Laboratory simulation and dynamics study of carbon dioxide geological storage system

Jifeng Zhao*, Mingxin Liu, Gang Su, Yongzhi Wu, Zhangying Liu, Lingjie Huang

Department of Environmental and Safety Engineering, Qingdao University of Science & Technology, Qingdao, 266042, China
*Corresponding author: 1463410660@qq.com

Abstract: In recent years, the issue of carbon dioxide disposal has become a national hot issue, and China has pledged to the international community to achieve the goal of carbon neutrality by 2060. In this paper, the relationship between the water-rock reaction rate of different ores and temperature and alkalinity is first studied by consulting relevant data. It is found that the reaction rate of quartz increases with the increase of temperature under neutral conditions, and the reaction rate of manganese-free ore increases with the alkalinity. At the same time, the kinetic parameters of the water-rock reaction were determined. Secondly, the underground storage model of carbon dioxide is established by using the law of conservation of mass and Darcy's law, and a case of solving the model is given. Finally, the sensitivity analysis of the model was carried out, and it was found that the model was not sensitive to carbon dioxide density and flow, but was more sensitive to soil porosity, and the sensitivity first decreased, then increased and finally stabilized.

Keywords: water-rock reaction kinetics, Conservation of mass, Darcy's Law, Sensitivity analysis

1. Introduction

In recent years, carbon dioxide treatment has become a national hot issue. China has made an international commitment to achieve the goal of carbon neutrality by 2060. At present, China is still in the middle and late stages of industrialization and urbanization. The next 15 years will be a key stage for China to basically realize modernization. Economic development still needs to maintain a reasonable growth rate. Energy demand will continue to grow[1]. The pressure of gas extraction and carbon reduction is enormous. Therefore, the team closely follows the pace of national development, and uses the law of conservation of mass, differential equations and other knowledge to establish an underground storage model of carbon dioxide, so as to realize the storage of carbon dioxide, so as to reduce the impact of the greenhouse effect caused by carbon dioxide on the natural environment and human production and life, and provide a basis for the site selection, excavation and equipment selection in the process of carbon dioxide storage through sensitivity analysis.
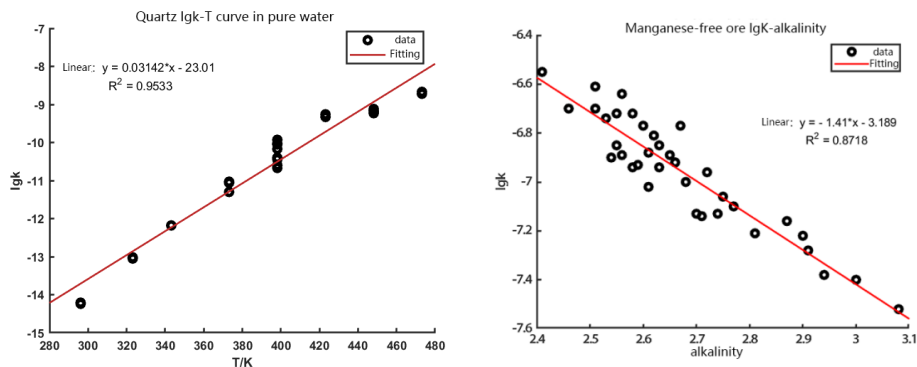
2. Methods

Figure 1: Variation diagram of reaction rate of quartz and manganese free ore under different conditions

Carbon dioxide can interact with many minerals (such as albite, calcite, etc.) during storage. The reaction rate is generally related to the pH, ionic strength, temperature and organic acid content of soil solution. The dissolution rate of common carbonate minerals is also related to the reaction temperature and CO_2 partial pressure.

As there are many minerals in the process of carbon dioxide storage, here only the data of quartz dissolution rate in pure H_2O changing with temperature and the diagram of reaction rate of manganese free ore changing with alkalinity are listed, as shown in the figure 1:

The change of reaction constants of other minerals is similar. It can be seen from Figure 1 that the reaction rate of ore increases with the increase of temperature, and shows an approximate linear relationship, while the reaction rate gradually decreases with the increase of alkalinity[2]. Therefore, it can be seen that the areas with higher ground temperature and lower pH should be selected as much as possible during the site selection of carbon dioxide storage.

