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Geochemical Modelling of the Evolution of Caprock Sealing Capacity at the Shenhua CCS Demonstration Project

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Abstract: CO₂ geological storage is considered as an important measure to reduce anthropogenic CO₂ emissions to the atmosphere for addressing climate change. The key prerequisite for long-term CO₂ geological storage is the sealing capacity of caprock. This study investigates the evolution of sealing capacity of caprock induced by geochemical reactions among CO₂, water and caprock using TOUGHREACT code based on the Heshanggou Formation mudstone at the Shenhua Carbon Capture and Storage (CCS) demonstration site of China. The results show that the self-sealing phenomenon occurs in the lower part of the caprock dominated by the precipitation of dawsonite, magnesite, siderite, Ca-smectite and illite. While the self-dissolution occurs in the upper part of caprock mainly due to the dissolution of kaolinite, K-feldspar, chlorite and Ca-smectite. Sensitivity analyses indicate that the precipitation of dawsonite, magnesite, siderite is highly advantageous leading to self-sealing of caprock, with albite and chlorite dissolution providing Na⁺, Mg²⁺ and Fe²⁺. The dissolution of K-feldspar dominates illite precipitation by providing required K⁺, and albite affects Ca-smectite precipitation. The self-sealing and self-dissolution of caprock are enhanced significantly with increasing temperature, while the effect of salinity on caprock sealing capacity is negligible perhaps due to the low salinity level of formation water.

Keywords: carbon capture and storage (CCS); CO₂ geological storage; CO₂-water-rock interaction; sealing capacity of caprock; self-sealing; self-dissolution; geochemical modelling; Shenhua CCS demonstration project

1. Introduction

The increasing concentration of anthropogenic CO₂ in the atmosphere has caused significant global climate change. CO₂ emission reduction has attracted extensive attention from the international community, especially the scientific community [1]. Among the existing emission reduction ways, carbon capture and storage (CCS) in geological formations such as deep saline aquifers, oil and gas reservoirs, and un-minable coal beds, is considered to be the most promising options for lowering anthropogenic emissions of CO₂ to the atmosphere on a large scale [2,3]. Recently, CCS technologies

have been extended to CCUS (carbon capture, utilization and storage) technologies, which can reduce CO₂ emissions and obtain economic benefits at the same time [4–6]. A series of CCS or CCUS operations and demonstration projects have been launched around the world, including the Sleipner site in the Norwegian part of the North Sea [7], the CO₂CRC Otway project in Victoria, Australia [8], the In Salah operation in Algeria [9], the Weyburn project in Canada [10]; Cranfield project in Mississippi, USA [11]; and the Shenhua CCS demonstration project in the Ordos Basin, China [12].

For the implementation of a large-scale CCS/CCUS project, the primary concern is the sealing capacity of caprock overlying the CO₂ storage reservoir, which improves the long-term safety of CO₂ geological storage [13]. The injected CO₂ can accumulate with time under the caprock due to its low permeability and high capillary entry pressure [14–16]. However, CO₂ may infiltrate into the initially water-saturated caprock when buoyancy pressure is higher than the capillary entry pressure. The intruded CO₂ dissolves into the formation fluid making an acidic medium which reacts with the caprock matrix, leading to mineral dissolution and precipitation and associated self-sealing and self-dissolution of caprock [17–20]. Such changes can significantly influence the sealing capacity of caprock and eventually affect the safe and long-term storage of CO₂.

It is crucial to understand the mechanism of the geochemical interactions among caprock minerals, water and CO₂ to characterize the evolution of caprock sealing capacity for long-term CO₂ storage. Many experimental studies have been performed to investigate the effect of geochemical reactions on mineral alterations and caprock permeability [21–26]. Batch and flow-through experiments have reported acidified CO₂-rich brines react with the caprock minerals resulting in the dissolution of primary minerals and the precipitation of secondary minerals, which are affected by mineral compositions and reservoir conditions. Alemu et al. [25] compared carbonate- and clay-rich shale batch reactions with CO₂ and water. They found that carbonate-rich shale is highly reactive, which may lead to porosity increase. According to [17], the geochemical reaction rates are accelerated whereas the mineral reaction mechanism is changed due to high temperature. These studies have determined significant mineral alterations and changes in pore structure and porosity/permeability of caprock due to the dissolution and precipitation of carbonate and clay minerals [17,21,25,27].

