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Effect of CO₂ Corrosion and Adsorption-Induced Strain on Permeability of Oil Shale: Numerical Simulation

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Abstract: Permeability is a crucial parameter for enhancing shale oil recovery through CO₂ injection in oil-bearing shale. After CO₂ is injected into the shale reservoir, CO₂ corrosion and adsorption-induced strain can change the permeability of the oil shale, affecting the recovery of shale oil. This study aimed to explore the influence of CO₂ corrosion and adsorption-induced strain on the permeability of oil shale. The deformation of the internal pore diameter of oil shale induced by CO₂ corrosion under different pressures was measured by low-pressure nitrogen gas adsorption in the laboratory, and the corrosion model was fitted using the experimental data. Following the basic definitions of permeability and porosity, a dynamic mathematical model of porosity and permeability was obtained, and a fluid–solid coupling mathematical model of CO₂-containing oil shale was established according to the basic theory of fluid–solid coupling. Then the effects of adsorption expansion strain and corrosion compression strain on permeability evolution were considered to improve the accuracy of the oil shale permeability model. The numerical simulation results showed that adsorption expansion strain, corrosion compression strain, and confining pressure are the important factors controlling the permeability evolution of oil shale. In addition, adsorption expansion strain and corrosion compression strain have different effects under different fluid pressures. In the low-pressure zone, the adsorption expansion strain decreases the permeability of oil shale with increasing pressure. In the high-pressure zone, the increase in pressure decreases the influence of expansion strain while permeability gradually recovers. The compressive strain increases slowly with increasing pressure in the low-pressure zone, slowly increasing oil shale permeability. However, in the high-pressure area, the increase in pressure gradually weakens the influence of corrosion compressive strain, and the permeability of oil shale gradually recovers.

Keywords: CO₂ corrosion; adsorption-induced strain; oil-bearing shale; permeability; numerical simulation



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1. Introduction

The success of the American shale oil extraction technology has considerably stimulated China's interest in developing shale oil exploration because of increasing energy demand [1,2]. China is rich in shale oil reserve, as approximately 5.5 billion tons of shale oil is available for exploitation. However, shale oil is an unconventional energy source with worrying mining disadvantages [3]. Problems associated with shale oil reservoirs include their low organic matter content, low-pressure coefficient, high shale content, clay expansion, and environmental pollution, as well as other problems related to volume fracturing [4,5]. Therefore, the use of waterless fracturing technologies (such as CO₂ fracturing) for extracting shale oil has been explored globally [6]. Shale oil production still faces problems, such as a sharp decline and low oil recovery. Wu et al. [7,8] noted that apparent permeability is a key parameter in evaluating an unconventional reservoir. Researchers have been working to solve these problems; a focus area is the change in shale permeability caused by carbon dioxide injection.

Exploring the effect of CO₂ adsorption on the permeability of the shale reservoir matrix, Wu et al. [9] found that CO₂ adsorption-induced pore wall expansion lowers the permeability of low-permeability shale, which limits the paths of fluid flow. Zhou et al. [10] noted that subcritical CO₂ (SubCO₂) and supercritical CO₂ (ScCO₂) have different effects on shale permeability, which decreased significantly after CO₂ saturation and decreased with increasing CO₂ reaction time. Compared with SubCO₂, ScCO₂ has a greater influence on the stress sensitivity of shale permeability. The weakening of the shale mechanical properties caused by ScCO₂ are also more pronounced. Zou et al. [11] studied the reaction of CO₂ with water-bearing shale under different conditions, which changed the porosity/permeability and mechanical properties of the shale. When CO₂ and water-bearing shale are mixed, shale minerals dissolve to form numerous large etching pores, which significantly increases porosity and permeability. Shen et al. [12] experimentally and numerically investigated changes in shale permeability during CO₂ throughput and injection. Experimental simulations showed that when the CO₂ huff and puff injection began, shale permeability decreased while crude oil recovery declined. In a previous work [13], we investigated changes in the physical and chemical properties of shale after CO₂ injection. The studies have shown that exposure to CO₂ deforms the pore properties of shale. For example, CO₂ corrosion increases the permeability and average pore size of shale. The shale deformation is mainly caused by CO₂ adsorption at low pressure. At higher pressures, however, deformation is mainly caused by gas pressure [13]. Previous research has focused on the effects of CO₂ on shale. CO₂ is adsorbed on shale and dissolves in shale oil when used to enhance shale oil development. The CO₂ corrosion and adsorption–pore deformation–permeation characteristics change, and the three processes interact with each other. Studies on the change in pore permeability under the combined action of oil, shale, and CO₂ have rarely been reported.

Therefore, in this study, the deformation of the internal pore size of oil-bearing shale induced by CO₂ corrosion-induced strain at different pressures was measured through a low-pressure nitrogen gas adsorption (N₂GA) experiment. The corrosion deformation model of CO₂ to oil-bearing shale under different pressures was then fitted. Further, a fluid–structure interaction mathematical model of CO₂-containing oil shale was established. Finally, finite element analysis was used to perform numerical simulations. The effects of CO₂ corrosion and adsorption expansion strain on the permeability of oil-bearing shale under the composite action of CO₂, oil, and shale are comprehensively investigated. This work has theoretical significance for the in-depth understanding of CO₂-enhanced shale oil development and improved shale oil recovery.

2. Experiments and Methods

2.1. Experimental Samples

Shale outcrop rock samples were collected from the Fuling area, Sichuan Basin. Organic carbon was determined according to the GB/T19145-2003 standard [14]. The organic carbon content lies between 0.47% and 3.06%, with a mean value of 1.56%. We prepared the sample according to the coal sample preparation method GB/T474 [15]. Firstly, the shale is crushed to pieces with a particle size of 10–20 mm. Second, an ST-E200 table jaw crusher was used for crushing the shale samples, and the 60–80 mesh powder was screened out. Then, the powder was dried in a constant temperature oven at 80 °C for 24 h. Finally, the dried sample powder is equally divided into four groups, each group is 30 g, and one group of the untreated sample is reserved as the reference group.