The reaction rate equations of various reaction mechanisms commonly used at present are:

$$r = -A\sum_{n}\left[U_n e^{-\frac{E_n}{RT}} f\left(a_{mn}\right) g_n\left(\Delta G_n\right) \right] \quad (1)$$

A is the surface area of the reaction, U_n is the Arrhenius coefficient of the nth reaction, E is the activation energy of the reaction, T is the temperature, R is the gas constant, $f\left(a_{mn}\right)$ is the activity of the m-th substance in the n-th reaction, $g_n\left(\Delta G_n\right)$ is the Gibbs free energy of the nth chemical reaction.

The Gibbs free energy of a mineral reaction can be expressed by the following formula:

$$g\left(\Delta G_r\right) = \left(1 - \left(\frac{Q}{K}\right)^p \right)^q \quad (2)$$

P and Q are empirical constant, which can be determined by test.

At present, most of the researches are about the reaction mechanism of mineral kinetics under the conditions of pure water (neutral), H^+ or OH^-. Because most of the soils in our country are alkaline, the complete rate equation under the alkaline condition is as follows:

$$r = -A\left[k_{acid}^{298.15} e^{\frac{-Eacid}{R}\left(\frac{1}{T}-\frac{1}{298.15}\right)} a_{H^+}^{n_1} \left(1-\Omega^{p1}\right)^{q1} + k_{neutral}^{298.15} e^{\frac{-E_{neut}}{R}\left(\frac{1}{T}-\frac{1}{298.15}\right)} \left(1-\Omega^{p2}\right)^{q2} + k_{base}^{298.15} e^{\frac{-E_{base}}{R}\left(\frac{1}{T}-\frac{1}{289.15}\right)} a_{H^+}^{n3} \left(1-\Omega^{p3}\right)^{q3} \right] \quad (3)$$

k is the rate constant, 'acid', 'neutral' and 'base' represent acidic, neutral and alkaline conditions respectively; $\Omega = Q/K$ is the mineral saturation index, n_1, n_3, p_1, p_2, p_3, q_1, q_2, and q_3 are empirical constants. In case of lack of data or other reaction mechanisms, corresponding components can be added or removed according to their own needs. A is the surface area of the reaction, which can be determined by test or experience.

In this paper, the following formula is used for calculation:

$$A = \frac{6}{\rho_d \bullet d_s} \quad (4)$$

ρ_d is the density of the mineral, d_s is the dynamic diameter of the mineral.

Through the above process and consulting relevant geological data, the kinetic parameters of water rock reaction at the site can be determined, and the reaction rate can be obtained by bringing the determined parameters into the rate equation.

3. Model

3.1 Establishment of sealing model

After carbon dioxide is stored underground, it can be described by the multicomponent multiphase flow model in porous media[3]. Due to the complex physical and chemical changes in the process of underground storage, for simplicity, it is assumed that there are only liquid and gas phases in the porous medium, the particle size of the soil remains unchanged, and the influence of thermal effect is ignored. Assuming that $m^{(1)}$ and $m^{(2)}$ are the mass of water and carbon dioxide per unit volume of porous medium respectively, they can be expressed as:

$$\begin{cases} m^{(1)} = \alpha\left(\rho_l S_l X_l^{(1)} + \rho_g S_g X_g^{(1)}\right) \\ m^{(2)} = \alpha\left(\rho_l S_l X_l^{(2)} + \rho_g S_g X_g^{(2)}\right) \end{cases} \tag{5}$$

α is the porosity of soil, ρ_l and ρ_g are the density of water and carbon dioxide respectively, S_l and S_g are the saturation of liquid phase and gas phase respectively. $X_l^{(1)}$ represents the volume fraction of the first component in the liquid phase, $X_g^{(1)}$ is the volume fraction of the first component in the gas phase, $X_l^{(2)}$ is the volume fraction of the second component in the liquid phase, and $X_g^{(2)}$ is the volume fraction of the second component in the gas phase.

According to the law of conservation of mass:

$$\begin{cases} \dfrac{\partial m^{(1)}}{\partial t} = -\nabla \bullet q^{(1)} \\ \dfrac{\partial m^{(2)}}{\partial t} = -\nabla \bullet q^{(2)} + Q - r + k_d L \end{cases} \tag{6}$$

