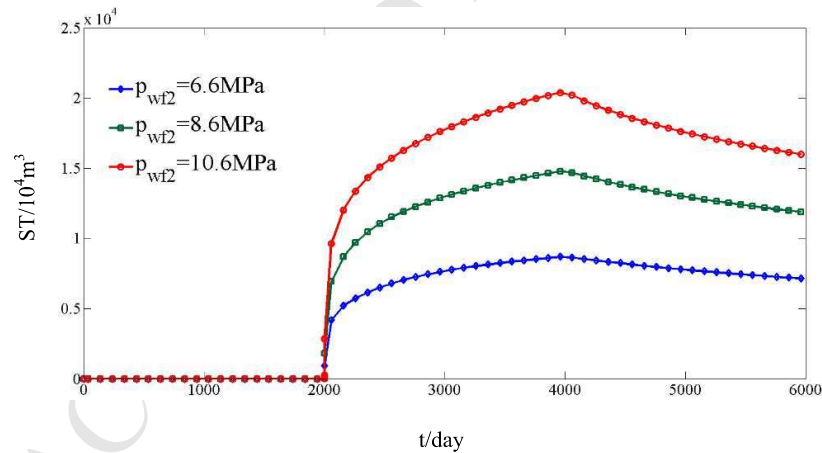


Fig. 13. The effect of injection pressure on CO<sub>2</sub> storage capacity.

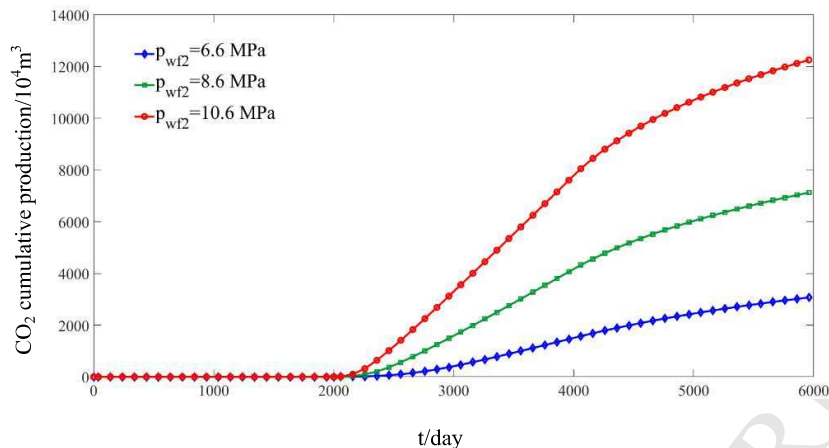


Fig. 14. The effect of injection pressure on CO<sub>2</sub> cumulative production curves.

Fig. 14 shows the effect of injection pressure of well-2  $p_{w12}$  on CO<sub>2</sub> cumulative production curves. The larger the value of injection pressure is, the CO<sub>2</sub> cumulative production is higher. The reason is that the higher injection pressure enforced the CO<sub>2</sub> flow, so the more CO<sub>2</sub> can be exploited from the production well.

#### 4.2.5. Volumetric fraction of kerogen $f_k$

Fig. 15 shows the effect of volumetric fraction of kerogen  $f_k$  on CH<sub>4</sub> cumulative production curves. The larger the value of  $f_k$  is, the more natural gas is obtained. The reason is that a larger volumetric fraction of kerogen indicates a higher total organic-carbon content, which means that more natural gas in dissolved state come out from organics, and more adsorbed gas was stored in kerogen cells. Thus, a shale gas reservoir with larger volumetric fraction of kerogen have more natural gas stored in shale formation.

Fig. 16 shows the effect of volumetric fraction of kerogen  $f_k$  on CO<sub>2</sub> storage capacity curves. The larger the value of  $f_k$  is, the less carbon dioxide is stored in shale formation. The reason is that a larger volumetric fraction of kerogen means that the volumetric fraction of inorganic matrix is small, which is the main storage space of CO<sub>2</sub>, then less CO<sub>2</sub> can be sequestered in shale formation.

