Influence of CO_2-water displacement characteristics on the storage efficiency and security of geological carbon storage

Yan Zhao[a,b*], Ruru Xi[a,b], Liu Yang[a,b], Qian Zhang[c], Xinyao Huang[d], Xiao Chen[e]

a. School of Water and Environment, Chang an University, Xi an 710054, *Shaanxi, People's Republic of China*

b. Key Laboratory of Subsurface Hydrology and Ecological Effects in Arid Region, Chang'an University, Ministry of Education, PR China

c. Petro China Changqing Oilfield Company Planning Department, Xi an 710018, *Shaanxi, People's Republic of China*

d. School of Earth Science and Resources, Chang an University, Xi an 710054, *Shaanxi, People's Republic of China*

e. School of Geological Engineering and Geomatics, Chang an University, Xi an 710054, *Shaanxi, People's Republic of China*

**Corresponding author: E-mail: yanzhao@chd.edu.cn*

Telephone: +86 18710443033

Abstract

In the mitigation of greenhouse gas emissions, the storage efficiency and security of geological carbon storage (GCS) are the focus of attention, and both of them are closely related to the displacement behavior between immiscible two phases. In this study, CO_2-water displacement experiments were conducted on six samples with various pore structures using NMR and MRI technology to characterize the fluid distribution and determine displacement patterns. The displacement property was found to be closely related to the pore structure and appears to be independent of mineral compositions. The two-phase displacement instability gradually evolved from tounging (logCa > -2.76) to capillary fingering (logCa < -1.85), and then further evolved into viscous fingering (logCa > -1.85). Nevertheless, pore structures with good connectivity and high-permeability channels will restrain the occurrence of unstable displacement even if logCa is in the favorable range. In addition, unstable displacement is seriously affected by the heterogeneity and anisotropy of the pore structure. With the tonguing phenomenon, displacement efficiency will present a distinct ladder-shaped increase with increasing pore size, whereas the capillary fingering and viscous fingering phenomena will induce a more complex and variable change rule. Compared with unstable displacement, the stable piston-like displacement tends to result in higher displacement efficiency. Furthermore, for rocks with high sealing efficiency that can be considered as caprocks, the pore structures are often dominated by micropores, and their displacement pattern is more likely to reflect time-consuming piston-like displacement, which will reduce the probability of premature CO_2 breakthrough.

1. Introduction

Under the threat of global warming, humans are facing severe pressure and challenges of carbon dioxide emission reduction (IPCC, 2005; Juanes et al., 2006; Li et al., 2013). Geological carbon storage (GCS) has been widely considered as an effective technology to mitigate greenhouse gas emissions (Bachu, 2000; Yang et al., 2019), for which the storage efficiency and security of GCS have been the focus of attention (Bachu et al., 2007; Goodman et al., 2011; Zhao et al., 2021). Both of these factors are closely related to the displacement of two phases. Many studies have confirmed that unstable displacement characterized by fingering flow, resulting from the low viscosity of $scCO_2$ relative to formation brine, is an important contributor to inefficient CO_2 storage (Zhang et al., 2011; Berg & Ott, 2012; Wang et al., 2012). Furthermore, unstable fingering flow of $scCO_2$ increases the probability of the premature breakthrough of CO_2 (Tsang et al., 2008; Song et al., 2012), and the high probability of CO_2 leakage can reduce the sealing efficiency of caprocks. Therefore, the displacement characteristics between CO_2-water at GCS conditions need to be thoroughly monitored and controlled to ensure efficient, safe, and permanent CO_2 storage (Nordbotten et al., 2005; Doughty et al., 2010; Juanes et al., 2010; MacMinn et al., 2010, 2011).