Q is the source term of CO_2, R is the reaction rate constant, k_d is the microbial metabolism constant (here it is assumed that the microorganisms are heterotrophic microorganisms), L is their quantity (about 108 microorganisms in 1g soil), $q^{(1)}$ and $q^{(2)}$ are the mass fluxes of the two components respectively:

$$\begin{cases} q^{(1)} = X_l^{(1)}\delta^{(1)} + X_g^{(1)}\delta^{(g)} \\ q^{(2)} = X_l^{(2)}\delta^{(2)} + X_g^{(2)}\delta^{(g)} \end{cases} \tag{7}$$
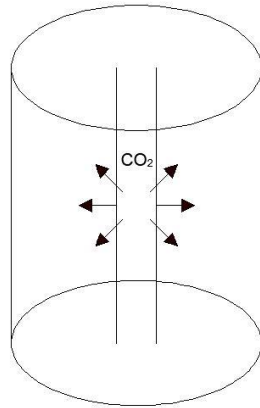
δ_1, δ_2 can be expressed by Darcy's Law:

$$\begin{cases} \delta_j^{(k)} = \rho_k v^{(k)} \\ v^{(k)} = -\dfrac{k k_r^{(k)}}{\mu_k}\left(\nabla P_k - \rho_k g\right) - k_T^k \nabla T \end{cases} \tag{8}$$

k is the liquid or gas phase, v is the dynamic viscosity, ∇ is the Laplace operator, which represents the sum of the derivatives of the spatial coordinates in each direction, and T is the soil thermodynamic temperature. At the same time, $k_r^k = k_r^k(S_k)$.

Considering the particularity of carbon dioxide storage, the mutual solubility of water and carbon dioxide can be ignored, $X_l^{(1)} = X_g^{(2)} = 1$, $X_g^{(1)} = X_l^{(2)} = 0$. Thus, the model can be transformed

into:

$$\begin{cases} \alpha \dfrac{\partial}{\partial t}(\rho_l S_l) = \nabla\left(\rho_l \dfrac{kk_r^l}{\mu_l}(\nabla P_l - \rho_l g)\right) \\[2mm] \alpha \dfrac{\partial}{\partial t}(\rho_g S_g) = \nabla\left(\rho_g \dfrac{kk_r^g}{\mu_g}(\nabla P_g - \rho_g g)\right) + Q - r + k_d L \\[2mm] S_l + S_g = 1 \\[2mm] P_c = P_g - P_l = P_c(S_l) \end{cases} \tag{9}$$

Figure 2: Schematic diagram of CO2 injection into reservoir

Figure 2 is a schematic diagram of CO_2 injection into the reservoir. Since the influence of gravity is ignored, CO_2 flows only along the radial direction, so this problem is essentially a one-dimensional problem. CO_2 is injected only at the injection point, so the source term can be ignored[4]. Meanwhile, most soil microorganisms are located in the surface soil (0-50cm), and the water rock reaction rate is slow, so the microbial metabolism and rate constant can also be ignored. The model can be simplified as:

$$\begin{cases} \alpha \dfrac{\partial S_l}{\partial t} = -\dfrac{\partial \omega^{(l)}}{\partial x} \\[2mm] \alpha \dfrac{\partial S_g}{\partial t} = -\dfrac{\partial \omega^{(g)}}{\partial x} \\[2mm] S_l + S_g = 1 \end{cases} \tag{10}$$

$\omega^{(l)}$ and $\omega^{(g)}$ are the volume fluxes of liquid phase and gas phase respectively:

$$\omega^{(l)} = -\frac{kk_r^{(l)}}{\mu_l}\frac{\partial P}{\partial x} \tag{11}$$

$$\omega^{(g)} = -\frac{kk_r^{(l)}}{\mu_l}\frac{\partial P}{\partial x} \tag{12}$$

For this example, it is a one-dimensional problem. The reservoir is cylindrical, so it needs to be solved in polar coordinates. The model is transformed into:

$$\alpha \frac{\partial S_l}{\partial t} + \frac{1}{2\pi\rho_g r} \frac{\partial \vartheta(S_l)}{\partial r} = 0$$

(13)

Where, $\vartheta(S_l) == \dfrac{1}{1 + \dfrac{k_r^{(g)}(S_l)\mu_l}{k_r^{(l)}(S_l)\mu_g}}$.

The above differential equation has no analytical solution and is discretized by upwind scheme to obtain:

$$S_l^{n+1}(x_{j+1}) = S_l^n(x_{j+1}) - \frac{\Delta t}{\Delta x} \frac{1}{2\pi\rho_g \alpha} \left(\vartheta\left(S_l^n(x_{j+1})\right) - \vartheta\left(S_l^n(x_j)\right) \right)$$

(14)

The initial value function is:

$$S_{l0} = \begin{cases} 0 & x = 0 \\ 1 & others \end{cases}$$

(15)

The boundary conditions are: $S_l(0, t) = 0$, $S_l(3000,t) = 1$, the time step is set to 0.05d and the space step is set to 60m.