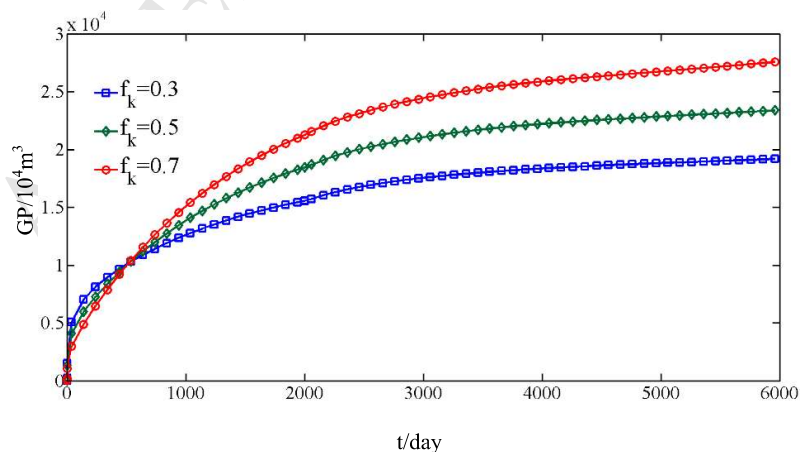


Fig. 15. The effect of volumetric fraction of kerogen  $f_k$  on CH<sub>4</sub> cumulative production curves.

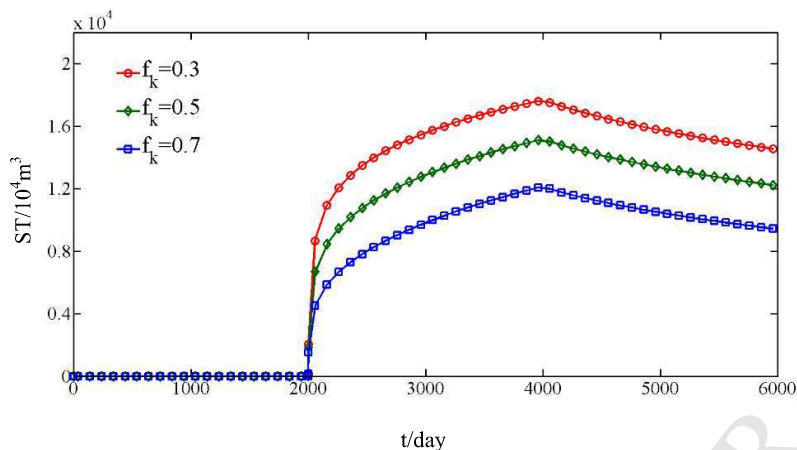


Fig. 16. The effect of volumetric fraction of kerogen  $f_k$  on  $\text{CO}_2$  storage capacity.

### 4.3. Injection opportunity

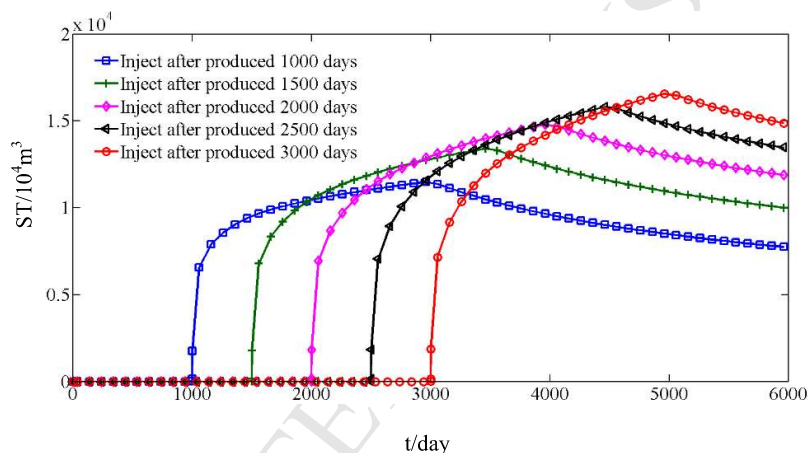


Fig. 17. The effect of injection opportunity on  $\text{CO}_2$  storage capacity.