A large number of laboratory and numerical simulation studies have been carried out to investigate two-phase flow fundamentals, including distribution characteristics and displacement efficiency. These studies reported that unstable displacement fingering is considerably affected by pore structure (Berg and Ott, 2012; Wang et al., 2012). Chang et al. (2019) pointed out that the complexity of unstable displacement arises largely from the heterogeneity and anisotropy of rocks, which can be regarded as important contributors to the uncertainty in storage capacity estimates. In addition, the two-phase displacement instability can be characterized by dimensionless capillary number (Ca), which represents the relative effect of viscous force and interfacial force acting on the interface between two immiscible liquids (Saffman and Taylor, 1958). Ca has been used in various micromodels to divide the pore-scale regimes of capillary fingering, viscosity fingering, and crossover (Lenormand et al., 1988; Ferer et al., 2005, 2007, 2011; Zhang et al., 2011; Chang et al., 2019, 2021). They claimed that viscous fingering dominated at higher capillary numbers, while capillary fingering and viscous fingering were observed at medium capillary numbers. The zone in which the type of unstable finger changes from capillary to viscous is usually denoted as the crossover zone (Ferer et al., 2004; Cottin et al., 2010). Zheng et al. (2017) summarized experimental and numerical results published in the past three decades and clearly proposed different relationships between non-wetting fluid saturation and Ca. Therefore, the reported displacement efficiency indicating by non-wetting fluid saturation or residual water saturation shows a wide range of variation (Bennion and Bachu, 2010; Chang et al. 2013; Bachu, 2013).

Significant attempts also have been made to reveal factors affecting sealing efficiency. The capillary sealing efficiency of caps for gases, in terms of capillary displacement pressure (P_d), has been studied using different approaches

(Ibrahim et al., 1970; Schowalter, 1979; Horseman et al., 1999; Gallé, 2000; Zhao and Yu, 2017a, b). Additionally, the quality of a seal is characterized by the effective permeability (k_{eff}) of the gas phase after breakthrough, which is a function of the gas/water saturation of the connected pore network (Hildenbrand et al., 2002). In other words, the fluid distribution characteristics during the two-phase displacement process will ultimately affect the capillary sealing efficiency. Zhao and Yu (2017a) claimed that different pore structure parameters can significantly affect the capillary displacement pressure and effective gas permeability. However, the change of pore size distribution with varying water saturation is complex and difficult to define. Consequently, the impact of displacement properties on sealing efficiency remains poorly understood. Therefore, additional analyses are required to assess the influence under GCS conditions.

Nuclear magnetic resonance (NMR) and magnetic resonance imaging (MRI) are noninvasive techniques that can be used to monitor protons in water trapped within porous media (Prather et al., 2016). On one hand, NMR signals are the superposition of water signals in pores of different sizes, and the T_2 spectrum can thus be correlated to pore sizes within saturated cores (Song et al., 2008; Mitchell et al., 2010). On the other hand, MRI facilitates the visualization of the spatial distribution of water in pores with different sizes at any stage of displacement (Baldwin and Yamanashi, 1989; Majors et al., 1995). Using these techniques, quantitative and accurate measurement and description of micro pores and positions involved in the specific migration and distribution of CO_2 and formation water in the reservoir can be realized. Previous studies show that vital information for understanding transport characteristics and determining properties that reflect multiphase displacements can be obtained through dynamic displacement experiments using NMR and MRI (Chen et al., 1992; Liu et al., 2011; Prather et al., 2016).

In this study, a series of displacement experiments were carried out on six different cores by introducing CO_2 into initially water saturated samples, and the distribution of the wetting phase (water) in the pores during the entire displacement process was determined through NMR imaging and relaxometry. In this manner, parameters such as T_2 distribution, $P_{d,}$ and k_{eff}, as well as images of water distribution were obtained, which provide direct information of different displacement stages. The main objectives of this study were to (1) investigate the impacts of pore characteristics, such as pore size distribution, heterogeneity, and anisotropy, on displacement properties, (2) analyze the relationship between the capillary number (Ca) and displacement patterns, and (3) compare the displacement efficiency and capillary sealing efficiency between different core samples with various pore size distributions. The findings are expected to provide deeper insights into the impact of two-phase displacement characteristics on the storage efficiency and security of GCS.

