1. INTRODUCTION

Global warming is becoming a serious threat to the environment, which are caused by the significant man-made emissions of greenhouse gases. CO₂ is definitely the representative of greenhouse gases due to human’s overreliance on traditional fossil fuels (coal, oil, and natural gas). Greenhouse gas control has become a focal point of the 21st Century. In the 2015 COP21, also known as the 2015 Paris Climate Conference, the issue of greenhouse gas control was also emphasized and attracts more and more attention from many aspects of the society. An important route in dealing with this issue is via a CO₂ geological storage as part of carbon capture, utilization, and storage (CCUS) systems. There is a strong case for the need of CCUS in the future energy mix if modern human society wishes to maintain economic development following its historic and current dependence on traditional fossil energy. There are different kinds of geological structures, such as deep saline aquifers, depleted oil and gas reservoirs, and deep unminable coal seams that can be storage candidates for the CO₂ geological storage process. CO₂ geological storage associated with deep saline aquifers has a promising future because of its wide distribution and enormous storage potentials. Many demonstration projects conducted in recent years have proved that the CO₂ storage in deep saline aquifers can be an effective method in eliminating the negative effects of greenhouse gas emissions. However, the safety, with regard to CO₂ leakage, has always been an eminent issue for public concern, with many potential pathways and unknown factors. The rock-fluid interactions may change the property of the caprock and weaken the seal layer. Hence, it is very important to monitor CO₂ migration and investigate the leakage mechanisms during CO₂ storage process. Meanwhile, geochemical processes could influence the CO₂ migration front, which may affect the timeliness of monitoring technologies, especially in a large scale. Geochemical reactions can change the permeabilities of storage reservoirs and leakage channels, which serve a key role in altering CO₂ migration rules.

In the early stage, CO₂ geological storage capacity and mechanisms are hot issues during the application of CCUS. The available storage structures mainly include deep saline aquifer, unminable coal seams, and depleted oil and gas reservoir etc. Combination of CO₂ storage and enhanced oil recovery (EOR) is also welcome, with benefits in both environment and economic efficiency. At the same time, it is theoretically feasible to inject CO₂ to replace CH₄ in natural gas hydrate deposits, which can serve as an alternative way to develop unconventional energy and eliminate CO₂ emissions.
Evaluation on CO₂ geological storage potential indicates that different storage geostructures have different storage capacities with various storage mechanisms. However, the leakage risks using different storage structures have diverse levels. The technical feasibility of CCUS has been demonstrated by field applications, but the economic and safety issues restrict the further development of CO₂ geological storage. Implementation of carbon tax can improve the economic efficiency. Nevertheless, the public always worries and doubts about the potential leakage risk associated with CO₂ geological storage projects. CO₂ leakage will eliminate the environmental benefits, which is provided by CO₂ geological storage activities or damage the ecosystem. Therefore, it is important to investigate the leakage behaviors and mechanisms with the presence of leakage channels.

Some research works have been carried out to study the leakage mechanisms and behaviors. Nordbotten et al. applied a novel framework for predicting the leakage channels connecting multiple subsurface permeable formations. The capabilities of the model on typical field data were demonstrated. Their results showed the flexibility and utility of the solution methods. Song and Zhang gave a comprehensive review of caprock-sealing mechanisms for a CO₂ geological storage project. The review exhibited that CO₂ leakage can be rapid and catastrophic through faults or fracture networks, whereas diffusive loss is usually low. Jordan et al. built a reduced-order model to predict CO₂ and brine leakages along the wellbores into the surface or the overlying aquifer. The influences of wellbore properties and the state of the CO₂ plume on leakage profiles are also investigated. The results indicate that minima in flow rates exhibited in the response surface are induced by a complex nonlinear phase behavior along the wellbore. CO₂ leakage can be increased with the presence of a shallow aquifer by comparing with the cases that CO₂ directly leak to the land surface. Class et al. carried out a benchmark study on the problem related to CO₂ storage in geologic formations. They applied different simulators to study the CO₂ leakage through an assumed leakage channel, methane recovery enhanced by CO₂ injection and a field-scale injection scenario into a heterogeneous formation. A description of the benchmark problems and a brief introduction on participating codes are provided in their study. The results of the benchmark study are also presented and discussed. Zhang et al. illustrated and analyzed the monitoring process of CO₂ storage safety and leakage in the CCS demonstration project of the Jilin oilfield in China. They demonstrated that the monitoring of targets should be focused on the reservoir, near-surface, and injection and production systems, as shown by field experience. It can not only prevent CO₂ leakage, but also avoid the blind expansion of monitoring program scopes by applying monitoring methods to ensure the integrity of wellbores. Their works can provide valuable guidance for the further enlarged Jilin project and other CO₂ EOR and geological storage operations.