Fig. 17 shows the effect of  $\text{CO}_2$  injection opportunity on  $\text{CO}_2$  storage capacity curves. The later the injection starting time is, setting injection duration fixed to 2000 days, the more carbon dioxide is sequestered in shale formation. This is because that the later injection starting time results in lower energy of shale formation around the  $p_{wf2}$ , which increases the  $\text{CO}_2$  storage capacity greatly. As is shown in Fig. 17, when the injection starting time increases from 1000<sup>th</sup> day to 3000<sup>th</sup> day, the increment of  $\text{CO}_2$  storage capacity decreases clearly. The reason is that  $\text{CO}_2$  storage capacity is determined by many factors, such as adsorption and the content of organics, which limits  $\text{CO}_2$  storage capacity greatly as the energy of shale formation decreases.

### 4.4. Injection strategy

Fig. 18 show the  $\text{CH}_4$  cumulative production curves of three cases with different injection strategies. We fixed the total period as 7000 days, then, the  $\text{CO}_2$  huff-n-puff patterns are shown as follows. There is no injection in Case 1, which means that the wells have produced for 7000 days, denoted as (P\_7000). One huff-n-puff is involved in Case 2, then, Case 2 includes production period, soak period and injection period, can be expressed as (P\_2000+I\_1500+S\_1500+P\_2000). Case 3 was denoted as (P\_1000+I\_500+S\_500+P\_1000+I\_1000+S\_1000+P\_2000).

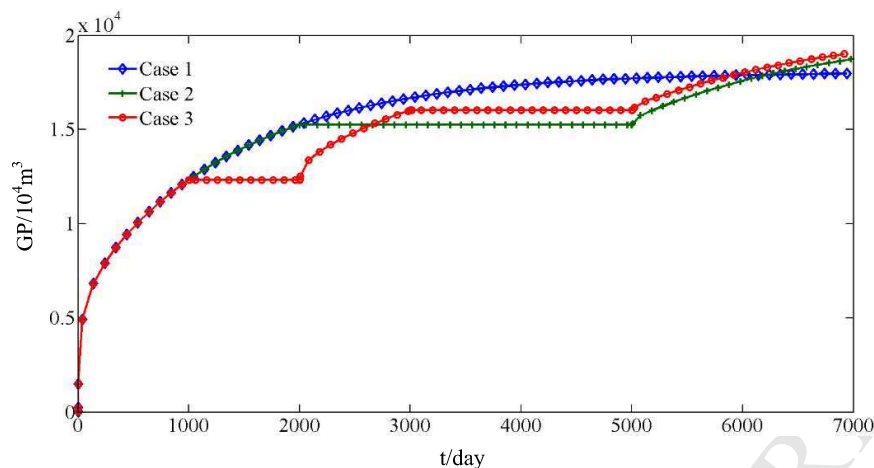


Fig. 18. The CH<sub>4</sub> cumulative production curves of three injection strategies.

As is shown in Fig. 18, it is clear that the ultimate cumulative CH<sub>4</sub> production of Case 1 is the lowest among these cases. Although the total injection period, total soak period and total production period are the same in Case 2 and Case 3, the Case 3 has higher ultimate cumulative CH<sub>4</sub> production. This is because that more huff-n-puff are involved in Case 3, and repeatedly implementing CO<sub>2</sub> huff-n-puff can improve reservoir re-pressurization and CH<sub>4</sub> replacement by CO<sub>2</sub>.