2. Theory for NMR Relaxometry and MRI

NMR refers to the response of proton nuclei to a magnetic field (Brownstein and Tarr, 1979). When subjected to a certain radio frequency (RF) pulse, the proton nuclei of fluids within rock samples absorb the energy of the magnetic field and jump from a low energy state to a higher energy state (Coates et al. 1999; Dunn et al.2002). The proton nuclei release energy and return to an equilibrium state through different relaxation mechanisms, producing different measurable NMR signals (Levitt 2001; Yan et al. 2019).

During these processes, the transverse relaxation time (T_2) can be measured by the Carr-Purcell-Meiboom-Gill (CPMG) sequence (Callaghan, 1991). The CPMG sequence consists of a 90° RF pulse and a series of 180° pulses, which create a train of spin echoes. These spin echoes produce an exponential decay envelope, which is determined by the transverse spin-spin T_2 relaxation (Callaghan, 1991). For samples with different pore sizes, as they show multiple T_2 values, a multiexponential decay envelope is obtained (Prather et al., 2016). Using an inverse Laplace transform (ILT) algorithm to solve the inverse problem, magnetization attenuation is converted to a T_2 distribution (Hurlimann et al., 2003; Washburn and Callaghan, 2006; Stingaciu et al., 2010). This transverse relaxation time can be defined as Eq. (1), in which the three terms on the right of the equation represent the surface relaxation from rock particles, volume relaxation from bulk fluids, and diffusion relaxation from molecular diffusion, respectively (Washburn and Cheng, 2017; Singer et al., 2018).

$$\frac{1}{T_2} = \rho_2 \left(\frac{S}{V}\right) + \frac{1}{T_{2B}} + \frac{D(\ GT_E)^2}{12} \quad (1)$$

where $_2$ is the surface relaxivity of pore surface, m/ms; S/V is the pore surface to volume ratio, m^2/g; T_{2B} is the transverse relaxation time of the bulk fluid, ms; D is the diffusion coefficient of fluid, m^2/ms; is the gyromagnetic ratio, $rad \cdot /(s \cdot T)$; G is the internal magnetic field gradient, gauss/cm; and T_E is the echo spacing, ms.

Spin-echo (SE) sequence is often used for acquiring MRI images. The execution of SE sequence can be divided into four steps: excitation, coding, phase refocusing, and echo acquisition. In the first step, a combination of 90° and 180° RF pulses are used to excite protons. A 90° RF pulse is first transmitted, followed by a 180° RF pulse at a certain interval. This process changes the precession direction of protons in the XY plane, reunites protons, and releases energy in the form of spin echo, resulting in spin echo signal. Subsequently, the echo signal is collected under the action of phase coding and frequency coding. The entire process is termed echo acquisition and the time consumed is termed echo time (TE). Thereafter, the 90° RF pulse is transmitted again after a period of time to repeat the above echo acquisition process. Here, the elapsed time between these two 90° RF pulses is called repetition time (TR). After spatial coding, the two-dimensional distribution function of the NMR signal can be obtained through two-dimensional Fourier transform, and the two-dimensional NMR image of the sample can then be obtained.

3. Samples and experiments

3.1 Core samples

Six cylindrical tight rock samples (Figure 1) were collected from the Ordos Basin in China, which has been regarded as a potential area for the deployment of large-scale CO_2 capture and storage (CCS) (Zhang et al., 2016, Zhao et al. 2021). They were set to have the same diameter (25 mm) and similar length (30 mm), and the basic properties of these six cores are listed in Table 1. The permeability and porosity were determined using Helium (He), and the method is described in detail by Zhao and Yu (2017a). Mineral composition was quantitatively analyzed through X-ray diffraction (XRD) analysis performed using a D/max-rA X-ray diffractometer. All samples were prepared and analyzed according to the SY/T 5163-2010 standard (Zeng et al., 2010), and the results of these measurements are shown in Table 2. The samples comprised four sandstone samples, one dolomite sample, and one shale sample. The sandstone samples were divided into quartz dominated (#5, #8) and quartz-plagioclase dominated sandstones (#2, #3). The dolomite sample (#9) is mainly composed of dolomite and the shale sample (#1) contains a large amount of clay minerals, as well as some quartz and feldspar. According to XRD results, the main clay minerals in all samples are chlorite, illite, and kaolinite.