Geochemical reactions can occur for hundreds to thousands of years and may make a significant contribution to alterations in permeability and thus the sealing capacity of caprock [13,28]. Consequently, several numerical models of geochemical reactions have been recently conducted to evaluate the sealing capacity of caprock [7,29–34]. Tian et al. [29] investigated the impact of heterogeneous mineralogical composition on the sealing capacity of caprock for a CO₂ geological storage site. They found that the spatial variation in mineral composition slightly enhanced the sealing capacity of the caprock. The work of Xiao et al. [30] suggested increased caprock sealing efficiency resulting from maximum porosity decreases ~25% at the reservoir-caprock interface due to mineral precipitation in the Morrow Shale under typical CO₂ enhanced oil recovery (CO₂-EOR) conditions, by considering the influence of hydrological and mineralogical heterogeneity. Most of these geochemical modelling studies report the dissolution of carbonate and feldspar minerals, along with secondary carbonate and clay minerals precipitation due to CO₂ charged brine reacting with caprock minerals. These geochemical processes could affect solid volume, and hydrodynamic and mechanical properties of the caprocks, which have the potential to affect porosity and permeability changes, thereby enhancing or weakening the sealing capacity of caprock [31,32,35]. Gherardi et al. [31] conducted reactive transport simulations in the caprock of a depleted gas reservoir for CO₂ storage using TOUGHREACT code (Version 1.2, Lawrence Berkeley National Laboratory (LBNL), Berkeley, CA, USA) [36]. They found that when free CO₂ enters into the caprock through existing fractures or high permeability zones, self-dissolution alteration occurs due to the dominant geochemical reaction of significant calcite and dolomite dissolution in caprock. By contrast, some calcite precipitation is predicted leading to further sealing of the storage reservoir when fluid-rock interactions occur under fully liquid-saturated conditions and a diffusion-controlled regime. Similarly, Tian et al. [32] evaluate the effects of generated random heterogeneous permeability

on the migration of CO₂ within the caprock, the alteration of minerals and the associated evolution of the caprock sealing efficiency.

The above studies suggest that the geochemical interactions among CO₂, water and caprock cause minerals alteration in caprock. The dominant mineral dissolution/precipitation reaction(s) may lead to porosity/permeability reduction or enhancement, and thus potentially contribute significantly to the evolution of sealing capacity of caprock, which can affect long-term safety of CO₂ storage. However, a number of factors, namely the caprock mineralogy, water chemistry, and formation properties (e.g., temperature, pressure, salinity and thickness) differ from site to site, which might accelerate or retard different geochemical reactions, thereby influencing the sealing capacity of caprock [16,20,31,34]. Therefore, the geochemical reactions which occur in caprock are site-specific and need to be investigated case by case. Moreover, due to the fact that CO₂-water-caprock geochemical processes are very slow under the actual storage conditions, laboratory experiments have certain limitations (e.g., short laboratory time scale and the increase of reactive surface areas). It is imperative to carry out numerical simulation of the geochemical reactions among CO₂, water and caprock to evaluate the long term caprock sealing capacity based on the actual site characteristics.

The main aim of this study was to investigate the evolution of seal capacity of mudstone caprock induced by geochemical reactions during long-term CO₂ storage. A vertical one-dimensional model was employed to represent the reservoir-caprock system based on the seismic, well testing and logging data of Heshanggou Formation (regional seals) and Liujiagou Formation (the upmost reservoir) at the Shenhua CCS demonstration site of China. Reactive transport modelling was conducted to analyze mineral dissolution and precipitation mechanisms and their impact on the changes in caprock sealing capacity using TOUGHREACT. Moreover, sensitivity analyses of key mineral composition, formation temperature and salinity variables were made. The results could have a novel scientific contribution for evaluating the caprock sealing and CO₂ storage potential in the large-scale implementation of CCS/CCUS projects from the perspective of geochemistry.

2. Site Characteristics of Shenhua CCS Demonstration Project

The Shenhua CCS project lies in the Chenjiacun village of Wulam Len town, EjinHoro county, about 40 km southeast of the Ordos City, Inner Mongolia and 17 km northwest to the Shenhua Coal Liquefaction Co., Ltd-CO₂ source [12]. It is tectonically located on the east section of the Yimeng Uplift of the northern part of the Ordos Basin (Figure 1). The Ordos Basin, covering an area of 250,000 km², is the second-largest sedimentary basin and an important energy base in China. The CO₂ storage capacity of deep saline aquifers in the Ordos Basin is estimated to be more than 10 billion tons [12,37]. The injection operation is structured so that CO₂ is injected into multiple layers from the Liujiagou Formation through to the Majiagou Formation, with Heshanggou Formation to Jurassic strata (mudstone, silty mudstone and shale) as the regional seals (Figure 1).

The bottom of the Heshanggou Formation is mainly composed of mudstone, which is the first barrier to prevent CO₂ escape. The average porosity and permeability of this section are 2.99% and 0.25 mD, respectively, which is a low porosity and low permeability formation. The top of the Liujiagou Formation is composed of light brownish red fine sandstone with brownish red mudstone, whose sandstone is mainly lithic arkose and feldspathic litharenite. The average porosity and permeability of the top Liujiagou Formation is 11.40% and 4.5 mD, respectively, which defines it as a low permeability formation [38].

Figure 1. Location and stratigraphic structure of Shenhua CCS demonstration area in the Ordos Basin, China (Modified from [37,38]).