In this paper, a geological scale 3D reactive flow simulation model is built to simulate the leakage processes though the assumed leakage channels in typical caprock–aquifer geological storage systems. The dissolution/precipitation reactions are coupled with fluid flow simulations in this model with considerations for reservoir minerals calcite, kaolinite, and anorthite. As an essential trigger for geochemical reactions, the changes in pH value are investigated during and after the CO₂ injection process. The influence of the reservoir temperature on CO₂ leakage is illustrated. CO₂ leakage potential through leakage channels with different permeabilities is evaluated. The effects of the distance between the CO₂ injection well and the leakage channel on the leakage potential are investigated.

2. REACTIVE FLOW SIMULATION MODEL

Literature researches indicate that the existence of a leakage channel is key risk point for CO₂ storage safety and the leakage mechanisms can be influenced by environmental and anthropogenic factors. It is meaningful to study the dynamic leakage behaviors and their mechanisms with the presence of a leakage channel in typical CO₂ geological storage systems. Meanwhile, the study on CO₂ leakage can provide a reference for the implementation of CO₂ monitoring methods and projects, which is beneficial for increasing the CO₂ geological storage safety and enhancing the public confidence in CO₂ geological storage. The background data of this study are according to topic 1, which is given at the Workshop on Numerical Models for CO₂ Storage in Geological Formations that took place from 2–4 April, 2008, in Stuttgart, Germany. Compositional simulator is adopted to set up the 3D reactive flow simulation model of typical caprock–aquifer system for investigating CO₂ leakage behaviors and mechanisms during the CO₂ geological storage process. The existence of leakage channels with high permeability inside the caprock or seal layer can induce an upward migration of CO₂ and increase the leakage risk potential. Hence, a 3D reactive flow simulation model is built for studying CO₂ leakage behaviors and mechanisms in typical caprock–aquifer system as shown in Figure 1.

Figure 1. 3D model to simulate CO₂ leakage during CO₂ geological storage in a typical caprock–aquifer system.
K is the activity product for aqueous reaction \( \alpha \).

\( a_R \) is the chemical amount of aqueous reactions; and \( k \) is the activity constant of the mineral reaction expressed by eq 3.

\( \alpha \) is the equilibrium constant of aqueous reaction \( \alpha \) of mineral reactions.

\( A \) is the following reactive rate formula is applied in this model:

\[
\frac{dz}{dt} = -\sum_{k=1}^{n} N_k (4 \pi r_k^3) \frac{dr_k}{dt}
\]

where \( r_k \) is the porosity; \( N_k \) is the amount of mineral particles per rock volume; and \( r_k \) is the dissolution reaction rate of mineral \( k \).

In order to reflect the relationship between porosity and permeability, the Kozeny–Carman equation is inserted into the reactive simulation model and its expression is as follows:

\[
k = k_0 \left( \frac{\phi}{\phi_0} \right) \left( \frac{1 - \phi}{1 - \phi_0} \right)^2
\]

where \( k \) is the real-time permeability; \( k_0 \) is the initial permeability; \( \phi \) is the real-time porosity; \( \phi_0 \) is the initial porosity; and \( n \) is the correlation coefficient. In this study, the value of \( n \) is assumed to be 1. With the presence of a stronger relationship between porosity and permeability, the influence of mineral reactions on reservoir properties can be enhanced with the value of \( n \) larger than 1. In addition, the equations and correlation coefficients of the aqueous and mineral reactions in this study are shown in Tables 1–3.