3.2 Experimental device

All experiments were performed using a nuclear magnetic displacement device, which mainly includes a core holder surrounded by a magnet (MacroMR12-150H-I, Niumag), a gas injection system, a liquid injection system, confining and back pressure units, a vacuum pump, an intermediate container, a metering system, and control computers. The flow loop is shown in Figure 2.

The MacroMR12-150H-I system has a magnetic field strength of 0.3 $\pm$ 0.05T (permanent magnets) and a resonance frequency of 12 MHz. The core sample is wrapped in a heat shrink sleeve and placed horizontally in the stainless steel core holder. In order to monitor the upstream and downstream pressures, two pressure gauges are installed at the inlet and outlet of the core holder. Liquids can enter the core holder at a constant flow rate through the liquid injection system, while gases are injected at a constant pressure through the gas injection system. The core holder is divided into two regions by the heat shrink sleeve. The inner region contains the rock core and injected liquid or gas, and the outer region contains the confining fluid. The confining fluid (Fluorinert) is pressurized by a ISCO syringe pump to maintain a pressure higher than that of the drainage fluids, restricting the drainage fluids from flowing around the outside of the core. Another ISCO syringe pump is used at the outlet of the core holder to control the initial pressure inside the core holder, and the injected gas or liquid flows out only when its pressure exceeds the back pressure. The vacuum system is used to remove air from the core holder and pipelines. The gas-liquid mixture flowing out of the core is separated by the gas-liquid separator, and

the water entrained in or dissolved in the gas can be absorbed by the silica gel dryer. Subsequently, the gas is passed through the gas flow meter to determine the instantaneous flow rate. The upstream/downstream pressure of the core holder and gas flow rate can be recorded by the control computer.

3.3 Experimental Methods

3.3.1 Pore structure analysis The pore structure characteristics of tight rocks have a vital impact on the displacement behavior between CO_2 and water (Chang et al. 2019), as well as the flow characteristics of the CO_2 phase (Zhao and Yu, 2017a). Correspondingly, the CO_2 migration and saturation distribution will ultimately affect the efficiency and security of carbon sequestration. It is commonly accepted that the NMR T_2 spectra of water-saturated cores are analogous to pore size distributions (Kleinberg and Vinegar, 1996; Coates et al., 1999). As volume relaxation is much slower than surface relaxation (T_{2B} T_2) when pores are saturated only with a single-phase fluid, the contribution of volume relaxation can be ignored in Eq. (1). Moreover, under uniform magnetic field (G is very small) and sufficiently short echo spacing (T_E is very small), the contribution of diffusion relaxation is also very small and can be ignored. Therefore, surface relaxation is considered to be the main mechanism of rock relaxation, and it has been employed in the estimation of pore size distribution (Yan et al. 2019). The simple relationship between T_2 values and pore sizes can be approximately expressed as Eq. (2). With the decrease of pore size, the surface relaxation effects and interactions of nuclei in small pores contribute to the decrease of T_2 (Prather et al., 2016). Hence, larger pores correspond to larger T_2 values (slower relaxation) and smaller pores correspond to smaller T_2 values (faster relaxation) (Kleinberg, 1996; Song et al., 2008).