3. Modelling Approach

3.1. Numerical Tool

All simulations are conducted using the TOUGHREACT/ECO2N code [36,39]. The numerical method for fluid flow and chemical transport simulation is based on the integral finite difference (IFD) method for space discretization. The resulting concentrations obtained from the transport simulations are then substituted into a chemical reaction model. The system of chemical reaction equations is solved on a grid-block basis by Newton-Raphson iteration. Thermodynamic data of aqueous species and minerals used in the simulations are taken from the EQ3/6 database [40], which have been derived from SUPCRT92. For local equilibrium constants and kinetic rates used in TOUGHREACT refer to [39]. Full details on the simulator are given in Xu et al. [36,39].

Porosity and permeability are the key parameters in CCS that can affect the CO₂ injectivity and caprock sealing. The variation of porosity is directly tied to the volume changes as a result of mineral alteration, which is calculated by:

$$\phi = 1 - \sum_{b=1}^{ab} fr_b - fr_u \quad (1)$$

where ab is the number of minerals; fr_b is the volume fraction of mineral b in the rock ($V_{\text{mineral}}/V_{\text{medium}}$, including porosity); and fr_u is the volume fraction of nonreactive rock.

Permeability changes are calculated from changes in porosity using ratios of permeabilities as per the Kozeny-Carman grain model [39], as follows:

$$k = k_i \frac{(1 - \phi_i)^2}{(1 - \phi)^2} \left(\frac{\phi}{\phi_i} \right)^3 \quad (2)$$

where k_i is the initial permeability; ϕ and ϕ_i are current and initial porosity, respectively.

3.2. Model Description

According to the underground conditions of the bottom Heshanggou Formation at depths of 1495–1545 m and the top Liujiagou Formation at depths of 1545–1555 m at the Shenhua CCS demonstration site, a vertical one-dimensional (1D) model representing 50 m thick caprock and 10 m thick reservoir is employed (Figure 2), which was developed in our previous studies [38,41]. The 60 m column is divided into a total of 52 layers in the vertical direction, with caprock of 51 layers of equal thickness and reservoir of 1 layer. The grid cells of the other two directions are 1 m. An infinite volume element of 10^{25} m^3 is set on the uppermost grid of the caprock, representing constant pressure boundary in the simulation that hydrogeological parameters of the caprock are stable. The volume of the reservoir is 10 m^3 . This setting can not only reflect the evolution of reservoir pressure and CO_2 gas saturation after shutting down the injection well, but also consider the effect of geochemical reactions on caprocks.

The formation pressure at a depth of 1550 m is estimated approximately at 15.0 MPa based on the well drilling measurements of Zhongshenjian 2#. For the convenience of calculation, the initial pressure for the model is set to be at static hydraulic pressure state. Then the hydrostatic pressure distribution in the caprock is set by hydrostatic equilibrium, with 14.5 MPa to 15 MPa from the top to the bottom of the caprock. After CO_2 injection, the pressure gradient of reservoir fluctuates between 0.32 MPa and 0.45 MPa. Therefore, the pressure of the reservoir is set to 15.5 MPa, exceeding the hydrostatic pressure of the caprock bottom by 0.5 MPa. The average temperature of 53°C is applied to the whole model. As key parameters that dominate the CO_2 migration and storage, the vertical permeabilities of the caprock and reservoir are set to $2.5 \times 10^{-17} \text{ m}^2$ and $4.5 \times 10^{-16} \text{ m}^2$, respectively, which are taken as 1/10 of the horizontal permeabilities [31]. The caprock is initially water-saturated, whereas the reservoir is assumed to be in two-phase conditions with CO_2 saturation of 0.8 [31,38]. Details in hydrogeological parameters used in the model are listed in Table 1.

Figure 2. Sketch of the 1D vertical model.

Table 1. Hydrogeological parameters used in the simulations [12,32,38].

Parameters	Formation	
	Caprock	Reservoir
Porosity	0.03	0.114
Horizontal permeability (10 ⁻¹⁵ m ²)	0.25	4.5
Vertical permeability (10 ⁻¹⁵ m ²)	0.025	0.45
Pore compressibility (Pa ⁻¹)	4.5 × 10 ⁻¹⁰	4.5 × 10 ⁻¹⁰
Rock grain density (kg/m ³)	2600	2600
Formation heat conductivity (W/m °C)	2.51	2.51
Rock grain specific heat (J/kg °C)	920	920
Temperature (°C)	53	53
Pressure (MPa)	14.5–15.0	15.5
Salinity (mass fraction)	0.016	0.046
Relative permeability		
Liquid (van Genuchten, 1980)		
$k_{rl} = \sqrt{S^*} \{1 - (1 - [S^*]^{1/m})^m\}^2$	$S^* = (S_l - S_{lr}) / (1 - S_{lr})$	
Residual liquid saturation	$S_{lr} = 0.30$	
Exponent	$m = 0.457$	
Gas (Corey, 1954)		
$k_{rg} = (1 - \hat{S})^2 (1 - \hat{S}^2)$	$\hat{S} = (S_l - S_{lr}) / (S_l - S_{lr} - S_{gr})$	
Residual gas saturation	$S_{gr} = 0.05$	
Capillary pressure (van Genuchten, 1980)		
$P_{cap} = -P_0 ([S^*]^{-1/m} - 1)^{1-m}$	$S^* = (S_l - S_{lr}) / (1 - S_{lr})$	
Residual liquid saturation	$S_{lr} = 0.20$	
Exponent	$m = 0.457$	
P ₀ (MPa)	2.0	1.0
P _{max} (MPa)	100	10