2.2. Apparatus and Methods

CO₂–oil–shale soaking experiments were performed in preparation for subsequent tests. The shale oil used in the experiment was obtained from the Fuling area of the Sichuan Basin. The CO₂–oil–shale interaction experiment was performed in a specially designed high-temperature and high-pressure shale-soaking device. The schematic of the experimental device is shown in Figure 1. The reaction conditions of shale samples in the

experiment were divided into untreated samples (reference group), 6-MPa CO₂ oil, 9-MPa CO₂ oil, and 15-MPa CO₂ oil. The experimental reaction time of each pressure point was set to 3 days, and the experimental temperature was 50 °C (higher than the supercritical temperature). The experimental characterization method and treatment scheme are shown in Figure 2.

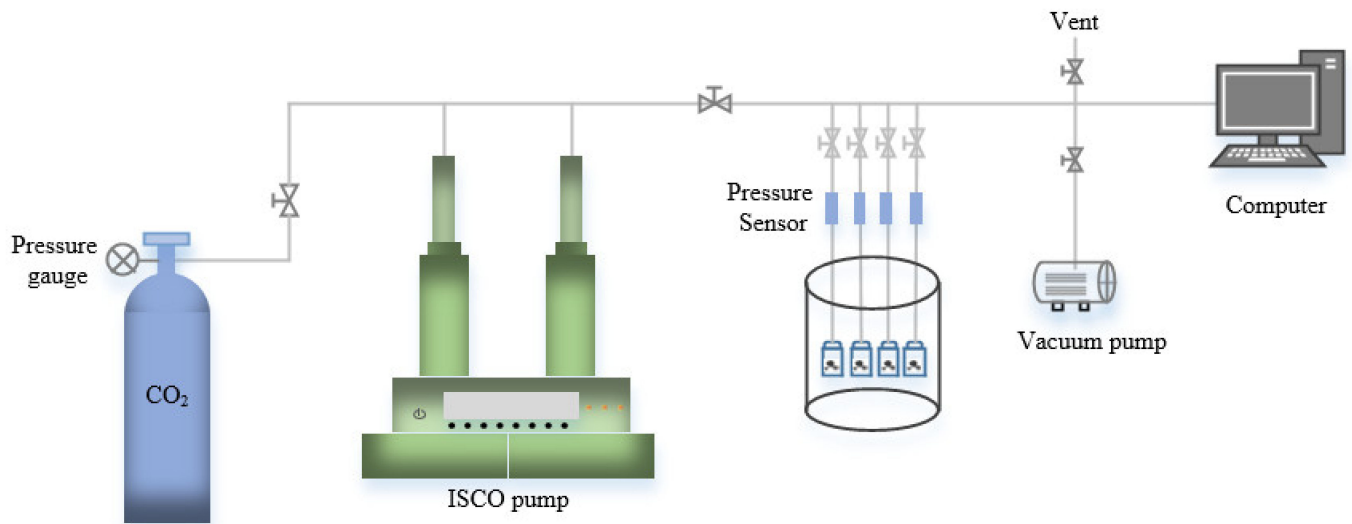


Figure 1. Experimental device for shale immersion.



Figure 2. Experimental characterization method and treatment scheme.

An N₂GA experiment was conducted to characterize changes in shale pore structure before and after CO₂–oil–shale interaction. The test was performed using ASAP 2020 automatic SSA and pore size analyzer (American Mack Company, United States of America). The pore size measurement range of the instrument was 0.35 to 500 nm. To ensure effective pore measurement, the shale samples between 60-mesh and 80-mesh were pulverized before the experiment and after vacuum degassing for 15 h. N₂ adsorption was performed at −196 °C and a relative pressure (P/P_0) of 0.01–0.99 to obtain the average pore diameter of shale under different CO₂ soaking pressures [16,17]. The results are shown in Table 1.

Table 1. N₂GA test results of shale samples.

Treatment Methods	TSSA (m ² /g)	TPV (m ³ /g)	R _a (nm)
Untreated	2.7948	0.0070	4.95
6 MPa-3 days	1.9077	0.0040	3.92
9 MPa-3 days	3.2366	0.0104	6.16
15 MPa-3 days	3.5957	0.0091	10.08

2.3. Model of Corrosion Deformation of Oil-Bearing Shale under the Influence of CO₂

Varying CO₂ pressure considerably affects the internal pore changes of oil shale. CO₂ reacts with the internal minerals of oil shale, dissolves and corrodes the inner wall of the oil shale pores, and produces a small amount of asphaltene precipitation, which changes the pore size. In general, the higher the CO₂ pressure, the stronger the dissolution reaction. According to the N₂GA test results, the average pore sizes R_a of the four samples under different pressures were 4.95, 3.92, 6.16, and 10.08 nm, respectively. Because the test was performed under isothermal conditions, deformation caused by thermal stress was not included.

By fitting the pressure p/K_s and average pore diameter R_a , according to the geometric equations:

$$\varepsilon_r = 5.4133 \times 10^{-7} \ln\left(\frac{p}{K_s}\right) + 4.4334 \times 10^{-6} \quad (1)$$

where ε_r is the corrosion compression strain in %; p is the pore pressure in MPa; K_s is shale solid skeleton modulus in MPa.

The corrosion deformation model can be converted into:

$$\varepsilon_r = a_r \ln\left(\frac{p}{K_s}\right) + b_r \quad (2)$$

where $a_r = 5.4133 \times 10^{-7}$, $b_r = 4.4334 \times 10^{-6}$, a_r and b_r are corrosion coefficients.