$$\frac{1}{T_2} = \rho_2 \left(\frac{S}{V}\right) \quad (2)$$

The method for determining pore size distribution was applied to the six samples. Fresh samples were cleaned with methanol and toluene to remove residual oil to the minimum level (Qu et al., 2006). Then, the samples were dried at 105°C in a high-temperature oven for 4 h to remove free fluids, and the samples were weighed as m_0. The samples were further dried in the oven for an additional hour to determine the weight m_i, and the value of $(m_i\text{-}\ m_0)/m_0$ was calculated. The above steps were repeated until $(m_i\text{-}\ m_0)/m_0$ 0.3, and the final weight of the samples was recorded as the dry weight (m). Subsequently, the dry sample was wrapped with the heat shrink sleeves and placed in the core holder. The core holder was then subjected to the CPMG sequence to obtain the background signal, which was used later for background subtraction (Prather er al., 2016). The parameters for NMR T_2 measurement were set as follows: polarization or wait time (TW) of 5000 ms; echo time (TE) of 0.1 ms; number of echoes (NE) of 15000; numbers of scans of 32. Following this, a vacuum condition (<-0.1 MPa) was maintained in the core holder with the dry sample inside for 5 h. Deionized water was introduced into the core holder, and the pressure was gradually increased to 20 MPa for at least 12 h to ensure that the core was

completely saturated. After measuring the weight m_s of the saturated sample, NMR measurement was repeated with the same parameters mentioned above.

3.3.2 Displacement experiments Displacement experiments with CO_2 were conducted on the six saturated core samples. The abovementioned two types of pulse sequences were used for characterizing the change of fluid saturation and distribution at the pore scale. As almost all signals originated from hydrogen protons, the signal strength of CO_2 was close to zero. This feature can be used to effectively distinguish CO_2 and water in pores. First, in order to compare the NMR T_2 spectra obtained during the displacement process and initial water-saturated conditions, the parameters applied in the previous experiment were maintained for CPMG measurements. In addition, MRI analyses were employed to visualize the CO_2 flow characteristics and observe the pore structure and saturation profiles during dynamic displacement. The parameters for SE measurements were set as follows: repetition time (TR) of 500 ms; echo spacing (TE) of 5.89 ms; image data matrix of 256 × 192; field of view (FOV) of 100 mm × 100 mm with a thickness of 10 mm. The core image can be obtained by filtering out interference signals from the original image data, performing mapping, and adding false colors (Li et al., 2020).

First, the T_2 spectrum distribution and MRI image were collected after the maximum saturation occurred. Then, the displacement experiments were started, and the flow direction was along the axial direction of the cylinder. Considering that the MacroMR12-150H-I system can withstand a working temperature range of only 23–27℃, the experimental temperature was set to 25℃. Displacement experiments in this study were performed by imposing an instantaneous high gas pressure gradient across the rock samples (Hildenbrand et al., 2002). A stable downstream pressure was controlled by applying back pressure, which was set to 20 MPa to simulate the formation pressure conditions of the coring depth (1500–2300 m). In order to control the displacement time and capture the change trend of MRI images for different core samples, CO_2 was injected into the inlet section of the core holder at two different pressures (22 and 25 MPa). The confining pressure was maintained 5 MPa higher than the gas injection pressure, which was essential to prevent CO_2 from flowing through the gap between the core and the sleeve. Additionally, the pressure at the ends of the core holder was recorded in real time by the computer, and the flow rate of gas breaking through the core was measured by the gas flowmeter.

During the displacement process, NMR signals were monitored and multiple MRI images on the sagittal plane were obtained (Figure 3). In this manner, images were taken along the direction of CO_2 flow such that saturation distributions along the length of the cores can be determined, which are especially suitable for observing the two-phase displacement behavior in cores (Chen et al., 1992). In addition, by selecting the sagittal plane instead of the coronal plane, one-sided information attributable to the radial heterogeneity of cores can be eliminated. With the progress of displacement, the signal strength of hydrogen

protons decreased gradually. When the signal strength in the core was close to the background signal, the distribution of different phases in the MRI image became difficult to distinguish, which indicated the end of displacement. The time consumed for complete displacement varied significantly among different cores, ranging from 2 h to 12 h. As the time required for imaging each core was approximately 15 min, the displacement process had to be suspended several times to acquire sufficient images.