## 5. Conclusions

This paper developed a multi-continuum quadruple porosity binary component model to investigate CO<sub>2</sub> storage and CO<sub>2</sub> enhanced shale gas recovery. According to the results presented above, the following conclusions are obtained:

- (1) The mathematical model for CO<sub>2</sub> geologic sequestration in shale gas reservoir is established with multiple flow mechanisms including dissolution, adsorption/desorption, viscous flow, diffusion, slip flow and stress sensitivity of hydraulic fractures. Moreover, this proposed model is coupled by quadruple media, including natural fractures, matrix system, clay cells and kerogen cells.
- (2) The transfer flow between matrix system and natural fractures is simulated by modified multiple interacting continua (MINC) method, and embedded discrete fracture model (EDFM) is introduced to simulate the gas flow in hydraulic fractures and the transfer flow between hydraulic fractures and natural fractures. This model was solved by finite difference method and quasi-Newton iterative method. The theoretical stability and convergence of solving method have been presented.
- (3) This model can match well with the production history of the fractured horizontal well of a shale gas reservoir, which means this proposed is reliable and practicable.
- (4) Sensitivity analysis of several uncertain parameters was given above, which offers meaningful theoretical reference on estimating carbon dioxide storage capacity and CO<sub>2</sub> enhanced shale gas recovery.
- (5) Injection opportunity and injection strategy for CO<sub>2</sub> sequestered in shale formation has been analyzed, which is helpful to determine the better CO<sub>2</sub> injection strategy for CO<sub>2</sub> enhanced shale gas recovery.

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## Nomenclature

$\phi_{fs}$	porosity of natural fracture system, dimensionless;
$\phi_m$	porosity of matrix system, dimensionless;
$\phi_k$	porosity of kerogen system, dimensionless;
$\phi_h$	porosity of hydraulic fracture system, dimensionless;
$p_{sc}$	pressure under the ground condition, Pa;
$p_i$	pressure under the initial reservoir condition, Pa;
$p_{L,i}$	Langmuir pressure of component $i$ , $i=1, 2$ , Pa;
$V_{L,i}$	Langmuir volume of component $i$ , $i=1, 2$ , Pa;
$\alpha$	shape factor of shale matrix element, $m^{-2}$ ;
$k_m$	shale matrix permeability, $m^2$ ;
$k_{fi}$	natural fracture absolute permeability, $m^2$ ;
$k_h$	hydraulic fracture permeability at initial condition, $m^2$ ;
$k_{H,i}$	Solubility coefficient, $m^3/(Pa \cdot m^3)$ ;
$D_{p,i}$	pressure driven diffusivity of component $i$ , $m^2/s$ ;
$D_{kn,i}$	Knudsen diffusivity of component $i$ in kerogen cells, $m^2/s$ ;
$D_{surf,i}$	surface diffusion coefficient of adsorbed gas in kerogen cells, $m^2/s$ ;
$\omega_1 \omega_2$	mole fraction of $CH_4$ and $CO_2$ , fraction, respectively;
$\mu_g$	shale gas viscosity, $Pa \cdot s$ ;
$Z_g$	gas compressibility factor;
$Q_1$	production rate of $CH_4$ , $m^3/s$ ;
$Q_2$	production rate of $CO_2$ , $m^3/s$ ;
$q_{ad,i}$	The amount of component $i$ remaining absorbed on the surface of kerogen, $kg/m^3$ ;
$q_{d,i}$	The amount of component $i$ remaining dissolved in organic matters, $kg/m^3$ ;
$q_i^{m-k}$	The mass rate of kerogen-matrix transfer flow, $kg/m^3$ ;
GP	cumulative production of $CH_4$ , $m^3$ ;
ST	cumulative storage capacity of $CO_2$ , $m^3$ ;
$N_f$	quantity of hydraulic fracture;
$x, y$	x- and y-coordinates, m;
t	time, s;
$M_1 M_2$	molar mass of $CH_4$ and $CO_2$ , respectively;
h	reservoir thickness, m;
$w_h$	hydraulic fracture width, m;
Subscript	
$i$	the gas species, with $i=1$ for methane and $i=2$ for carbon dioxide.
k/m/f/h/c	Represents kerogen cells/matrix system/natural fractures/hydraulic fractures/clay cells.