3.3. Initial Mineralogy and Water Geochemistry

The mass fraction of clay minerals in the bottom of the mudstone caprock (Heshanggou Formation) varies greatly from 13% to 56% generated by XRD quantitative analysis of core samples taken from Zhongshenjian 2#. However, the relative proportion of clay minerals is basically the same, which are mainly composed of smectite and illite, followed by kaolinite and chlorite. Non-clay minerals are mainly composed of quartz, K-feldspar, albite and a small amount of carbonate minerals. The content of clay minerals in the caprock is set to 30% by fraction of volume to meet the format of TOUGHREACT in defining the mineral abundance in this work. The content of clay minerals in the top of the reservoir (Liujiagou Formation) is 30%, and non-clay minerals are mainly quartz and feldspar. Almost all possible secondary minerals are considered in the simulations according to previous studies [37,39]. The details of mineral compositions of the caprock and reservoir are shown in Table 2, which is similar to our previous study [38].

The water chemistry of the caprock (Heshanggou Formation) and reservoir (Liujiagou Formation) was derived from water samples that were extracted from Zhongshenjian 2# at the Shenhua CCS demonstration site and presented in Table 3. Batch geochemical modelling of water-rock interaction was performed to equilibrate the formation water with primary minerals (Table 2) until the desired water chemistry was obtained, where the saturation indices (SI) equal or approximately equal zero. The resulting water chemistry was used as the initial condition for the reactive transport simulation.

Table 2. Initial mineral volume fractions and possible secondary mineral phases for caprock and reservoir.

Mineral	Chemical Composition	Volume Fraction (%) of Solid Rock	
		Caprock	Reservoir
Primary			
Illite	$K_{0.6}Mg_{0.25}Al_{1.8}(Al_{0.5}Si_{3.5}O_{10})(OH)_2$	11.0	15.6
Kaolinite	$Al_2Si_2O_5(OH)$	3.8	4.7
Ca-smectite	$Ca_{0.145}Mg_{0.26}Al_{1.77}Si_{3.97}O_{10}(OH)_2$	10.3	5.4
Chlorite	$Mg_{2.5}Fe_{2.5}Al_2Si_3O_{10}(OH)_8$	4.9	4.2
Quartz	SiO_2	30.0	33.5
K-feldspar	$KAlSi_3O_8$	7.0	10.5
Albite	$NaAlSi_3O_8$	8.0	15.0
Calcite	$CaCO_3$	2.2	9.0
Oligoclase	$CaNa_4Al_6Si_{14}O_{40}$	0	2.0
Secondary			
Anhydrite	$CaSO_4$		
Pyrite	FeS_2		
Hematite	Fe_2O_3		
Siderite	$FeCO_3$		
Ankerite	$CaMg_{0.3}Fe_{0.7}(CO_3)_2$		
Dawsonite	$NaAlCO_3(OH)_2$		
Magnesite	$MgCO_3$		
Dolomite	$CaMg(CO_3)_2$		
Halite	$NaCl$		

Notes. The total volume fraction of reactive minerals should be less than or equal to 1.0. When the total volume fraction of reactive minerals is less than 1.0, the insufficient volume fraction of the whole rock is the default unreactive minerals during the simulation.

Table 3. Initial total dissolved component concentrations (mol/kg H₂O) for caprock and reservoir.

Component	Caprock	Reservoir
Ca ²⁺	9.424×10^{-2}	3.628×10^{-1}
Mg ²⁺	1.495×10^{-2}	3.728×10^{-2}
Na ⁺	1.620×10^{-1}	3.398×10^{-1}
K ⁺	9.256×10^{-4}	8.756×10^{-4}
Fe	6.107×10^{-5}	4.000×10^{-5}
SiO ₂ (aq)	1.783×10^{-4}	1.967×10^{-5}
C	3.308×10^{-3}	4.134×10^{-4}
SO ₄ ^{2−}	2.141×10^{-2}	2.161×10^{-2}
Cl [−]	3.467×10^{-1}	1.119
pH	6.94	5.35

Notes. Iron is the sum of Fe²⁺, Fe³⁺ and their related complexities; C is the sum of CO₂ (aq) and its related species such as CO₃^{2−} and HCO₃[−].

