Research Article

Dynamic Evaluation Method of Caprock Microscopic Sealing in CO₂ Sequestration Project

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The existing statistical evaluation methods of caprock sealing ability in CO₂ sequestration engineering only take into account the sealing ability of caprocks before sequestration but cannot reflect the retained sealing ability of caprock after hydrochemical reactions. A microscopic sealing evaluation method of caprock was established based on the microscopic mechanism of chemical reaction and the breakthrough pressure of caprock which, changes with the time of CO₂ sequestration, was taken as the dynamic evaluation index. The results show that the change of microstructure parameters such as the average pore radius after dissolution is the essential reason that affects the variation of the caprock microscopic sealing property. Dissolution or precipitation of different caprock minerals during the chemical reaction process is the key factor that determines the decrease or increase of caprock microscopic sealing property. The evaluation method can reflect the change of microscopic sealing property of the caprocks in different areas as the sealing time goes and provides an efficient and practical quantitative evaluation method for the initial formation site selection and safety sealing in the later stage.

1. Introduction

CCUS (carbon capture, utilization, and storage) technology is widely used in major oilfields as a significant method of energy conservation and pollution emission reduction combined with the displacement of reservoir oil. From the interest of oil and gas field development, oil recovery has been increased by more than 10% through the CO₂ flooding technology in China [1]. However, from the interest of environmental protection, although CO₂ underground storage can reduce the greenhouse gas content of the air, whether it can be safely stored in the formation has become a new problem facing humanity.

In recent years, scholars at home and abroad have carried out a large number of related studies on geochemistry problems related to the site selection and application of CO₂ flooding and burial projects. Figure 1 shows the three ways that trapped CO₂ mainly leaks and escapes through in the reservoir: permeation and escape from caprock, diffusion and escape from caprock, and escape from caprock fractures or abandoned wells [2–4]. The change of gas saturation generally goes through two stages: first, it increases from the bottom of the barrier layer to the top successively with time, until it breaks through the caprock, leakage occurs, and then decreases gradually. The changes of rock physical properties are consistent with the spatial distribution characteristics of CO₂ gas saturation [5].

CO₂ sequestration capacity is mainly controlled by permeability, connectivity, pore volume, injection well type, and other factors of caprock [6]. Based on the current geological model, these are the most influential parameters to determine the potential for successful CO₂ geological storage of CO₂. However, CO₂ leakage also has a substantial impact on the geochemical evolution of caprock [7]. CO₂-water-rock chemical reaction process is often accompanied by mineral dissolution and precipitation, seriously threatening the safety of CO₂ geological sequestration. When CO₂ fluids driven by buoyancy migrate upward through the microcracks of rocks and form channels, chemical reactions cause a large number of mineral dissolution and alter the caprock microstructure.
On the contrary, precipitation of secondary minerals can further improve the caprock sealing ability. Li et al. [8] simulated the diffusion and migration processes of CO$_2$ in the formation under long-term storage and found that CO$_2$ invaded the caprock from 10 to 46 meters with different formation conditions and initial minerals. Kong et al. [9] simulated and calculated the transport of CO$_2$ in the formation and the change of gas saturation at different positions. CO$_2$ was injected at 24 MPa continuous constant inject pressure for 10000 years. The gaseous CO$_2$ entered the caprock after ten years in large quantities and reached 69 meters away from the injection point, and the vertical migration dimension reached 125 m after 120 years.

Therefore, the evaluation of caprock sealing safety should not only include the blocking effect on the CO$_2$ vertical transport but also include the studies on the damage caused by the acidic solution of CO$_2$ and the caprock sealing property changes after long-term sequestration.

The caprock sealing mechanism mainly includes micro-sealing and macrosealing. In addition to strong microsealing ability, the caprock also needs to have a specific sufficient thickness and macrodistribution area to seal CO$_2$ in the formation system effectively [10–14]. At the present stage, most evaluation methods of caprock sealing property are multifactor evaluation methods based on statistics [15], such as the fuzzy evaluation method or weighted analysis method. The main disadvantage of these methods, which is suitable for solving problems with many uncertain factors, is that the subjective factors account for a relatively high proportion in the evaluation and the accuracy is relatively low. However, these methods are no longer suitable for the caprock microsealing mechanism. Other plans start from the breakthrough pressure and integrate the sedimentary environment, logging data, pore structure parameters, laboratory test parameters, and different kinds of rock data; the classification evaluation standards of caprock sealing capacity were established, respectively, and provided a theoretical basis for the gradual quantitative evaluation of caprock safety [16–21].