3. Flow-Solid Coupling Model for CO₂-Bearing Oil Shale

3.1. Model Assumptions

In order to solve the problem of mutual coupling between CO₂ migration in oil shale and shale solid deformation, the following assumptions are introduced into the model:

1. CO₂ adsorption saturation in oil shale;
2. The adsorption of CO₂ by shale conforms to the Langmuir equation;
3. CO₂ is considered an ideal gas and the temperature remains constant as it flows through the reservoir;
4. Seepage in shale obeys Darcy's law;
5. Shale is a transversely isotropic elastic-plastic porous medium with small deformation of shale skeleton and pores;

3.2. Porosity Model

Porosity is the ratio of the porous media volume to the total porous media volume. The resulting porosity n , according to its definition, is [18]:

$$\begin{aligned} n &= \frac{V_p}{V_b} = \frac{V_{p0} + \Delta V_p}{V_{b0} + \Delta V_b} = 1 - \frac{V_{s0} + \Delta V_s}{V_{b0} + \Delta V_b} \\ &= 1 - \frac{1 - n_0}{1 + \varepsilon_V} \left(1 + \frac{\Delta V_s}{V_{s0}}\right) \end{aligned} \quad (3)$$

where V_p is the shale pore volume, V_b is the total volume of shale, V_{p0} is the initial pore volume of shale, V_{b0} is the initial total volume of shale, n_0 is the initial porosity, ε_V is the shale volumetric strain, and V_s is the volume of a solid skeleton in a porous medium.

The internal deformation of shale is primarily composed of three components: temperature-induced deformation, CO₂ pressure deformation, and adsorption expansion stress caused by deformation. However, there are significant differences in the average pore size of oily shale under different CO₂ pressures, so the deformation caused by the corrosion and

compression stress of CO₂ must be addressed. Assuming this deformation process is isothermal, the amount of change in solid particles of shale is [19]:

$$\Delta V_s = -V_s(\varepsilon_p - \varepsilon_s + \varepsilon_r) \quad (4)$$

The following formula expresses the shale deformation caused by CO₂ pressure, adsorption expansion stress, and corrosion compression stress [20,21]:

$$\varepsilon_p = \frac{\Delta p}{k_s} \quad (5)$$

where ε_p is the strain caused by CO₂ pressure in %, Δp is the CO₂ change value in MPa, and k_s is the solid skeleton modulus of shale in MPa.

The expression for the adsorption expansion strain is as follows:

$$\varepsilon_s = \frac{2a_s\rho_sRT}{3V_mk_s} \ln(1 + b_s p) \quad (6)$$

where ε_s is the adsorption expansion strain in %, a_s is the limit adsorption capacity in m^3/t , b_s is the adsorption constant in MPa^{-1} , R is the gas molar constant, T is the shale temperature in K, V_m is the gas molar volume ($22.4 L/mol$), p is pore pressure in MPa, and ρ_s is the apparent density of shale.

Corrosion compression strain can be expressed as:

$$\varepsilon_r = a_r \ln\left(\frac{p}{k_s}\right) + b_r \quad (7)$$

where ε_r is the corrosion compression strain in %, a_r and b_s are the corrosion constants, p is pore pressure in MPa, and k_s is the solid skeleton modulus of shale in MPa.

Substituting Equations (5)–(7) into Equation (2), porosity can be obtained as follows:

$$n = 1 - \frac{1 - n_0}{1 + \varepsilon_v} (1 - \varepsilon_p + \varepsilon_s - \varepsilon_r) \quad (8)$$

3.3. Permeability Model

Permeability is essential for describing the ease with which gases can move through shale. Therefore, to accurately describe the fluid transport in shale, it is necessary to develop a correct permeability model.

The stress state of CO₂-containing oil shale is closely related to its permeability. The following Carman–Kozeny's fundamental equation describes the connection between permeability and porosity [22]:

$$k = \frac{n}{K_z S_p^2} = \frac{n^3}{K_z \Sigma^2} \quad (9)$$

Approximately, the total surface area of particles per unit volume of shale rock mass does not change during the stress–strain process [19]:

$$\frac{k}{k_0} = \frac{1}{1 + \varepsilon_v} \frac{1}{(1 + \Delta A_s)^2} \left(\frac{V_{p0} + \Delta V_p}{V_{p0}} \right)^3 \quad (10)$$

where ΔA_s is the change in the total surface area of the pores in cm^2 .

According to Equations (3), (8)–(10), the permeability expression for the CO₂-containing oil shale can be obtained as follows:

$$k = \frac{k_0}{1 + \varepsilon_v} \left[1 + \frac{\varepsilon_v + (\varepsilon_p - \varepsilon_s + \varepsilon_r)(1 - n_0)}{n_0} \right]^3 \quad (11)$$

where k_0 is the initial permeability of the CO₂-containing oil shale.

3.4. Effective Stress of the CO₂-Bearing Oil Shale

In addition, the internal minerals of shale react to the CO₂ pressure, resulting in corrosion and compressive stress. Finally, the stress distribution of shale alters. Therefore, when studying the fluid–structure interaction of CO₂-containing oil shale, adsorption expansion, and corrosion compression stress must be considered simultaneously. Assuming that oil shale is an elastomer with the same mechanical properties, its pore pressure is identical in all directions; therefore, the stress of the shale is identical in all directions. Furthermore, its relationship with force conforms to Hooke's law. Therefore, the following equations can be used to calculate the adsorption expansion stress and corrosion compression stress of shale:

$$\sigma_s = E\varepsilon_s = \frac{2Ea_sRT}{3V_mk_s} \ln(1 + b_sp) \quad (12)$$

$$\sigma_r = E\varepsilon_r = Ea_r \ln\left(\frac{p}{k_s}\right) + b_r \quad (13)$$

where E is the elastic modulus of shale in MPa.