4. Results

4.1 T_2 distribution

4.1.1 Pore Size Distribution The NMR T_2 spectra of the six saturated core samples are shown in Figure 4. The range of T_2 values accessible by the current NMR device is between 0.01 ms and 10 s. The pore size distributions determined using NMR showed various shapes among different samples. In general, it could be divided into unimodal distribution and bimodal distribution. Sample #5 exhibited a bimodal distribution with two populations centered on 0.87 and 14.18 ms. Sample #3 also exhibited a bimodal distribution with two populations centered on 1.05 and 135.1 ms. Samples #1, #2, #8, and #9 exhibited unimodal distributions with peaks at 0.28, 0.46, 15.70, and 2.41 ms, respectively. According to the concentration and dispersion of signal intensity, it can be concluded that Samples #1, #2 and #9 show narrow peaks, indicating that the pore size distribution is relatively homogeneous. The NMR signals of water in Sample #1 were concentrated in the relaxation time between 0.03 ms and 1.38 ms. Regarding Samples #2 and #9, the signals were concentrated within relaxation time ranges of 0.26–2.45 ms and 0.13–13.67 ms, respectively. Conversely, the broader T_2 distribution of the other three samples can be explained to be a result of large differences in pore size and strong heterogeneity. For Samples #3, #5, and #8, the relaxation time ranges corresponding to the concentrated NMR signals were 0.05–943.79 ms, 0.18–439.76 ms, and 0.28–270.50 ms, respectively.

T_2 cutoff (T_{2c}) is a T_2 value that can be applied to distinguish pore types (Jorand et al., 2011; Tanino and Blunt, 2012). For sandstones, such as Samples #1, #3, #5, and #8, T_{2c} = 3 ms is the conventional cutoff for partitioning microporosity associated with clay-bound water (Straley et al., 1997; Dunn et al., 2002), and a new T_{2c} defined as 33 ms facilitates the segregation of bound water and free water (Jorand et al., 2011). In other words, the T_{2c} of 3 ms is applied for sandstones in order to distinguish between micropores and mesopores, while 33 ms is regarded as the cutoff between mesopores and macropores (Allen et al. 2000; Jorand et al., 2011). In this study, T_{2c} for shale was selected according to the classification standard of sandstone. For carbonates, such as Sample #9, previous measurements suggest that inter-particle porosity can be distinguished from secondary porosity within a broad range of T_{2c} from 60 to 100 ms (Straley et al., 1997; Westphal et al., 2005). In this study, the pore distribution of micropores was estimated by setting T_{2c} = 72 ms, which is consistent with the local minimum of T_2 in Tanino and Blunt (2012). As shown in Figure 4,

notable NMR signals for Sample #9 were almost concentrated in the relaxation time of 0.13–13.67 ms. Therefore, in this study, although no T_2 cutoff was set for discriminating mesopores and micropores for carbonates, it has little effect on the analysis of pore size distribution characteristics for samples with almost only micropores. With these values of T_{2c}, the distribution probability of macropores, mesopores, and micropores for sandstone and shale as well as the distribution probability of micropores for dolomite could be determined, as shown in Figure 4.

4.1.2 CO_2-water displacement The same procedure of the NMR T_2 test was followed during displacement experiments with CO_2. Figure 5 shows the NMR T_2 spectra from the entire experimental process for the six samples. Water in all pores was found to be mobilized with increasing displacement time. The displacement time of different cores widely varied, which is attributable to the properties of cores and their pore size distribution characteristics. The end of displacement was marked by the distribution of different phases in the MRI image becoming almost impossible to distinguish (Figure. 7), which means that vast majority of water has been displaced and CO_2 has reached the outlet end of the core, and the longest time of displacement lasted nearly 12 h. Except for Sample #8, the change of signal intensity of other samples was less than 4.3% within 12 h (Figure 6). In particular, this process lasted only 120 min to 200 min for Samples #3 and #5.