The above model is solved by MATLAB software, and the following results are finally obtained:
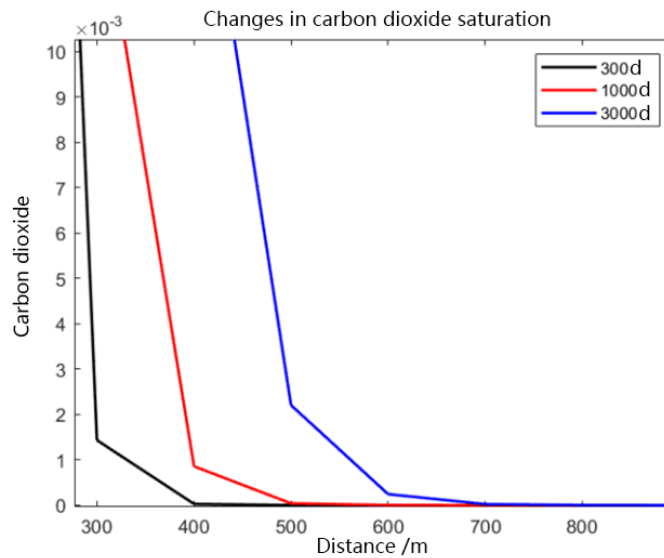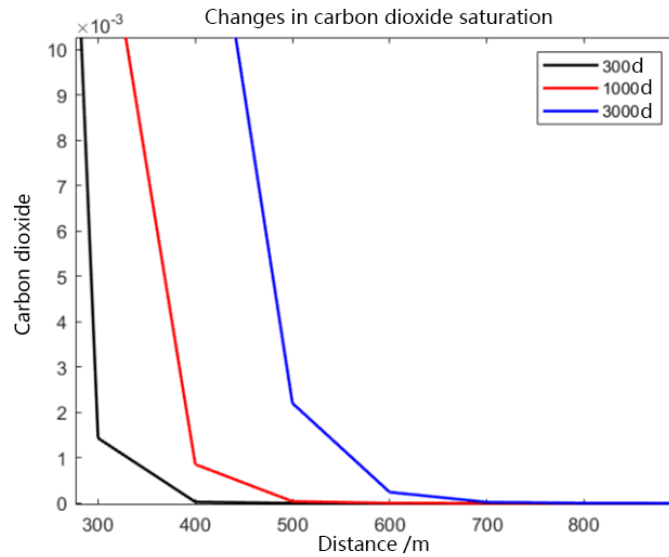

Figure 3: Variation diagram of CO2 radial saturation

It can be seen from

Figure *3* that as time goes on, carbon dioxide continues to diffuse outward, and the diffusion rate continues to slow down. At the same time, within a certain period of time, the saturation of carbon dioxide first drops rapidly, then quickly flattens out at a certain distance, and finally tends to 0. The gentle transition point continues to move backward with the extension of time, which may be related to the soil porosity[5]. Large porosity, small carbon dioxide resistance, small porosity and large resistance. Therefore, in order to ensure the effect of carbon dioxide storage, the soil porosity should be low, but considering the power consumption when injecting carbon dioxide, the porosity should not be too low.

4. Sensitivity analysis of model

According to the above established model, it is known that it is related to the density, viscosity, flow, pressure and temperature of carbon dioxide. Change the density of carbon dioxide from $691kg/m^3$ to $695kg/m^3$, the step $\Delta\rho$ is set to $0.5kg/m^3$, and bring it into the established model. The results are shown in the following figure:
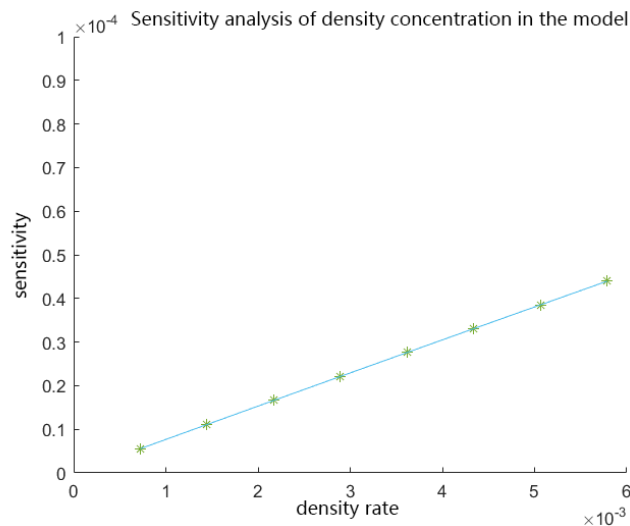

Figure 4: Sensitivity analysis of model to carbon dioxide density

It can be seen from Figure 4 that when the carbon dioxide density changes by one thousandth, the solution result of the model changes by less than one hundredth, and the model is not sensitive to the carbon dioxide density. Therefore, although the carbon dioxide density increases with the increase of pressure, and the pressure changes by 100% and the density changes by nearly 102%, it has little impact on the storage system.