In the above evaluation methods of the caprock sealing capacity, the evaluation criteria obtained by laboratory experiments are not in line with the actual strata numerically. This is due to the significant difference between the actual formation states and the laboratory conditions, which is mainly reflected in the following two aspects: first, the rock skeleton is stressed by the overlying strata, and most of the pores are in a compressed state; second, the temperature environment of the formation will also change with the temperature system of each layer, and the temperature at different depths varies greatly; liquid viscosity and gas phase will also change with the temperature. The parameters of the caprock are obviously different from those at standard temperature and pressure. Therefore, these methods are only applicable to stable gas which does not react with formation. Without taking into account the influence of chemical reaction on the caprock microstructure after CO$_2$ invasion, these methods have difficulty evaluating the microscopic sealing property of caprock accurately under long-term sealing and reacting conditions.

In this paper, the change of breakthrough pressure with time is taken as the dynamic evaluation index, and the micro-sealing evaluation method is established based on the microscopic mechanism of caprock chemical reactions. The caprock microscopic sealing property of an oilfield is analyzed and evaluated by using the actual data of CO$_2$ flooding and sequestration project with this method.

2. Microscopic Sealing Evaluation Method of CO$_2$ Geological Sequestration

2.1. Mechanism of Caprock Microscopic Sealing. The mechanism of caprock microscopic sealing includes capillary
sealing, hydrocarbon concentration sealing, and overpressure sealing. For CO₂ sequestration formation, when the barrier layer is not capable of generating hydrocarbon and there are no overpressure sites, the mechanism of caprock microscopic sealing is mainly embodied as capillary seals. It depends on the difference in capillary pressure between the reservoir and the caprock. The higher the difference is, the stronger the physical sealing ability will be [22]. At present, the breakthrough pressure, permeability, porosity, density, specific surface area, and micropore structure of rocks are widely used to evaluate the microsealing ability of caprock. The breakthrough pressure is the most direct and fundamental microscopic sealing parameter among them. The functional relationship between breakthrough pressure and porosity, permeability, density, median pore radius, and specific surface area, and micropore structure of rocks are roughly divided into carbonate minerals, feldspar minerals, clay minerals, and quartz. Each mineral has complex chemical reactions with CO₂ based on its specific dissolution or formation conditions. Therefore, the initial mineral composition and chemical reaction mechanism are the key factors to evaluate the caprock microscopic sealing ability. The dynamic variation rule of rock porosity and permeability can be obtained by calculating the process of mass conservation principle is used to calculate the change of caprock breakthrough pressure under the influence of chemical reactions, and the sealing performance of the caprock is classified according to different value ranges of the gas column that the rock can seal.

2.2 Evaluation Method of Caprock Microscopic Sealing. The caprock microscopic sealing process of CO₂ can be equivalent to the process of rock microstructure change under acidic conditions. The mineral composition in caprocks can be roughly divided into carbonate minerals, feldspar minerals, clay minerals, and quartz. Each mineral has complex chemical reactions with CO₂ based on its specific dissolution or formation conditions. Therefore, the initial mineral composition and chemical reaction mechanism are the key factors to evaluate the caprock microscopic sealing ability. The dynamic variation rule of rock porosity and permeability can be obtained by calculating the process of mass conservation of each mineral during CO₂ sequestration. The relationship between rock microstructure and breakthrough pressure is used to calculate the change of caprock breakthrough pressure under the influence of chemical reactions, and the sealing performance of the caprock is classified according to different value ranges of the gas column that the rock can seal.

During the CO₂-water-caprock reaction, the volume fraction of each mineral changes, and then the porosity changes at each time step of the calculation. The mass conservation principle is used to calculate the mass and volume changes of every mineral phase and update the volume fraction.

\[
\phi_{j,t+\Delta t} = \phi_{j,t} + V_j \times R_{j,t+\Delta t} \times \Delta t, \quad (2)
\]
\( \phi_{j,i,t} \) is the volume fraction of mineral \( j \) in region \( i \) at \( t \) time, \( V_j \) is the molar volume of mineral \( j \), and \( R_{j,i,t+\Delta t} \) is the reaction velocity of mineral \( j \) in region \( i \) at \( t \) time.