Moreover, based on the effective stress principle, considering the stress generated by adsorption and corrosion, the effective stress equation of CO₂-containing oil shale can be expressed as follows:

$$\sigma'_{ij} = \sigma_{ij} - \alpha p \delta_{ij} - \sigma_s \delta_{ij} - \sigma_r \delta_{ij} \quad (14)$$

where σ'_{ij} is the effective stress of CO₂-containing oil shale in MPa, σ_{ij} is the overall stress of CO₂-containing oil shale in MPa, and α is the Biot coefficient.

3.5. Stress Field Equations

Assuming the oil shale containing CO₂ is an isotropic linear elastic medium, the stress field varies according to the following equations:

Equilibrium equation

$$\sigma_{ij,j} + F_i = 0 \quad (15)$$

where F_i is the bulk stress in N/m³.

Substituting Equation (13) into Equation (14) yields:

$$\sigma'_{ij,j} + (\alpha p \delta_{ij})_{,j} + \sigma_s \delta_{ij,j} + \sigma_r \delta_{ij,j} + F_i = 0 \quad (16)$$

(1) Geometric equations

$$\varepsilon_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i}) \quad (17)$$

(2) Stress–strain relationship

During elastic deformation, shale follows Generalized Hooke's law according to the model's underlying assumptions:

$$\sigma'_{ij} = \lambda \delta_{ij} \varepsilon_V + 2G \varepsilon_{ij} \quad (18)$$

where λ is the Lamé constant, G is the modulus of shear, and δ_{ij} is the Krocker number.

Four factors primarily cause shale deformation: ground stress, CO₂ pressure, adsorption expansion stress, and corrosion compression stress; therefore, the strain of shale can be expressed as:

$$\varepsilon_{ij} = \frac{1}{2G} \left(\sigma' - \frac{v\Theta'}{1+v} \delta_{ij} \right) - \frac{\Delta p}{3k_s} \delta_{ij} + \frac{2a_sRT}{9V_mk_s} \ln(1 + b_sp) \delta_{ij} - \frac{1}{3} \left(a_r \ln\left(\frac{p}{k_s}\right) + b_r \right) \delta_{ij} \quad (19)$$

Equation (18) yields the expression for effective stress σ'_{ij} as follows:

$$\sigma'_{ij} = \lambda \varepsilon_V \delta_{ij} + 2G \varepsilon_{ij} + \frac{2G}{3k_s} \Delta p \delta_{ij} - \frac{4G a_s R T}{9 V_m k_s} \ln(1 + b_s p) \delta_{ij} + \frac{2G}{3} \left(a_r \ln \left(\frac{p}{k_s} \right) + b_r \right) \delta_{ij} \quad (20)$$

Based on Equations (15) and (19) for joint solution and collation, the stress field equation of the shale mass containing CO₂ oil is obtained as follows:

$$\begin{aligned} \frac{G}{1-2\nu} u_{j,ji} + G u_{i,jj} + \left(\alpha + \frac{2G}{3k_s} \right) p_{,i} + \left\{ \left[\frac{2E}{3} - \frac{4G}{9} \right] \frac{a_s b_s \rho_s R T}{V_m k_s (1 + b_s p)} \right\} p_{,i} \\ + \left\{ \left[E + \frac{2G}{3} \right] \frac{a_r}{p} \right\} p_{,i} + F_i = 0 \end{aligned} \quad (21)$$

where ν is the Poisson's ratio.

3.6. Seepage Field Equation

(1) Equations of motion

When CO₂ moves in a porous medium with low permeability, the seepage on the solid pore inner wall exhibits a non-zero velocity, defying the linear Darcy's theorem; this phenomenon is known as the Klinkenberg effect. Considering the Klinkenberg effect and the assumption that CO₂ and oil are completely miscible, the equation of motion of CO₂ in oil shale can be expressed as follows:

$$V = -\frac{k_m}{\mu_m} \left(1 + \frac{m}{p} \right) \nabla p \quad (22)$$

where k_m is the permeability of the fluid in shale in m^2 , μ_m is the dynamic viscosity coefficient of a mixed fluid in $Pa \cdot s$, m is the Klinkenberg coefficient in MPa, and ∇p is a pressure gradient.

According to the miscibility criterion [23]:

$$\mu_m = \frac{\mu_{oil}}{[M^{1/4} - (M^{1/4} - 1)C]^4} \quad (23)$$

$$M = \frac{\mu_{oil}}{\mu_{CO_2}} \quad (24)$$

where μ_{oil} is the dynamic viscosity coefficient of the oil in $Pa \cdot s$, μ_{CO_2} is the dynamic viscosity coefficient of CO₂ in $Pa \cdot s$, and M is the mixing ratio of a fluid.

(2) Equation of state

$$\rho = \frac{\rho_n p}{p_n z} \quad (25)$$

where ρ is the density of the fluid in kg/m^3 , ρ_n is the density of fluids under standard conditions in kg/m^3 , and p_n is the fluid pressure under standard conditions in MPa.

(3) Continuity equation

$$\frac{\partial Q}{\partial t} + \nabla \cdot (\rho V) = 0 \quad (26)$$

where Q is the fluid content in shale in m^3/kg .

(4) Equation of fluid content in shale

Considering that CO₂ in the fluid exists in an adsorptive and free state and that the proportion of oil in the fluid is much smaller than that of CO₂, it is assumed that the fluid

in shale is composed of adsorptive state Q_a and free state Q_b , which can be expressed as follows:

$$Q_a = \frac{a_s b_s p}{1 + b_s p} \rho_s \rho_n \quad (27)$$

$$Q_b = \rho n = \frac{n \rho_n p}{\rho_n z} \quad (28)$$

where n is the porosity in shale in %.