### 3. RESULTS AND DISCUSSION

#### 3.1. Influence of Geochemical Reactions on CO\(_2\) Leakage

By comparing with the scenario without considering geochemical reactions, the leakage behaviors can be analyzed with the presence of geochemical reactions. At the same time, the mineral trapping mechanism during CO\(_2\) geological storage process can also be exhibited at some extent. As shown in Figure 2, grid (15, 13, 1/5, 1, 1), and grid (15, 13, 1/5, 5, 1) are selected as the no.1 and no.2 reference points for monitoring the change in CO\(_2\) saturation, respectively. The distance between the leakage channel and the CO\(_2\) injection well is set to 100 m. The permeability of leakage channel is assumed to be \( 1000 \times 10^{-3} \) \( \mu \)m\(^2\).
CO₂ saturation decreases from 0.69047 to 0.68997 at the no.1 reference point with considering geochemical reactions after 20 years of CO₂ injection. This phenomenon indicates that the beneficial mineral reactions can trap CO₂ during CO₂ geological storage processes to some extent. Given that the selected CO₂ injection period is relatively short and the relationship between porosity and permeability is a weak correlation, the mineral trapping mechanism is not very significant with relatively small changes in CO₂ saturation. However, the total storage capacity of CO₂ based on mineral trapping mechanisms can be considerable in view of actual injection volume and storage period. Therefore, it is beneficial to enlarge the positive effects of mineral trapping mechanisms on the CO₂ permanent storage by mastering the mineral distribution and total amount when selecting storage sites.

3.2. Changes in pH. A change in pH is induced after CO₂ dissolves in water. pH is an important parameter to evaluate the tendency of different geochemical reactions. At the same time, the change in pH can reflect the CO₂ migration front at some extent in CO₂ storage projects. Hence, monitoring the change in pH can provide an alert for CO₂ leakage and predict the potential zones for special reactions, which need an environment of low pH. The distance between the CO₂ injection well and the leakage channel is set to be 100 m. Permeability of the leakage channel is assumed to be 1000 × 10⁻³ μm². Reservoir temperature of 60 °C is adopted in this reactive flow simulation model. As can be seen in Figure 3, a low pH region becomes larger with the continuous injection of CO₂ during the storage process and can spread to the aquifer overlaying the caprock with the presence of a leakage channel.

Therefore, monitoring changes in low pH areas can reflect the degree of CO₂ escape and can also provide an early warning of some harmful reactions that require a low pH environment. Based on modeling and experimental studies, a decrease in aqueous pH associated with CO₂ leakage into the overlying aquifer will induce increased aqueous concentrations of a wide range of metals (such as Pb, Cd, Cu, Fe, Mn, Zn, Cr, V, and U). CO₂-induced decrease in pH can also weaken the integrity of the injection and production wells by damaging their cement ring and wellbore. After 20 years of CO₂ injection, the pH can be as low as 4.7 in the aquifer overlaying the caprock.

### 3.3. Influence of Leakage Channel Permeability

Leakage channels with different permeabilities can induce CO₂ leakage at different scales. It is of great significance to study the influence of permeability of the leakage channel on the CO₂ leakage performance during the CO₂ storage process. Four kinds of leakage channels with the permeability of 1, 10, and 1000 × 10⁻³ μm², respectively, are selected to study the influence of leakage channel permeability on CO₂ leakage behaviors. The distance between the CO₂ injection well and the leakage channel is set to be 100 m and the reservoir temperature is assumed to be 60 °C.

As can be achieved in Figure 4, the CO₂ leakage risk increases with increasing permeability of the leakage channel, which can be expressed by an enlarged distribution range of CO₂ in the overlying aquifer. It is notable that the leakage risk can be reduced significantly with the presence of a relatively...
lower permeability \((10 \times 10^{-3} \mu m^2)\), which indicates that CO\textsubscript{2} leakage can be controlled with blocking the leakage channel to some extent, and it is unnecessary to plug the leakage channels thoroughly. In addition, the leakage control costs can also be reduced with applying a relatively small amount of blocking materials.

**3.4. Influence of Distance between Leakage Channel and CO\textsubscript{2} Injection Well.** For some storage cases, there may exist some potential leakage channels, which can be triggered by the injection activity. These kinds of potential leakage channels can keep a close state without CO\textsubscript{2} injection, which provide barriers for the subsurface fluid migration. However, CO\textsubscript{2} injection activity may disturb the relatively stable state of leakage channels that leads the leakage channels to an open state. Therefore, the influence of distance between the leakage channel and CO\textsubscript{2} injection well on the leakage performance is estimated.