According to the law of chemical kinetics, the rate of mineral dissolution or precipitation reaction follows the formula [26]:

\[
R_\beta = \tilde{A}_\beta k_\beta \left( 1 - \frac{Q}{K_{\text{eq},\beta}} \right), \quad \beta = 1, \ldots, \xi_{mn},
\]

where \( \xi_{mn} \) is the amount of reactions, \( R_\beta \) is the velocity of reactions, mol/L·s\(^{-1}\), \( A \) is the reactive surface area of mineral, m\(^2\), \( k_\beta \) is the reaction rate constant, and \( K_{\text{eq}} \) is the equilibrium constant of reaction. Kharaka and Yousif [27] and Busienger and Delany [28] listed the numerical value of \( K_{\text{eq}} \) as a function of temperature. \( Q/K_{\text{eq},\beta} \) is the saturation index of the reaction, if \( Q/K_{\text{eq},\beta} - 1 \), mineral dissolution occurs. Otherwise mineral precipitation occurs; \( Q \) is the activity product:

\[
Q_\beta = \prod_{k=1}^{n_{aq}} a_k^{\nu_k},
\]

where \( n_{aq} \) is the number of ions in the solution, \( a_k \) is the activity of the reactive component, \( \nu_k \) is the stoichiometric coefficient of equilibrium reaction, the stoichiometric coefficient of reactants is negative, and the product is positive.

The formation or consumption rates of different minerals can be calculated by multiplying \( A \) by the respective metrolgy coefficients:

\[
R_{k_\beta} = \nu_{k_\beta} \times R_\beta.
\]

\( k_\beta \) is the rate constant of chemical the reaction:

\[
k_\beta = k_{0_\beta} \exp \left[ \frac{-E_{\alpha_\beta}}{R(1/T - 1/T_0)} \right],
\]

where \( E_{\alpha_\beta} \) is the activation energy of reaction \( \beta \), \( R \) is the molar gas constant, and \( k_{0_\beta} \) is the reaction rate constant of reaction \( \beta \) at \( T_0 \) (298.15 K usually); it can be calculated by the Arrhenius equation:

\[
k_{0_\beta} = A(T)e^{-\left(\frac{E_{\alpha_\beta}}{RT}\right)}.
\]
The change in the volume of every single mineral can be obtained by multiplying reaction rate by molar volume; the changes in caprock porosity caused by chemical reactions can be replaced by the changes in the volume of the minerals involved in the chemical reactions. The rock porosity can be calculated by the following equation:

\[ \phi = 1 - \frac{N_m}{\sum_{m=1}^{N_m} \phi_m}, \]  

where \( N_m \) is the number of mineral species in the rock and \( \phi_m \) is the volume fraction of every mineral.

Matrix permeability changes are calculated from changes in porosity using ratios of permeabilities calculated from the Carman-Kozeny relation and ignoring changes in grain size, tortuosity, and specific surface area [29]:

\[ k = k_0 \left( \frac{1 - \phi_0}{1 - \phi} \right)^{1/3}, \]

where \( \phi_0 \) and \( \phi \) are, respectively, the rock porosity in the grid before and after the reactions and \( k_0 \), \( k \) are, respectively, the rock permeability in the grid before and after reactions, m\(^2\).

According to Darcy’s law, the permeability of rock is

\[ Q = \frac{knA\Delta p}{\mu L}. \]

Combined with the Darcy law equation, the relation between the pore median radius and the permeability can be obtained by the following equation [31]:

\[ k = \frac{\pi r^4}{8\tau}, \]

where \( \tau \) is tortuosity; it represents the degree of tortuosity of the channel.

By combining the above equation, the relationship between rock breakthrough pressure and dynamic changes in porosity and permeability caused by dissolution can be calculated:

\[ P_c' = \frac{2\sigma \cos \theta}{\sqrt{\left(8\pi k_0 (1 - \phi_0)\right)/\pi(1 - \phi)^2 \cdot (\phi/\phi_0)^{3/2}}}. \]