## References

- Boosari, S. S. H., U. Aybar and M. O. Eshkalak (2015). Carbon dioxide storage and sequestration in unconventional shale reservoirs. *Journal of Geoscience and Environment Protection* 3(01): 7.
- Cao, P., J. Liu and Y. K. Leong (2017). A multiscale-multiphase simulation model for the evaluation of shale gas recovery coupled the effect of water flowback. *Fuel* 199: 191-205.
- Chen, Z., X. Liao, X. Zhao, X. Feng, J. Zang and L. He (2015). A new analytical method based on pressure transient analysis to estimate carbon storage capacity of depleted shales: A case study. *International Journal of Greenhouse Gas Control* 42: 46-58.
- Edwards, R. W., M. A. Celia, K. W. Bandilla, F. Doster and C. M. Kanno (2015). A model to estimate carbon dioxide injectivity and storage capacity for geological sequestration in shale gas wells. *Environmental science & technology* 49(15): 9222-9229.
- Gallo, Y. L. and T. A. Carballo (2016). Quantitative Assessments of CO<sub>2</sub> Injection Risks for Onshore Large Scale CO<sub>2</sub> Storage. *Spe Europec Featured at Eage Conference and Exhibition*.
- He, J., W. Teng, J. Xu, R. Jiang and J. Sun (2016). A quadruple-porosity model for shale gas reservoirs with multiple migration mechanisms. *Journal of Natural Gas Science and Engineering* 33: 918-933.
- He, J., W. Teng, J. Xu, R. Jiang and J. Sun (2016). A quadruple-porosity model for shale gas reservoirs with multiple migration mechanisms. *Journal of Natural Gas Science & Engineering* 33: 918-933.
- Heller, R. and M. Zoback (2014). Adsorption of methane and carbon dioxide on gas shale and pure mineral samples. *Journal of Unconventional Oil and Gas Resources* 8: 14-24.
- Javadpour, F. (2009). Nanopores and Apparent Permeability of Gas Flow in Mudrocks (Shales and Siltstone). *Journal of Canadian Petroleum Technology* 48(8): 16-21.
- Javadpour, F., D. Fisher and M. Unsworth (2007). Nanoscale Gas Flow in Shale Gas Sediments. *Journal of Canadian Petroleum Technology* 46(10): 55-61.
- Jiang, J., Y. Shao and R. M. Younis (2014). Development of a multi-continuum multi-component model for enhanced gas recovery and CO<sub>2</sub> storage in fractured shale gas reservoirs. *SPE improved oil recovery symposium, Society of Petroleum Engineers*.
- Kang, S. M., E. Fathi, R. J. Ambrose, I. Y. Akkutlu and R. F. Sigal (2011). Carbon dioxide storage capacity of organic-rich shales. *Spe Journal* 16(04): 842-855.
- Kim, T. H., J. Cho and K. S. Lee (2017). Evaluation of CO<sub>2</sub> injection in shale gas reservoirs with multi-component transport and geomechanical effects. *Applied Energy* 190: 1195-1206.
- Li, L. and S. Lee (2008). Efficient Field-Scale Simulation of Black Oil in a Naturally Fractured Reservoir via Discrete Fracture Networks and Homogenized Media. *Spe Reservoir Evaluation & Engineering* 11(4): 750-758.
- Liu, M., C. Xiao, Y. Wang, Z. Li, Y. Zhang, S. Chen and G. Wang (2015). Sensitivity analysis of geometry for multi-stage fractured horizontal wells with consideration of finite-conductivity fractures in shale gas reservoirs. *Journal of Natural Gas Science & Engineering* 22: 182-195.
- Merey, S. and C. Sinayuc (2016). Analysis of carbon dioxide sequestration in shale gas reservoirs by using experimental adsorption data and adsorption models. *Journal of Natural Gas Science and Engineering* 36: 1087-1105.