According to Equations (6), (22)–(28), the joint solution yields the seepage field equation for CO₂-containing oil shale, as follows:

$$\left[2n + \frac{2a_s b_s p_0 \rho_s}{(1 + b_s p)^2} - \frac{4a_s b_s \rho_n RT(1 - n_0)p}{3V_m k_s (1 + b_s p)} \right] \frac{\partial p}{\partial t} + 2\alpha p \frac{\partial \varepsilon_V}{\partial t} - \nabla \cdot \left[\frac{k_m}{\mu_m} \left(1 + \frac{m}{p} \right) \nabla p^2 \right] + \frac{2(1 - n_0)p}{k_s} \frac{\partial p}{\partial t} = 0 \quad (29)$$

Together, Equations (6)–(8), (11), (21) and (29) constitute a fluid–structure interaction model of CO₂-containing oil shale.

4. Numerical Simulation Analysis

According to the fluid–solid coupling model of CO₂-containing oil shale, the full-coupling model was solved using COMSOL Multiphysics.

4.1. Geometric Model

Figure 3 illustrates a plane-strain geometric model established according to the actual occurrence conditions of CO₂ in shale. The model is a 20-m square with a 20-cm diameter well at the center. The boundary conditions of the CO₂-bearing shale reservoir are as follows: (1) uniaxial strain; (2) constant overburden stress at the top boundary; (3) the wellbore pressure is applied at the boundary of well; (4) no flow condition is applied at other boundaries.

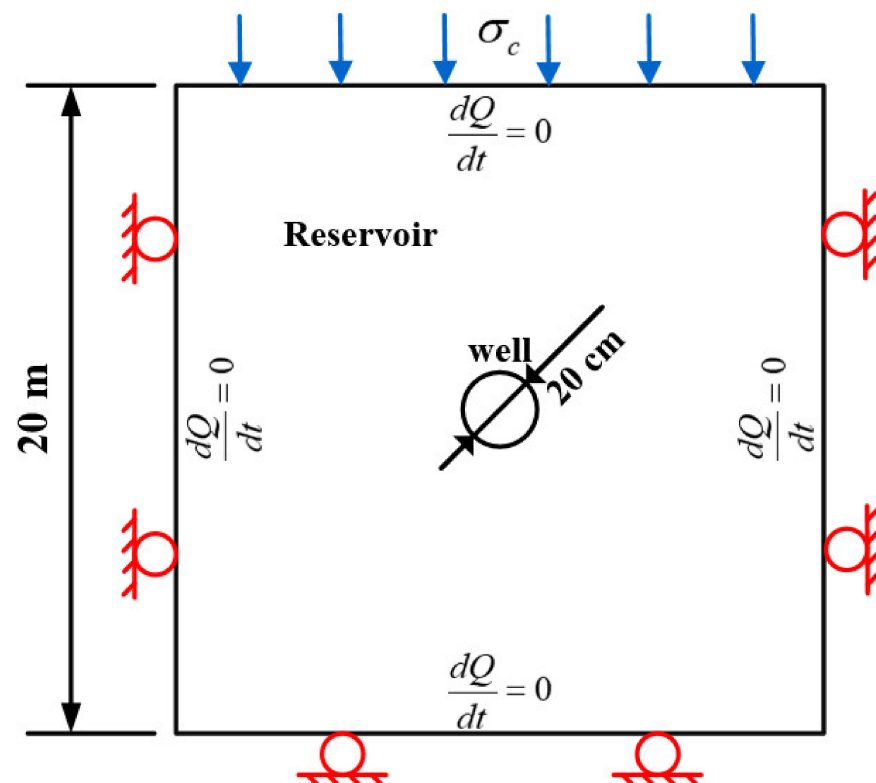


Figure 3. Geometric model and boundary conditions.

4.2. Model Parameters

The parameters of the fluid–solid coupling of CO₂-containing oil shale are shown in Table 2.

Table 2. Numerical simulation parameters.

Parameter	Value	Units
Elastic modulus, E	30	GPa
Poisson's ratio, ν	0.25	-
Shale density, ρ_s	2630	kg/m ³
Klinkenberg coefficient, m	0.25	MPa
Initial porosity, n_0	0.2	%
Initial permeability, k_0	3.7996	m ²
Adsorption constant, a_s	0.0317	m ³ /kg
Adsorption constant, b_s	1.75	MPa ⁻¹
Fluid viscosity, μ_m	1.38×10^{-5}	Pa · s
Fluid density, ρ_m	1.977	kg/m ³
Confining pressure σ_c	9	MPa
Initial pressure, p_0	16	MPa
Flowing bottom-hole pressure, p_w	0.1	MPa

4.3. Analysis of Model Simulation Results

Figure 4 illustrates the permeability evolution of CO₂-bearing oil shale based only on an adsorption-induced strain case. In a non-corrosion and sorption-induced strain case, the permeability of CO₂-bearing oil shale increases linearly. In an adsorption-induced strain case, the permeability decreases with increasing pressure under low pressure. However, under high pressure, the permeability increases with increasing pressure. This phenomenon occurs because, in the low-pressure area, the internal pores of shale are considerably affected by adsorption expansion, decreasing shale permeability with increasing pressure. However, in the high-pressure area, the influence of adsorption expansion strain on shale pores gradually weakens with the increase in pore pressure, and the shale permeability gradually recovers. Therefore, the evolution trend of the high-pressure zone is the same as that non-corrosion and sorption-induced strain case: the evolution of permeability increases with increasing pore pressure. Wang et al. and Robertson and Christiansen [24,25] also found that as pore pressure increases, permeability decreases at low pressure but increases at high pressure. Thus, our result is consistent with previous experimental results.