The breakthrough pressure of formation rocks after \( \text{CO}_2 \) injection can be converted to equivalent air column sealing height. The air column sealing height is taken as the evaluation index, and the specified grade of the caprock [32] can be used to evaluate the caprock microscopic sealing property. When the height of the \( \text{CO}_2 \) column accumulates at the bottom of the caprock and exceeds the maximum sealing height of the layer, the caprock capillary pressure will be broken; \( \text{CO}_2 \) will displace the fluid in the upper formation until it escapes through the caprock, leading to the failure of the microscopic sealing ability. Smith’s (1966) formula can be used to obtain the height of the sealing gas column at the caprock-reservoir interface under breakthrough pressure:

\[ T_h = \frac{P_c'}{\left(\rho_w - \rho_{\text{co}_2}\right) g}, \]

where \( T_h \) is the air column height. Figure 4 illustrates the behavior of the breakthrough pressure (BP) with effective porosity (a) and permeability (b).
where \( \rho_w \) is the density of the formation water, \( \text{kg/m}^3 \); \( \rho_{co2} \) is the density of supercritical \( \text{CO}_2 \) fluid; \( g \) is the acceleration of gravity, \( 9.8 \text{ N/kg} \); \( T_h \) is the column height of gas sealing under \( P_g \), \( \text{m} \).

When the above method is applied to evaluate the microscopic sealing property of \( \text{CO}_2 \) storage formation, a specific analysis should be carried out in combination with different initial mineral compositions and geological conditions of the formation. For example, some caprocks have a high content of feldspar minerals, the dissolution of primary minerals is higher than that of secondary minerals, and the caprock microscopic sealing ability becomes worse. However, if the clay mineral content of some caprock is high, the precipitation reaction will be dominant and the pore volume will expand after fluid saturation, which is helpful in improving the sealing ability of caprock [33].

### 3. Application and Results

#### 3.1. Simulation Methods

X oilfield is one of the most essential oil-bearing basins in China, containing precious oil and gas resources. With the development of the \( \text{CO}_2 \) flooding project, the rate of oil and gas recovery increases year by year. At the same time, considering that \( \text{CO}_2 \) geological storage is an effective method to slow down the national greenhouse effect; if oil and gas are exhausted, the original oil and gas reservoirs will provide enough storage space for \( \text{CO}_2 \). According to geological data, \( \text{CO}_2 \) injection layer in X oilfield belongs to low porosity and ultra-low permeability medium and deep clastic rock reservoir. The main caprock and its sealing performance play an important role in controlling \( \text{CO}_2 \) sequestration. In this section, the mudstone caprock of the second layer of this oilfield is selected as an example, and the above evaluation method is used to dynamically evaluate the impact of \( \text{CO}_2 \) storage on its microscopic sealing property.

##### 3.1.1. Model Description

In this paper, a two-dimensional radial model with injection well as the left boundary, vertical formation thickness of 273 m, and horizontal distance of 1000 m is established by using the software TOUGHREACT, a numerical simulation software for reactive solute transport. The dynamic process of chemical reaction in the reservoir and the barrier after \( \text{CO}_2 \) storage is simulated. The change of rock breakthrough pressure is simulated by calculating the changes of microstructure parameters such as porosity, permeability, and pore throat radius caused by a chemical reaction to describe the dynamic change process of the microsealing ability of the caprock with the storage time.

The physicochemical reaction process between \( \text{CO}_2 \), brine, and minerals after \( \text{CO}_2 \) injection into the formation mainly includes the following three steps:

1. Solute migration process: when \( \text{CO}_2 \) is injected into the reservoir, convection and diffusion of the ions in the acid solution will occur. Convection is the migration process of ions in solution with pore water flow. In this simulation, buoyancy is the only force driving fluid natural convection except for solute transport. The change in concentration gradient causes a diffusion phenomenon. The ions will diffuse from high concentration zone to low concentration zone and finally, tend to equilibrium.

2. Chemical reaction process: when the ions migrate to the surface of minerals, they will react with minerals, dissolve to form free ions, or precipitate to form secondary minerals. The transport reaction process of reactive ions in a chemical solution obeys the law of mass conservation, that is, the decrease of solute concentration through any unit is equal to the sum of convection, diffusion, and reaction [34].

\[
\frac{\partial (\phi C_j)}{\partial t} = \nabla (D \phi \nabla C_j - \phi \nu C_j) + \sum_{j=1}^{M_j} \phi R_j = 0, \quad (15)
\]

where \( \phi \) is the porosity of rock; \( C_j \) is the concentration of material \( j \), \( \text{mol} \cdot \text{L}^{-1} \); \( D \) is the diffusion coefficient, \( \text{m}^2 \cdot \text{s}^{-1} \); \( R_j \) is the reaction rate of material \( j \), \( \text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1} \); \( M_j \) is the amount of materials.