- Moinfar, A., A. Varavei, K. Sepehrmoori and R. T. Johns (2014). Development of an Efficient Embedded Discrete Fracture Model for 3D Compositional Reservoir Simulation in Fractured Reservoirs. *Spe Journal* 19(2): 289-303.
- Pruess, K. (2010). GMINC-A mesh generator for flow simulations in fractured reservoirs. Lawrence Berkeley National Laboratory.
- Pruess, K. and T. Narasimhan (1982). A practical method for modeling fluid and heat flow in fractured porous media.
- Sun, H., J. Yao, S.-h. Gao, D.-y. Fan, C.-c. Wang and Z.-x. Sun (2013). Numerical study of CO<sub>2</sub> enhanced natural gas recovery and sequestration in shale gas reservoirs. *International Journal of Greenhouse Gas Control* 19: 406-419.
- Svrcek, W. Y. and A. K. Mehrotra (1982). Gas solubility, viscosity and density measurements for Athabasca bitumen. *Journal of Canadian Petroleum Technology* 21(04).
- Swami, V. and A. Settari (2012). A pore scale gas flow model for shale gas reservoir. SPE Americas Unconventional Resources Conference, Society of Petroleum Engineers.
- Warren, J. and P. J. Root (1963). The behavior of naturally fractured reservoirs.
- Weniger, P., W. Kalkreuth, A. Busch and B. M. Krooss (2010). High-pressure methane and carbon dioxide sorption on coal and shale samples from the Paraná Basin, Brazil. *International Journal of Coal Geology* 84(3-4): 190-205.
- Wilke, C. R. (1950). A Viscosity Equation for Gas Mixtures. *Journal of Chemical Physics* 18(4): 517-519.
- Wu, M., M. Ding, J. Yao, S. Xu, L. Li and X. Li (2017). Pressure transient analysis of multiple fractured horizontal well in composite shale gas reservoirs by boundary element method. *Journal of Petroleum Science & Engineering* 162.
- Wu, Y.-S., G. J. Moridis, B. Bai and K. Zhang (2009). A multi-continuum model for gas production in tight fractured reservoirs. SPE Hydraulic Fracturing Technology Conference, Society of Petroleum Engineers.
- Xiao, C., L. Tian, Y. Yang, Y. Zhang, D. Gu and S. Chen (2016). Comprehensive application of semi-analytical PTA and RTA to quantitatively determine abandonment pressure for CO<sub>2</sub> storage in depleted shale gas reservoirs. *Journal of Petroleum Science & Engineering* 146: 813-831.
- Xu, R., K. Zeng, C. Zhang and P. Jiang (2017). Assessing the feasibility and CO<sub>2</sub> storage capacity of CO<sub>2</sub> enhanced shale gas recovery using Triple-Porosity reservoir model. *Applied Thermal Engineering* 115: 1306-1314.
- Zhu, G. P., J. Yao, H. Sun, M. Zhang, M. J. Xie, Z. X. Sun and T. Lu (2016). The numerical simulation of thermal recovery based on hydraulic fracture heating technology in shale gas reservoir. *Journal of Natural Gas Science & Engineering* 28: 305-316.

- Developing a multi-continuum quadruple porosity binary component gas model
- Considering multiple flow mechanisms for binary component gas
- Solving this model by finite difference method and quasi-Newton iterative method
- Estimating CO<sub>2</sub> storage capacity and CO<sub>2</sub> enhanced shale gas recovery
- Simulating fracture-matrix transfer flow by modified multiple interacting continua method

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