To fully study the effect of corrosion on CO₂-bearing oil shale, we compared two models: one considering the effect of only adsorption and another considering the effect of both adsorption and corrosion. The comparison illustrated in Figure 5 shows that under the low-pressure condition, the permeability of the model that considers the effect of only adsorption decreases with increasing pore pressure. However, the permeability also decreases with increasing pore pressure in the model that considers the combined influence of adsorption and corrosion; the decrease was less than that of the model that considers only the adsorption effect. With an increase in pressure, the permeability difference between both models increases. This may be because the corrosion intensity of CO₂ under low-pressure conditions increases with increasing pore pressure, resulting in higher permeability of shale than that without considering corrosion-induced strain. During the transition from low pressure to high pressure, the corrosion strength weakens continuously with the increase in pore pressure. The permeability difference between the two cases tends to flatten out. Therefore, at the later stage of the reaction, the permeability curves of both models show an evolutionary trend of a relatively parallel increase with increasing pressure.

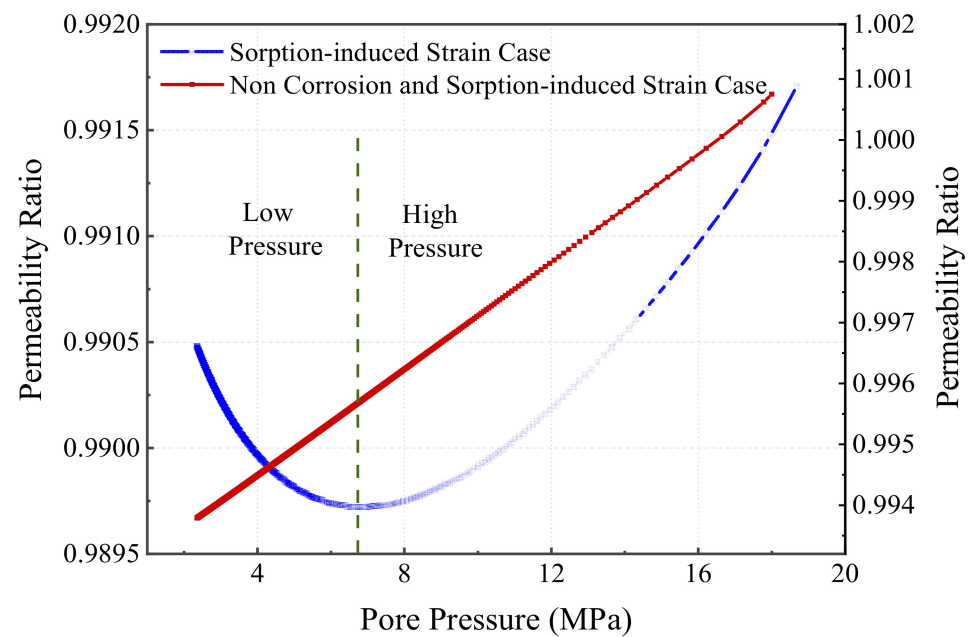


Figure 4. Permeability change curve of CO₂-bearing oil shale considering sorption-induced strain case.

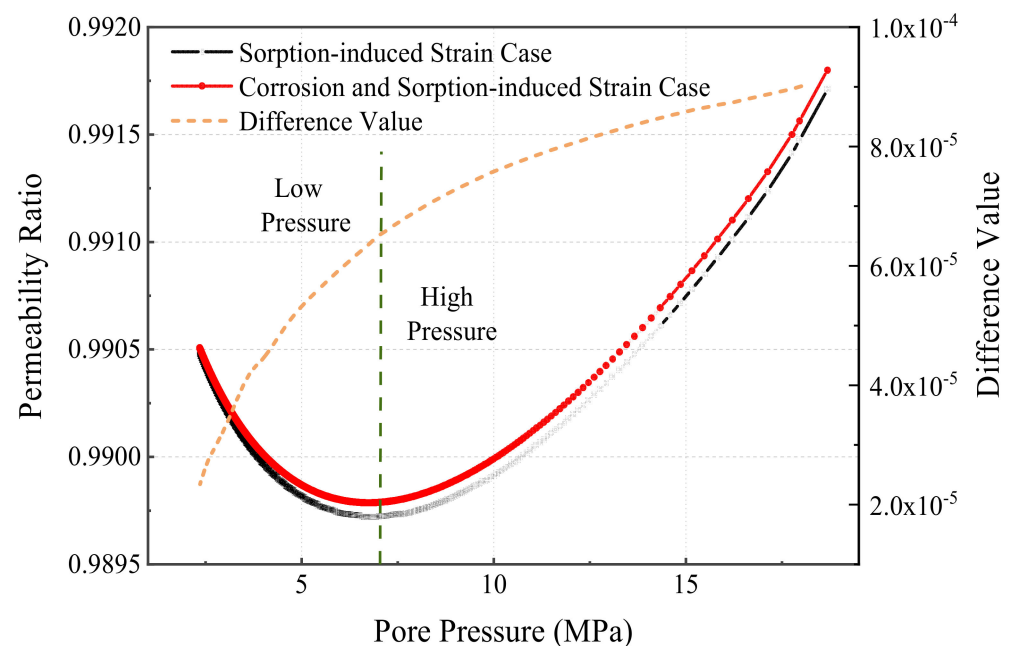


Figure 5. Permeability change curve of CO₂-bearing oil shale considering sorption-induced strain case as well as corrosion and sorption-induced strain.

The simulation of the permeability evolution of CO₂-bearing oil shale under different confining pressures showed clear differences in the permeability evolution curve under different confining pressures. Figures 6 and 7 show that with the increase in confining pressure, the permeability evolution of shale decreases. This may be because the larger the confining pressure of shale is, the larger the pore deformation is, and the shale pores are compressed, resulting in lower permeability. In the low-pressure area, the permeability of the high-confining pressure decreases more significantly than that of the low-confining pressure. This may be because under high-confining pressure, the shale skeleton deformation is more severe, resulting in greater variation in permeability. However, with the increase in pore pressure, the pressure difference between the inner and outer pores of

shale decreases continuously. Therefore, in the high-pressure area, the permeability trends of oil-bearing shale under different confining pressures are relatively parallel.