3. Physical properties of rock alteration process: under the reaction process of solution migration, minerals in rocks will have dissolution reaction and precipitate reaction. Dissolution is mineral dissolution and the generated ionic substances will migrate out of the pores, resulting in porosity increase. Precipitation will lead to a large number of secondary mineral particles attached to the surface of minerals or block small pores with solute migration. The final result leads to the change of rock microstructure, which can seriously affect the ability of rock to maintain breakthrough pressure.

##### 3.1.2. Parameters Used in the Simulation

The mudstone data in the X area shows that the depth of the caprock is about 2400-2590 m, and the depth of the reservoir is about 2590-2653 m. The rocks are assumed to be isotropic homogeneous materials and there is no abnormal high temperature or high pressure. The remaining parameters are shown in Table 1.

Before the \( \text{CO}_2 \)-water-rock reaction, the initial mineral content in the model and the initial solution ion concentration at the boundary are shown in Table 2. In order to facilitate the comparison of the migration rule and reaction process of \( \text{CO}_2 \) and the brine in the reservoir and caprock, the same initial ion concentration was set in both reservoir and barrier layer during this simulation, and each mineral is evenly distributed in the reservoir and the barrier according to its mass fraction.

##### 3.1.3. Initial and Boundary Conditions

The mesh pressure of the caprock was set as the initial hydrostatic pressure, and the initial saturation of \( \text{CO}_2 \) saturation is set as 0. Because the whole reaction process is carried out in a closed...
environment, only considering the inflow of CO₂ and no mass exchange with the outside, the solution concentration will gradually change with the reaction time, and this changing law is subject to the chemical rate equation of water-rock reaction, so the initial conditions ($t=0$) are

$$S_{\text{gCO}_2}(t)|_{\text{at}}=0, \quad C_i(t)|_{\text{at}}=C_0 - R_k \beta.$$  \hspace{1cm} (16)

There are 24 grids in the horizontal direction and 17 grids in the vertical direction, with 408 grids in total. Small grids are used in the reservoir and the upper caprock that is near the injection well, and large grids are used in other areas. The boundary conditions and the grid division of the numerical simulation model are shown in Figure 5. The left side is the flow inlet, and no flow boundary will be set at the right, top and bottom at any time. The injection volume of carbon dioxide is set as 30 t/d.

### Table 1: Parameters of reservoir and caprock.

| Stratum                  | Upper caprock | Reservoir | Caprock at bottom |
|-------------------------|---------------|-----------|-------------------|
| Depth (m)               | 2400–2590     | 2590–2653 | 2653–2673         |
| Accumulated thickness (m)| 190          | 63        | 20                |
| Density (kg·m⁻³)        | 2600          | 2400      | 2600              |
| Porosity                | 0.072         | 0.15      | 0.02              |
| Permeability (m²)       | $6.9 \times 10^{-20}$ | $1.3 \times 10^{-17}$ | $8 \times 10^{-21}$ |

The ratio of horizontal to vertical permeability

|                        | Upper caprock | Reservoir | Caprock at bottom |
|------------------------|---------------|-----------|-------------------|
| Average temperature (°C)| 90            | 97.3      | 100               |
| Median pore radius (μm) | 0.036         | 0.1       | 0.015             |

### Table 2: Initial mineral and hydrochemical composition of X oilfield formation.

| Initial mineral content of reservoir (%) | Quartz | Feldspar | Plagioclase | Dolomite | Carbonatite | Calcite | Dawsonite | Kaolinite | Illite | Montmorillonite |
|-----------------------------------------|--------|----------|-------------|----------|-------------|---------|-----------|-----------|-------|----------------|
| K-feldspar                              | 7.65   | 37.35    |             |          |             |         |           |           |       |                |
| Plagioclase                             | 9.46   |          |             |          |             |         |           |           |       |                |
| Dolomite                                | 7.16   |          |             |          |             |         |           |           |       |                |
| Carbonatite                             | 4.73   |          |             |          |             |         |           |           |       |                |
| Kaolinite                               | 1.73   |          |             |          |             |         |           |           |       |                |
| Illite                                  | 0.57   |          |             |          |             |         |           |           |       |                |
| Montmorillonite                         | 1.17   |          |             |          |             |         |           |           |       |                |