3.4. Simulation Scenarios

After CO₂ is injected into the deep saline aquifers, it may enter the caprock under the action of formation pressure, buoyancy and injection pressure, resulting in complex CO₂-water-rock interactions which influence caprock sealing on a geological timescale. We performed all simulations for 5000 years to approximate a scenario of long-term CO₂ storage. Mineral composition and formation properties such as temperature, salinity are the key factors that influence the geochemical reaction and caprock sealing capacity, which need further study. Therefore, a series of simulation scenarios were generated by varying one factor relative to a base case (the first simulation using the parameters given in Tables 1–3). These are analyzed to assess how caprock permeability and mineralized CO₂ are affected by these parameters, which are listed in Table 4.

Table 4. Summary of the simulation cases.

Simulation Scenarios	Variable Changed	Alternative Value
Case 1.1	Content of K-feldspar	0
Case 1.2	Content of albite	0
Case 2.1	Temperature (°C)	63
Case 2.2	Temperature (°C)	73
Case 3.1	Salinity (mass fraction)	0.036
Case 3.2	Salinity (mass fraction)	0.056

4. Results and Discussion

4.1. Distribution of Gaseous CO₂, Dissolved CO₂ and Mineralised CO₂ within the Caprock

After intruding into the caprock, CO₂ can be trapped by three phases: gas phase, aqueous phase, and mineral phase (Figure 3a–c). The CO₂ gas migrates upward under the action of formation pressure, buoyancy and injection pressure over time. Meanwhile, CO₂ dissolves gradually into the formation water forming carbonic acid, H₂CO₃, which subsequently dissociates into bicarbonate and carbonate ions, HCO₃[−] and CO₃^{2−}. It decreases pH in the aqueous phase of CO₂ altering the initial geochemical equilibrium in the caprock. The spatial variation of CO₂ concentration will affect the distribution of pH and the extent of CO₂-water-rock interactions [9,32]. It can be seen that pH quickly drops from 6.9 to 4.8 following the dissolution of CO₂ into groundwater at the bottom of caprock (Figure 3b,d).

Figure 3. Distribution of gaseous CO₂ (a), dissolved CO₂ (b), mineralized CO₂ (c) and pH values (d) for different times.

Over time, CO_2 gas phase decreases, but CO_2 continues to dissolve in the formation water enhanced by upward migration of the CO_2 . It can be seen that gaseous CO_2 does not penetrate the caprock and is always enclosed in the caprock during the simulation time (Figure 3a). Then, an increasing proportion of CO_2 is trapped in mineral phases through the formation of carbonate minerals during the process of CO_2 -water-rock interactions. As shown in Figure 3c, CO_2 sequestered in mineral phases increases gradually from 100 years to the end of the simulation, which is favorable for caprock sealing. Mineral dissolution and precipitation processes are critical for the evolution of caprock sealing performance [35,42], which is very important for long-term CO_2 geological storage.

4.2. Evolution of the Sealing Capacity of Caprock

During the CO_2 -water-rock geochemical reactions, the dissolution and precipitation of minerals may lead to changes in caprock porosity and permeability, potentially altering the fluid flow pattern, which could affect the sealing capacity of caprock and thus long-term CO_2 geological storage [39,43]. The spatial distribution of permeability in caprock is shown in Figure 4, which is consistent with the spatial distribution of CO_2 gas saturation (Figure 3a). It can be seen that the permeability tends to decrease in the lower part of the caprock (less than 30 m) while increase in the upper part of the caprock. The decrease is mainly because that CO_2 infiltrates into the bottom of caprock during long-term storage, resulting in the volume of precipitated minerals (e.g., CO_2 trapping minerals, Figure 3c) exceeds that of those dissolved [21,44]. This improves the caprock sealing security (self-sealing). However, in the upper part of caprock unaffected by CO_2 , the increase in permeability is caused by the long-term water-rock interaction that leading to more mineral dissolution than precipitation. Then, self-dissolution occurs which may decrease the caprock sealing to a certain extent.

Figure 4. Spatial distribution of permeability in caprock for different times.

4.3. Analysis of Self-Sealing and Self-Dissolution for Caprock Alteration

The self-sealing in the lower part of the caprock is induced by more mineral precipitation than dissolution. Among the precipitated minerals, the clay minerals are Ca-smectite and illite, and carbonate minerals are mainly dawsonite, magnesite and siderite, and other silicate mineral such as quartz (Figure 5). The precipitation of carbonate minerals plays a key role in caprock permeability change. As shown in Figures 5e–g and 4, the precipitation of dawsonite, siderite and magnesite are highly consistent with the variation of caprock permeability, which agree well with the distribution of CO_2 mineral trapping in caprock (Figure 3c). It can be inferred that the precipitation of carbonate minerals in pores is a common cementation process in mudstone caprock that can reduce or even close advection

pathways, which is highly advantageous leading to self-sealing of caprock. It is also determined by Charlet et al. [43] and Lo Ré et al. [45]. The precipitation of illite is also favorable for caprock sealing, but its variation is not consistent with other precipitated minerals (Figure 5b). This might be because the precipitation of illite is less affected by CO₂ in the system. Lo Ré et al. [45] have also observed illite precipitation both in their water-rock and CO₂-water-rock interaction experiments by XRD and SEM analysis, which confirm our results. The dissolution of chlorite, albite, kaolinite, K-feldspar and calcite may increase the caprock permeability to a certain extent. However, they can provide Mg²⁺, Fe²⁺, Na⁺, AlO₂⁻, K⁺ and Ca²⁺ for the precipitated minerals as mentioned above [17,31,46].