The CO_2 injection flow rate is also an influencing factor of the model, so that the flow rate changes from 1000kg/s to 2000kg/s in steps of 100kg/s. The above data are brought into the model and other parameters remain unchanged. The results are shown in Figure 5:
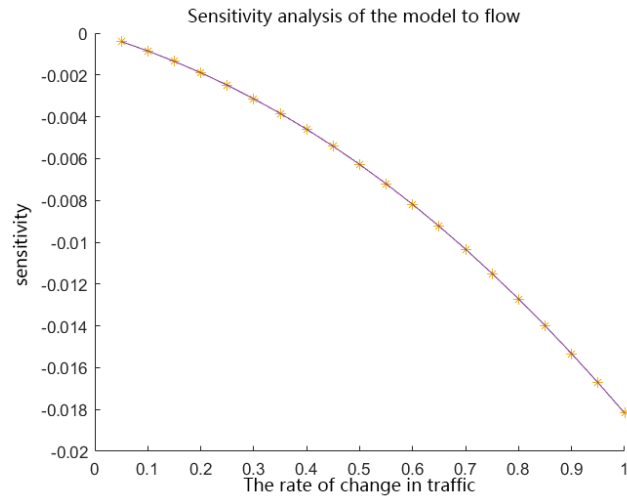

Figure 5: Sensitivity analysis of model to carbon dioxide flow

It can be seen from Figure 5 that when the flow changes by 10%, the result changes by 0.2%, and when the flow changes by 100%, the result changes by 1.8%. The model result is insensitive to the carbon dioxide flow. With the increase of the flow change rate, the change of the model solution results also increases, which indicates that to make the carbon dioxide storage system operate smoothly, it is necessary to keep the flow near a certain level without too large fluctuation.

For carbon dioxide storage, the soil porosity not only affects the injection of carbon dioxide, but also affects the dynamic process of water rock reaction. The soil porosity is changed from 0.01 to 1 in steps of 0.05. The results are shown in Figure 6:
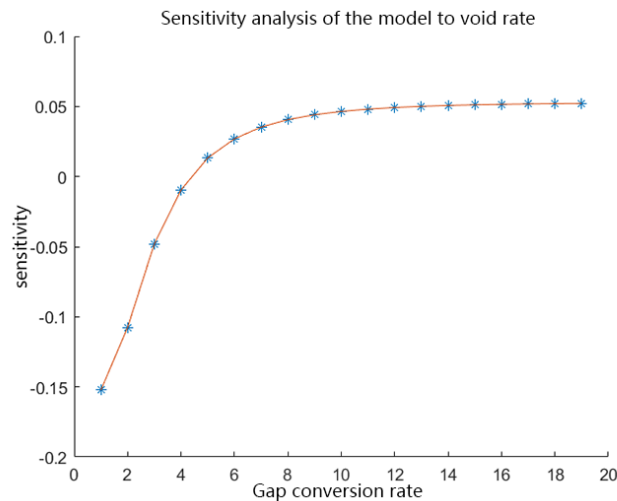

Figure 6: Sensitivity analysis diagram of model to soil porosity

It can be seen from Figure 6 that as the change rate of porosity increases, its impact on the model solution results first decreases, then increases, and then tends to be stable, which is consistent with the actual situation. When the porosity is greater than a certain degree, the soil pore size is greater than the pore size of carbon dioxide molecules, so the further increase of porosity will not affect the carbon dioxide storage system.

5. Conclusion

Through the above process, we can finally get the mathematical model of carbon dioxide storage.

However, the model is complex and can only be solved by numerical method. In practical work, it should be properly simplified. In the case solution given in this paper, it can be seen that with the extension of storage time, carbon dioxide continues to diffuse outward, and the diffusion rate continues to slow down. At a certain time, the saturation of carbon dioxide first decreases rapidly, then flattens rapidly at a certain distance, and finally tends to zero. Finally, through sensitivity analysis, it is found that the model is not sensitive to carbon dioxide density and flow, but sensitive to soil porosity, and the sensitivity first decreases, then increases, and finally tends to be stable.

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