| Initial mineral content of caprock (%)  | Quartz | Feldspar | Plagioclase | Dolomite | Carbonatite | Calcite | Dawsonite | Kaolinite | Illite | Montmorillonite |
|----------------------------------------|--------|----------|-------------|----------|-------------|---------|-----------|-----------|-------|----------------|
| K-feldspar                              | 4.85   | 28.93    |             |          |             |         |           |           |       |                |
| Plagioclase                             | 9.55   |          |             |          |             |         |           |           |       |                |
| Dolomite                                | 12.37  |          |             |          |             |         |           |           |       |                |
| Carbonatite                             | 3.5    |          |             |          |             |         |           |           |       |                |
| Kaolinite                               | 4.64   |          |             |          |             |         |           |           |       |                |
| Illite                                  | 8.16   |          |             |          |             |         |           |           |       |                |
| Montmorillonite                         | 8.33   |          |             |          |             |         |           |           |       |                |

| Initial composition of formation water (mol·kg⁻¹ H₂O) | H⁺          | Al³⁺        | Fe²⁺        | K⁺       | Mg²⁺        |
|------------------------------------------------------|--------------|-------------|-------------|----------|-------------|
| H⁺                                                   | $1.64 \times 10^{-8}$ |             |             |          |             |
| SiO₂                                                 | $8.64 \times 10^{-4}$ |             |             |          |             |
| Reaction equation [35–37]                             | log $K_{eq}$ | Reaction rate constant $k$ |
| Quartz $\iff$ SiO₂(aq)                                | -2.762       | -15.63      |
| Kaolinite + 6H⁺ $\iff$ H₂O + 2Al³⁺ + 2SiO₂(aq)       | 4.3024       | 11.52       |
| Calcite + H₂O + CO₂ $\iff$ Ca²⁺ + 2HCO₃⁻             | 1.235        | -10.03      |
| Dolomite + 2H⁺ $\iff$ Ca²⁺ + Mg²⁺ + 2HCO₃⁻            | 2.2247       | -9.744      |
| K-feldspar + 2H⁺ + 9H₂O $\iff$ 2K⁺ + 4H₂SiO₄ + kaolinite | -0.481       | -12.13      |

3.2 Results and Discussion

3.2.1. Gas Saturation. Under the action of pressure gradient and buoyancy, CO₂ migrated from the bottom of the reservoir to the top in a relatively short time and spread widely in the horizontal direction. Most of the CO₂ plume was still in the reservoir, and its diffusion range was about 250 m along the horizontal direction of the reservoir during the first ten years (Figure 6(a)). Only a small amount of CO₂ entered the upper reservoir, and the lateral migration distance was about 20 m. The maximum gas saturation in the whole caprock area was about 0.65 at the bottom of the upper caprock. After 50 years (Figure 6(b)), the CO₂ plume near the wellbore had passed through the top of the reservoir and entered mainly the upper caprock, about 90 m away from the bottom of the caprock, and the maximum CO₂ saturation reached 0.75. In the horizontal direction, CO₂ migrated far along with the reservoir-caprock interface, and its distribution range reached 450 m, which indicated that the bottom of the
Figure 5: Schematic diagram of formation grid division.

Figure 6: Migration of CO\textsubscript{2} in formation during 100 years storage.
The caprock was subject to particular dissolution effect, and the risk of CO₂ leakage increase. The CO₂ had reached the top of the upper caprock 100 years later (Figure 6(c)), and the gas saturation is distributed within the range of 0.1~0.6. However, CO₂ saturation near the wellbore at the bottom of caprock reached 0.9, which had formed the CO₂ leakage channel. Moreover, the CO₂ concentration at reservoir-caprock interface had been large and distributed in a wide range, which proved that the bottom of the upper caprock had been seriously eroded, and the microscopic sealing ability had been greatly reduced. Especially, CO₂ near the injection well had reached the top of the caprock and there is a considerable risk of leakage.

3.2.2. Mineral Content, Porosity, and Permeability. No.317 grid was used as the monitoring grid, which was located at the bottom of the upper caprock near the injection point. The curves of mineral content, porosity, and permeability at this point are shown in Figures 7 and 8.