It can be seen that the precipitation of carbonate minerals (CO₂ trapping minerals) consumes CO₂ in caprock, resulting in the decrease in CO₂ gas saturation and caprock permeability, which is favorable for enhancing the sealing performance of caprock.

Figure 5. Cont.

Figure 5. Volume fraction change of clay minerals (a–d), carbonates (e–g) and other silicate minerals (h–j) within the caprock.

Dissolution has occurred in the upper part of caprock (Figure 4). This is mainly due to the dissolution of kaolinite, K-feldspar, chlorite and Ca-smectite during the long-term water-rock interactions. Meanwhile, the precipitation of illite, albite and quartz in the upper part of the caprock can slow down the increase of permeability, but the total amount of mineral dissolution is more than that of mineral precipitation, which results in the increase of permeability in the upper part of the caprock. This is in agreement with experimental studies conducted by Szabó et al. [20] and Lo Ré et al. [45].

The intrusion of CO_2 into the caprock changes the geochemical behavior of some minerals. As shown in Figure 5, Ca-smectite and albite in the lower part of caprock show an opposite trend compared with their behaviors in the upper part. It can be seen that CO_2 -water-rock interaction promotes the precipitation of Ca-smectite and quartz and dissolution of chlorite to a certain extent. Meanwhile, it changes albite from precipitation to dissolution and inhibits the dissolution of kaolinite. As can be seen from Figure 6, the changes in concentration of K^+ , Ca^{2+} , Na^+ , Mg^{2+} , Fe^{2+} and AlO_2^- in the system are complex. The ion concentrations vary generally greater in the lower part of the caprock induced by CO_2 than in the upper part without CO_2 . Concentrations of K^+ , Na^+ , Mg^{2+} , and Fe^{2+} appear to increase initially and then decrease irregularly over time in the lower part of the caprock, while AlO_2^- concentration decreases initially then increases over time. This suggests the complex mutual transformation of K^+ , Na^+ , Mg^{2+} , Fe^{2+} and AlO_2^- -bearing minerals during CO_2 -water-caprock geochemical process [22,42]. Ca^{2+} concentration decreases irregularly over time and is relatively constant at the end of the simulation, suggesting that steady state is established between the fluid and calcium-bearing minerals [45].

Figure 6. Concentrations (in mol/kg H₂O) of aqueous chemical components within the caprock. (a) K⁺; (b) Ca²⁺; (c) Na⁺; (d) Mg²⁺; (e) Fe²⁺; (f) AlO₂⁻. Note that the values of ion concentrations are presented on a log scale except for the high concentrations of Na⁺.

The dissolution of albite, K-feldspar, chlorite and calcite supplies required ions for the precipitation of illite, Ca-smectite, dawsonite, magnesite and siderite in the caprock. It can be seen that the dissolution behavior of K-feldspar is highly consistent with that of illite precipitation (Figure 5b,j), suggesting the dissolution of K-feldspar corresponds with illite formation. The study of Xu et al. [34] also shows that illite precipitates due to the dissolution of K-feldspar. It can be inferred that the dissolution of K-feldspar (KAlSi₃O₈) provides K⁺ for the precipitation of illite (K_{0.6}Mg_{0.25}Al_{1.8}(Al_{0.5}Si_{3.5}O₁₀)(OH)₂).

The dissolution of chlorite has a great effect on Mg^{2+} and Fe^{2+} -bearing minerals precipitation, which can provide Mg^{2+} and Fe^{2+} for the precipitation of illite, Ca-smectite, magnesite and siderite [37,47]. Calcite dissolution could provide the required Ca^{2+} for the precipitation of calcium-bearing minerals. Dissolution of feldspar, chlorite and calcite, and the formation of dawsonite are also observed in the Permian Supai Formation of the Springerville-St. John CO_2 field, USA [48], which is in general agreement with our results.

It can be inferred that the self-sealing and self-dissolution of caprock depend on minerals dissolution and precipitation over the long-term CO_2 -water-rock interactions. When mineral precipitation is greater than dissolution, the caprock permeability decreases, leading to the self-sealing phenomenon, which is favorable for enhancing the sealing capacity of caprock. On the contrary, when mineral dissolution is greater than precipitation, the caprock permeability increases, thus self-dissolution phenomenon occurs that may decrease the sealing capacity of the caprock.