Changes of CO\textsubscript{2} saturation in the no.2 reference point with the presence of different distances between the leakage channel and the CO\textsubscript{2} injection is applied to investigate the distance influence on leakage behaviors in this study. The leakage channel is assumed to be open in this reactive flow simulation process. The reservoir temperature is set to be 60 °C. The permeability of leakage channels is assumed to be \(1000 \times 10^{-3} \mu m^2\). The distances of leakage channels and CO\textsubscript{2} injection wells are set to be 20 m, 25 m, 30 m, 40 m, 60 m, 75 m, 90 m, and 100 m. As can be achieved in Figure 5, the leakage is postponed with increasing the distance. However, the leakage levels tend to be consistent with injecting more CO\textsubscript{2}.

**3.5. Influence of Reservoir Temperature.** It is of a certain guiding significance to investigate the influence of temperature on leakage behaviors for the selection of geological storage reservoirs and understanding the safety of geological storage reservoirs with different temperatures.

Changes of CO\textsubscript{2} saturation in the no.2 reference point are applied here to study the influence of reservoir temperature on the leakage performance. The distance between the leakage channel and the CO\textsubscript{2} injection well is assumed to be 100 m and the permeability of leakage channel is set to be \(1000 \times 10^{-3} \mu m^2\). As can be seen in Figure 6, the CO\textsubscript{2} leakage rate accelerates with the increase in reservoir temperature, which can be exhibited by the steepening curve of CO\textsubscript{2} saturation. Moreover, the leakage level enlarges with the presence of a higher reservoir temperature that can be achieved by the comparison of the CO\textsubscript{2} saturation at higher reservoir temperatures and lower reservoir temperatures after 20 years of CO\textsubscript{2} injection in the no.2 reference point. Hence, storage reservoirs with relatively lower reservoir temperatures are recommended to be candidates for CO\textsubscript{2} geological storage when other conditions are similar, which may slow down the leakage rate or reduce the leakage risk with the presence of a potential leakage path. However, deeper storage can also decrease the leakage risk of CO\textsubscript{2} to the atmosphere. Therefore, it is important to avoid the storage reservoirs with abnormally high temperatures.

**4. CONCLUSIONS**

CO\textsubscript{2} geological storage has become one of the research priorities worldwide in recent years, which can reduce greenhouse gas emissions. During the CO\textsubscript{2} storage process, existing or newly generated leakage channels are inevitable because of natural and man-made geological activities. Hence, the storage safety in terms of CO\textsubscript{2} leakage has always been an eminent issue for concern. In this study, a 3D reactive flow simulation model is built to investigate the influence of geochemical reactions, reservoir temperature, and the permeability of leakage channels on leakage behaviors. The influence of distance between the injection well and the leakage channel on leakage risk is also evaluated. At the same time, changes in pH during the leakage process are exhibited. The following conclusions can be drawn from the above study.

1. The leakage risk can be reduced with the presence of geochemical reactions. Storage reservoirs with suitable minerals are recommended to be the candidates for CO\textsubscript{2} geological storage. A low pH region enlarges with the continuous injection of CO\textsubscript{2}, which can reflect the front of CO\textsubscript{2} migration. Therefore, monitoring the change in pH can give an alert on CO\textsubscript{2} leakage and predict the potential zone for harmful reactions, which need an environment of low pH.

2. The leakage level reduces with decreasing the permeability of the leakage channel. Leakage risk can be reduced significantly with the presence of a relatively lower permeability \((10 \times 10^{-3} \mu m^2)\), which indicates that CO\textsubscript{2} leakage can be controlled without plugging the leakage channels thoroughly.

3. The occurrence of a leakage phenomenon can be postponed with increasing the distance between the CO\textsubscript{2} injection well and the leakage channel. However, the
leakage level tends to be consistent with injecting more CO₂.

(4) CO₂ leakage rate accelerates with increasing reservoir temperature. The leakage level enlarges with the presence of higher reservoir temperature. Hence, storage reservoirs with relatively lower reservoir temperatures are recommended to be candidates for CO₂ geological storage when other conditions are similar.

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