Under the acidic environment provided by CO₂, feldspar minerals mainly undergo dissolution reaction, accompanied by the precipitation of clay minerals. These minerals provided ions Ca²⁺, Na⁺, Mg²⁺, and Fe²⁺ for the formation solution and then promoted the precipitation of kaolinite and quartz. At the early stage of the reaction, the content of dolomite tended to decrease from fast to slow, and the volume fraction of calcite decreased at the early stage of the reaction, and then increased. The reason may be that dolomite was a preferential dissolution. Although it provided Ca²⁺ for calcite precipitation, the dissolution rate of calcite was still higher than that of calcite precipitation. Therefore, the concentration of Ca²⁺ in formation solution remained stable, which was generally reflected as a dissolution phenomenon. As the reaction time went on, the dolomite continued to dissolve, leading to the increasing concentration of Ca²⁺ in the solution, inhibiting the dissolution of calcite, and leading to the reverse movement of calcite equilibrium reaction to generate precipitation. Although the change degree of mineral volume fraction varied in about 100 years, the amount of mineral dissolution was always more significant than that of precipitation.

The porosity and permeability had a similar increasing tendency; on the one hand, CO₂ increased the pore pressure and made the pores of caprock expand; on the other hand, the increase of porosity and permeability was caused by the particle volume reduction during the dissolution and precipitation of different minerals. According to the chemical kinetic reaction process, the dissolution amount of the primary mineral was greater than the precipitation amount of the secondary mineral, which increased the pore volume, porosity, and permeability of caprock, and gradually tended to be stable with the time of storage. However, the influence of CO₂ on the rock’s physical properties will be finally reflected in the changes of rock microstructure such as pore radius, which further affects the breakthrough pressure of caprock.

3.2.3. Breakthrough Pressure. After CO₂ fluid filled the formation and chemical reaction occurs, the breakthrough pressure of formation decreased on the whole, and the distribution of breakthrough pressure at different positions was consistent with the expansion of CO₂ fluid. Equation (12) is used to calculate the distribution of the change value of breakthrough pressure caused by chemical reactions in the formation, as shown in Figure 9. After the simulation, due to the dominant role of dissolution in the whole reaction process, as the porosity and permeability increase, the rock breakthrough pressure at different positions decreases to various degrees. The rock breakthrough pressure corresponding to the location of the maximum CO₂ saturation decreased from 9.811 MPa to 6.20 MPa.

In the simulation process, CO₂ was not fully filled in the whole caprock layer, if the entire caprock is taken as the research object, the calculated average breakthrough pressure change value will be far less than the actual situation, so the caprock within 50 m of the horizontal distance from the injection point is taken as the research area, and the average breakthrough pressure of the caprock in this area is converted into the equivalent gas column sealing height by Equation (13) and the result is shown in Figure 10.

According to the evaluation index (Table 3), the microscopic sealing capacity of caprock downgraded from I to II. With the increase of storage time, the microscopic sealing ability will continue to reduce and cause irreversible damage.

To maintain the high microscopic sealing property of the caprock under the long-term CO₂ storage condition, the caprock with enough initial breakthrough pressure can be selected reasonably in the initial site selection according to the simulation results and index of gas sealing evaluation criteria. Because most of the caprocks contain natural cracks, microfissures, and fault systems, their physical sealing ability will be greatly reduced. Therefore, the actual microscopic
sealing ability of caprocks will be generally lower than the theoretical value.

4. Conclusions

In this paper, a microscopic sealing evaluation method of caprock under CO₂ sequestration is established and the following insights are obtained:

(1) The essential change of the caprock microscopic sealing ability caused by CO₂ fluid is the change of microstructure, such as the rock pore radius. The breakthrough pressure of caprock after chemical reaction can be used as a dynamic evaluation index to predict the microscopic sealing property of the caprock under the action of chemical reaction accurately. It also provides an efficient and practical quantitative evaluation method for the initial site selection and safety storage evaluation in the later stage.
(2) The microscopic sealing property of the caprock after CO₂ storage is mainly related to the initial mineral composition of the rocks. The dissolution or precipitation amount of the caprocks composed of different minerals in the chemical reaction process is the crucial factor that determines the improvement or decrease of the microscopic sealing property.

(3) The evaluation method in this paper was used to evaluate the effect of microsealing of mudstone caprock after CO₂ storage. The results show that the breakthrough pressure of the caprock decreases gradually with the increase of storage time, and the variation trend is roughly the same as that of porosity and permeability, indicating that the evaluation method can describe the dynamic microsealing capacity of caprock successfully.

(4) Most of the formation rocks contain natural fractures and microfracture systems, and their microscopic sealing ability will be greatly reduced. Therefore, the macroscopic geological characteristics of the actual formation should be fully considered when evaluating the microscopic sealing ability of the caprocks.

Data Availability
The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest
The authors declare that they have no conflicts of interest.

Authors’ Contributions
Xu Han is the first author.

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