4.4. Sensitivity Analyses

4.4.1. Influence of Mineral Composition

Through the above analysis, it is found that K-feldspar is the key mineral causing the self-dissolution and self-sealing of the caprock. In order to investigate the influence of K-feldspar on the sealing capacity of caprock, we set the content of K-feldspar to 0, that is, there is no K-feldspar in the caprock (Case 1.1). As presented in Figure 7a, the permeability of the caprock decreases obviously compared to the base case. It can be seen that the permeability decreases to 52% of initial permeability at the end of the simulation (i.e., 5000 years) without K-feldspar dissolution. However, mineralized CO_2 increases compared to the base case (Figure 7b), which could explain the decrease of permeability in the lower part of caprock from another aspect. As can be seen from Figure 7c, there is no illite precipitation when K-feldspar is absent as a primary mineral. This confirms that illite formation is due to the dissolution of K-feldspar, which is consistent with previous studies [7,34,47]. Those studies also suggest that K^+ and AlO_2^- required for illite precipitation are supplied by the dissolution of K-feldspar that agree well with our results. Meanwhile, the dissolution of albite and precipitation of Ca-smectite in the lower part of the caprock are promoted in the absence of K-feldspar (Figure 7d,e).

In order to investigate the abundance of albite on the sealing capacity of caprock, we set the content of albite to 0 (Case 1.2). It can be seen that the minimum value (0.144 mD) of caprock permeability reduces to 56% of the initial value in the base case (Figure 7a). As shown in Figure 7e, the precipitation of Ca-smectite decreases significantly in the lower part of the caprock in the absence of albite. Simultaneously, the minimum value of caprock permeability decreases to 0.17 mD at the bottom of the caprock, approximately 68% of the initial value, while the permeability increases to 136% of the initial value at the top of the caprock (Figure 7a). This is mainly because that the precipitation of Ca-smectite is limited to a great extent without albite dissolution, however, it promotes the dissolution of K-feldspar and the precipitation of illite (Figure 7c,f). It can be seen that mineralized CO_2 also decreases compared to the base case (Figure 7b), which can be explained that there is no albite dissolution providing sufficient Na^+ for dawsonite precipitation [49]. An example by Tambach et al. [50] also shows that the Na^+ released from albite is consumed by dawsonite precipitation, and K-feldspar is transformed into illite. This is in good agreement with our modelling results.

Therefore, it can be inferred that the dissolution of K-feldspar provides required K^+ for illite precipitation, and albite is the key mineral affecting Ca-smectite precipitation. When K-feldspar is absent in the system, self-dissolution is obviously weakened in the upper part of the caprock, and self-sealing is obviously enhanced in the lower part of the caprock, which is favorable for long-term CO_2 storage. When albite is absent in the system, self-dissolution of the caprock is enhanced, and self-sealing is weakened, which is not conducive to the sealing capacity of the caprock and the long-term CO_2 storage.

Figure 7. Spatial distribution of permeability (a), and mineralized CO₂ (b), and abundance (in volume fraction) of illite (c), albite (d), Ca-smectite (e), K-feldspar (f) within the caprock at the end of the simulation (i.e., 5000 years) obtained with three different mineral compositions.

4.4.2. Influence of Formation Temperature

The formation temperature varies with the depth of the aquifer and has a great effect on caprock sealing during long-term CO₂ geological storage. As shown in Figure 8a, the increase of temperature accelerates the decrease of permeability at the base of the caprock, and the vertical distribution range of permeability at the base also decreases with increasing temperature. Meanwhile, the permeability in the upper part of the caprock reaches 0.53 mD by the end of the simulation, increasing more than 210% from the initial value when the formation temperature is 73 °C. The results

suggest that self-sealing and self-dissolution of the caprock are enhanced with increasing formation temperature. This is mainly because the reaction rate of minerals increases greatly with the increase in temperature, thus strengthening the dissolution and precipitation of minerals, leading to significant changes in caprock permeability [25,33,35,51]. Under the domination of mineral precipitation in the CO₂-water-rock interaction, the precipitation further increases as the temperature increases, enhancing the self-sealing of caprock. For the upper part of the caprock, mineral dissolution dominates the water-rock interaction process increasing with increasing temperature, which leads to significant self-dissolution [20]. Similar observations are also reported by Liu et al. [17] and Jayasekara et al. [16] in experiment interactions between CO₂, caprock and brine.

Figure 8. Changes in caprock permeability (a), mineralized CO₂ (b) and CO₂ gas saturation (c,d) within the caprock for different temperatures.