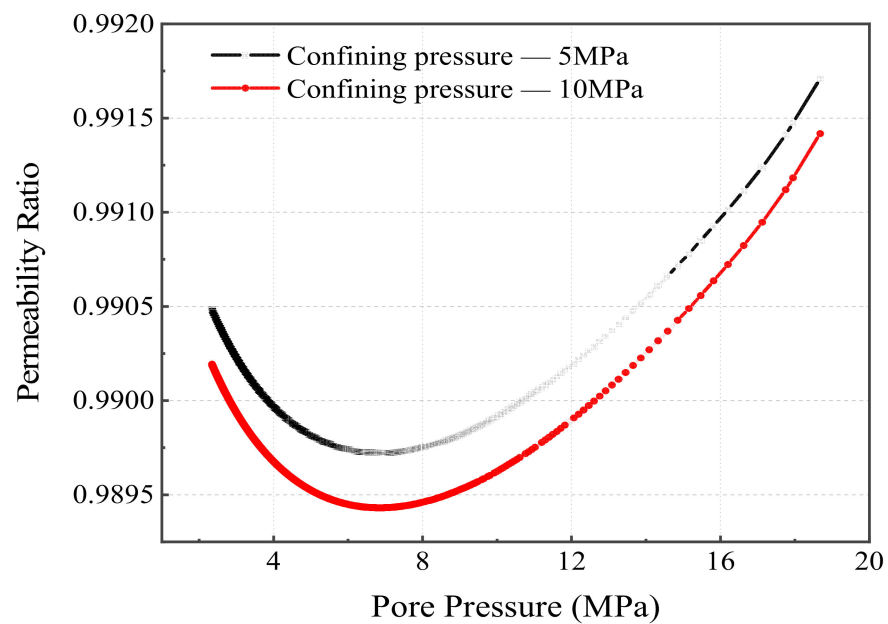


Figure 6. Permeability change curve under different confining pressures considering sorption-induced strain case.

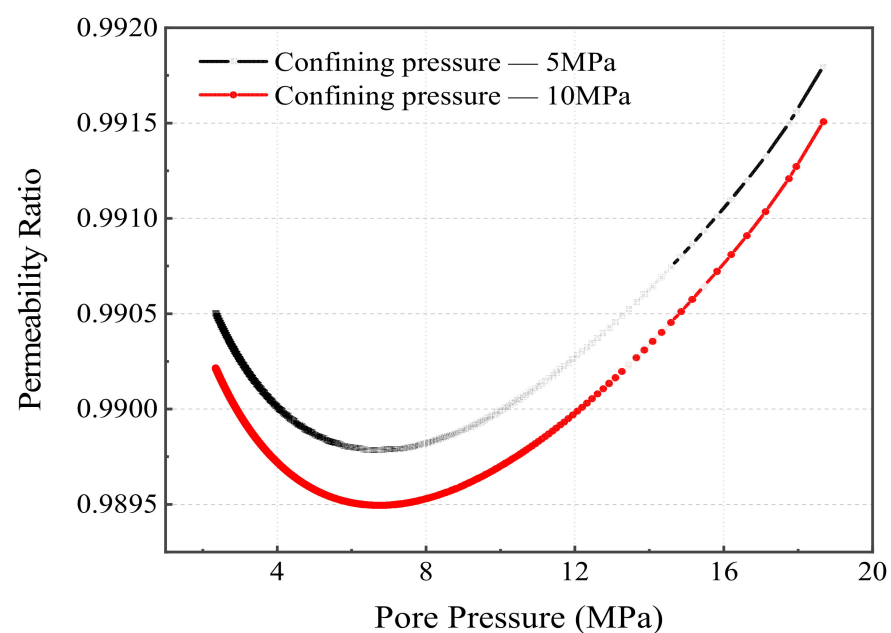


Figure 7. Permeability change curve under different confining pressures considering corrosion and sorption-induced strain.

5. Conclusions

In this study, the CO₂ corrosion-induced strain deformation of the internal pore diameter of oil shale was measured under different pressures through N₂GA tests. According to the laboratory data, the corrosion deformation model of oil shale pore diameter caused by CO₂ under different pressures was fitted. A mathematical model of the fluid–solid coupling of CO₂-containing oil shale was established, and the full coupling model was solved using COMSOL Multiphysics. The major conclusions of the study are as follows:

- (1) CO₂ corrodes the inner wall of the oil shale pores and increases the average pore size of oil shale. The corrosion strength increases with the increase in CO₂ pressure. A pressure increase of 0 to 15 MPa is accompanied by an average pore diameter increase of 4.95 to 10.08 nm.
- (2) Beginning from basic definitions of permeability and porosity, a dynamic mathematical model of porosity and permeability was obtained, and a fluid–solid coupling mathematical model of CO₂-containing oil shale was established according to the basic theory of fluid–solid coupling. The model considers the influence of adsorption expansion strain and corrosion compression strain on permeability evolution, and it improves the accuracy of the oil shale permeability model.
- (3) Numerical simulation results showed that adsorption expansion strain, corrosion compression strain, and confining pressure are important factors affecting the permeability evolution of oil shale. In the low-pressure zone, the adsorption expansion strain decreases the permeability of oil shale with increasing pressure. Compressive strain slowly increases oil shale permeability in the low-pressure zone. In the high-pressure zone, the influence of adsorption expansion strain and corrosion compression strain are gradually weakened, and the permeability of oil shale is gradually recovered.