It can be seen that CO₂ gas saturation decreases gradually from the base to the top of the caprock (Figures 3a and 8c,d). Meanwhile, the upward migration distance of gaseous CO₂ in caprock decreases with increasing temperature. There is basically no gaseous CO₂ after 100 years when the formation temperature is 73 °C. Then, the CO₂-water-rock interaction begins to weaken due to the dissolved CO₂ in caprock not being replenished over time and consumed gradually. Although the maximum value of mineralized CO₂ increases with increasing temperature, reaching 27.5 kg/m³ medium (Figure 3i), the vertical distribution decreases significantly, corresponding to the upward migration of gaseous CO₂ (Figure 8d). Thus, the total mineralized CO₂ within the caprock may decrease significantly with increasing temperature. These results suggest that the increase of formation temperature accelerates the geochemical process of CO₂, caprock and brine, which can consume CO₂ quickly and slow down the upward migration of CO₂ effectively within the caprock [16,33]. However, self-dissolution in the

upper part of the caprock is enhanced significantly due to the higher temperature, which may decrease the sealing capacity of the caprock.

4.4.3. Influence of Salinity

The effect of salinity on caprock sealing is evaluated by evaporating the initial formation water to increase salinity to 3.6 and 5.6 wt.% dissolved NaCl. As shown in Figure 9, the changes in caprock permeability and mineralized CO₂ are nearly the same for the different salinities. Although the salinity of the formation water increases to 5.6 wt.%, the effect on the caprock sealing and mineralized CO₂ is negligible. It is quite consistent with [46] that the formation water salinity has a negligible effect on the mineralization potential for CO₂. However, it is different from other studies where the increase of salinity enhances the ionic strength of the solution, reducing mineral dissolution and increasing mineral precipitation (e.g., deposition of different types of evaporites in rock pores) in the caprock, leading to a significant reduction in caprock permeability and decrease in CO₂ storage capacity at high salinity concentrations in brine [52–54]. This is probably because the salinity level in our study is so low that there is no significant effect on mineral alteration and consequent permeability changes and mineralized CO₂.

Figure 9. Changes in caprock permeability (a) and mineralized CO₂ (b) within the caprock for different salinity.

5. Conclusions

This study investigates the evolution of seal capacity of caprock induced by mineral alteration using TOUGHREACT based on the Heshanggou Formation mudstone at the Shenhua CCS demonstration site of China. The following conclusions can be drawn:

- (1) The CO₂ gas migrates upward under the action of formation pressure, buoyancy and injection pressure over time, then gradually decreases due to dissolution and the formation of carbonate minerals. Gaseous CO₂ does not break through the caprock and is always enclosed in the caprock during the simulation time. Mineralized CO₂ increases gradually from 100 years to the end of the simulation that is favorable for caprock sealing.
- (2) The self-sealing phenomenon occurs in the lower part of the caprock dominated by the precipitation of dawsonite, magnesite, siderite, Ca-smectite and illite during long-term CO₂-water-rock geochemical reactions, which is favorable for enhancing the sealing capacity of the caprock. On the contrary, self-dissolution occurs in the upper part of caprock mainly due to the dissolution of kaolinite, K-feldspar, chlorite and Ca-smectite, which may decrease the sealing capacity of caprock.

- (3) The precipitation of dawsonite, magnesite, siderite and other carbonate minerals can reduce or even close advection pathways with albite and chlorite providing Na^+ , Mg^{2+} and Fe^{2+} , which is highly advantageous, leading to self-sealing of the caprock. K-feldspar and albite are the key minerals causing the self-dissolution and self-sealing of the caprock. The dissolution of K-feldspar dominates illite precipitation by providing required K^+ , and albite affects the precipitation of Ca-smectite. When K-feldspar is absent as a primary mineral, the self-dissolution is weakened in the upper part of the caprock, and the self-sealing is obviously enhanced with mineralized CO_2 increasing in the lower part of the caprock, which is favorable for long-term CO_2 storage. When albite is absent, the self-dissolution of the caprock is enhanced, and self-sealing is weakened with mineralized CO_2 decreasing, which is not conducive to long-term CO_2 storage.
- (4) Formation temperature has a great effect on the sealing capacity of caprock. The self-sealing and self-dissolution of caprock are enhanced with increasing temperature because the kinetic reaction rate of minerals increases greatly with the increase of temperature strengthening the dissolution and precipitation of minerals. Meanwhile, the upward migration distance of gaseous CO_2 in the caprock decreases with increasing temperature due to the accelerated geochemical process of CO_2 , caprock and brine. However, the self-dissolution in the upper part of the caprock is enhanced significantly due to the high temperature that may result in a decrease of the sealing capacity of the caprock. The effect of salinity on the caprock sealing and mineralized CO_2 is negligible in this study mainly because the salinity level of the formation water in the Heshanggou Formation is so low.

In summary, we present a geochemical modelling study of the evolution of caprock sealing capacity in the Heshanggou Formation mudstone at the Shenhua CCS pilot of China. Results from this study are useful for the evaluation of geochemical behavior of caprock for practical implementations of CCS, providing a useful insight for screening the most effective caprocks and assessing the safety of long-term CO_2 geological storage by considering caprock compositions and in situ conditions. As future recommendations, it is necessary to determine the kinetic rate and thermodynamic properties of minerals as well as the process of precipitation and dissolution of the caprock matrix.

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