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References

1. Nianyin, L.; Chao, W.; Suiwang, Z.; Jiajie, Y.; Yinong, D. Recent advances in waterless fracturing technology for the petroleum industry. *J. Nat. Gas. Sci. Eng.* **2021**, *92*, 103999. [\[CrossRef\]](#)
2. Wang, X.; Zhang, G.; Tang, W.; Wang, D.; Wang, K.; Liu, J.; Du, D. A review of commercial development of continental shale oil in China. *Energy Geosci.* **2022**, *3*, 282–289. [\[CrossRef\]](#)
3. Wang, Q.; Zhao, J.; Hu, Y.; Ren, L.; Zhao, C. Shut-in time optimization after fracturing in shale oil reservoirs. *Pet. Explor. Dev.* **2022**, *49*, 671–683. [\[CrossRef\]](#)
4. Hu, S.; Bai, B.; Tao, S.; Bian, C.; Zhang, T.; Chen, Y.; Liang, X.; Wang, L.; Zhu, R.; Jia, J.; et al. Heterogeneous geological conditions and differential enrichment of medium and high maturity continental shale oil in China. *Pet. Explor. Dev.* **2022**, *49*, 257–271. [\[CrossRef\]](#)
5. Liu, K.; James, J.S.; Zhang, Z. A simulation study of the effect of clay swelling on fracture generation and porosity change in shales under stress anisotropy. *Eng. Geol.* **2020**, *278*, 105829. [\[CrossRef\]](#)
6. Muhammed, R.M.; Berihun, M.N.; Hesham, A.; Shiferaw, R.J.; Babatunde, K.A. A state-of-art review on waterless gas shale fracturing technologies. *J. Pet. Sci. Eng.* **2021**, *196*, 108048.
7. Xu, J.; Chen, Z.; Wu, K.; Li, R.; Liu, X.; Zhan, J. On the flow regime model for fast estimation of tight sandstone gas apparent permeability in high-pressure reservoirs. *Energy Sources Part A Recovery Util. Environ. Eff.* **2019**, *1*, 1–12. [\[CrossRef\]](#)
8. Xu, J.; Wu, K.; Li, R.; Li, Z.; Li, J.; Xu, Q.; Li, L.; Chen, Z. Nanoscale pore size distribution effects on gas production from fractal shale rocks. *Fractals* **2019**, *27*, 1950142. [\[CrossRef\]](#)
9. Wu, W.; Zoback, M.D.; Kohli, A.H. The impacts of effective stress and CO₂ sorption on the matrix permeability of shale reservoir rocks. *Fuel* **2017**, *203*, 179–186. [\[CrossRef\]](#)
10. Zhou, J.; Tian, S.; Zhou, L.; Xian, X.; Yang, K.; Jiang, Y.; Zhang, C.; Guo, Y. Experimental investigation on the influence of sub- and super-critical CO₂ saturation time on the permeability of fractured shale. *Energy* **2020**, *191*, 116574. [\[CrossRef\]](#)
11. Zou, Y.; Li, S.; Ma, X.; Zhang, S.; Li, N.; Chen, M. Effects of CO₂-brine-rock interaction on porosity/permeability and mechanical properties during supercritical-CO₂ fracturing in shale reservoirs. *J. Nat. Gas Sci. Eng.* **2018**, *49*, 157–168. [\[CrossRef\]](#)

12. Shen, Z.; Sheng, J.-J. Experimental and numerical study of permeability reduction caused by asphaltene precipitation and deposition during CO₂ huff and puff injection in Eagle Ford shale. *Fuel* **2018**, *211*, 432–445. [[CrossRef](#)]
13. Ao, X.; Lu, Y.; Tang, J.; Chen, Y.; Li, H. Investigation on the physics structure and chemical properties of the shale treated by supercritical CO₂. *J. CO₂ Util.* **2017**, *20*, 274–281. [[CrossRef](#)]
14. GB/T 19145-2003; Determination of Total Organic Carbon in Sedimentary Rock. Standardization Administration of China: Beijing, China, 2003.
15. Han, L. *Method for Preparation of Coal Sample*; China Standards Press: Beijing, China, 2009.
16. GB/T 21650.2-2008; Pore Size Distribution and Porosity of Solid Materials—Part 2: Analysis of Mesopores and Macropores by Gas Adsorption. Standardization Administration of China: Beijing, China, 2008.
17. Yuan, Y.; Rezaee, R.; Yu, H.; Zou, J.; Liu, K.; Zhang, Y. Compositional controls on nanopore structure in different shale lithofacies: A comparison with pure clays and isolated kerogens. *Fuel* **2021**, *303*, 121079. [[CrossRef](#)]
18. Li, P.; Kong, X.; Lu, D. Mathematical modeling of flow in saturated porous media on account of fluid-structure coupling effect. *J. Hydrodyn.* **2003**, *18*, 419–426.
19. Lu, P.; Sheng, Z.W.; Zhu, G.W. Characterization of and experimental study on the permeability of rock-samples during complete Stress-strain course. *J. Univ. Sci. Technol. China* **2002**, *32*, 7.
20. Wu, S.; Zhao, W. Analysis of effective stress in adsorbed methane-coal system. *Chin. J. Rock Mech. Eng.* **2005**, *24*, 5.
21. Shi, D. *Study on Coupling Mechanism of Seepage and Stress in Shale Gas Reservoir Based on Dual Media Model*; Southwest Petroleum University: Chengdu, China, 2019.
22. Kong, X. *Advanced Seepage Mechanics*; China University of Science and Technology Press: Hefei, China, 2010.
23. Sheng, J. Coupled Multiphysics model of CO₂ injection for enhanced oil recovery. *Chin. J. Rock Mech. Eng.* **2006**, *30*, 1893–1897.
24. Wang, S.; Elsworth, D.; Liu, J. Permeability evolution in fractured coal: The roles of fracture geometry and water-content. *Int. J. Coal Geol.* **2011**, *87*, 13–25. [[CrossRef](#)]
25. Robertson, E.P.; Christiansen, R.L. Modeling laboratory permeability in coal using sorption-induced strain data. *SPE Reserv. Eval. Eng.* **2007**, *10*, 260–269. [[CrossRef](#)]

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