The NMR T_2 spectra of samples with unimodal distribution showed a similar downward trend. With the progress of displacement, a small amount of water in mesopores and macropores was completely displaced first in Samples #1, #2, and #9, and the same situation occurred in some macropores (relaxation time $>$ 300 ms) of Sample #8. The NMR signal intensity in the remaining pores decreased gradually in the entire range of relaxation time. Although Samples #3 and #5 exhibited bimodal distributions, their T_2 distributions showed different change trends with displacement time. The NMR signal intensity of macropores, mesopores, and micropores in Sample #3 decreased almost at an equal rate, indicating that the piston-like displacement behavior may occur in this sample. In contrast, the displacement behavior was more complex in Sample #5 and the decrease rate of signal intensity in mesopores and macropores was higher than that of micropores, indicating unstable displacement.

A displacement rate curve (Figure 6) was drawn with the percentage content of NMR signal intensity (ratio of the decrease value of NMR signal intensity to the initial signal intensity) as the ordinate and displacement time as the abscissa. The displacement rates of Samples # 3, #5, and #8 were found to be much higher than those of the other three samples. The signal intensity of these three samples decreased to less than 45% of the initial value within 1.17 h, while that of the other three samples decreased by only 7–16% within 1 h. When the local capillary pressure is higher than the threshold entry pressure, pores with wetting fluid will be displaced by the non-wetting fluid, and thus, the largest

pores that provide the least resistance to capillary displacement typically get displaced first (Hildenbrand et al., 2002, Chang et al., 2021). The displacement rate in the early stage is closely related to the proportion of meso-macro pores in the core. Therefore, Sample #8 with the smallest proportion of micropores showed the fastest displacement rate in the first hour of displacement. Yang and Yu (2020) reported that the mobility of water strongly depends on the pressure gradient. During the displacement process, the inlet pressure of Sample # 8 was consistent with that of Samples # 3 and #5, both of which were kept at 22 MPa. However, after 1 h of displacement, the NMR signal intensity of Sample # 8 was only about 15–19% that of the other two samples (Fig. 6). The remaining water in Sample # 8 may be adsorbed on mineral surfaces under the action of interfacial forces (Li et al., 2019; Woodruff & Revil, 2012), and further displacement of adsorbed water would require a larger pressure gradient (Yang & Yu, 2020; Zhao et al., 2021). In other words, the displacement rate of Sample #8 decreased significantly due to the insufficient displacement pressure after 1 h. In addition, the inlet pressure was maintained at 25 MPa during the displacement experiments of Samples #1, #2 and #9, and the displacement rate of Sample #9 decreased sharply after 2 h. This can also be attributed to the variation of the mobility of absorbed water in smaller pores with the pressure gradient. The magnitude of the disjoining pressure of water absorbed in Sample #9, with extra low porosity and permeability (Table 1), is likely to be much larger than that in Samples #1 and #2.

4.2 MRI imaging

The MRI images of six samples versus displacement time are shown in Figure 7, which was used to investigate fluid saturation distributions and to monitor the fluid flow characteristics in situ during displacement experiments. The bright areas (yellow to red) indicate high water saturation, and the dark areas (blue) indicate low water saturation. The signal intensity corresponding to different colors in each sample is shown on the right side, and the corresponding displacement time is shown at the bottom of each image. The images in Figure 7 show that CO_2 enters Samples #1, #2, #3, and #9 with a piston-like displacement, leaving residual water saturation of 30.88%, 24.53%, 17.03%, and 27.10%, respectively. With the increase of CO_2 injection volume, instability of the displacement front, reflected by the appearance of the tonguing and fingering phenomenon, occurred in Samples #5 and #8, and the residual water saturation was 21.13% and 20.08%, respectively.

Previous studies have reported that this instability may occur in immiscible fluid displacement due to the difference in viscosity and density (Saffman & Taylor, 1958; Homsy, 1987). Furthermore, the instability is also sensitive to porous media characteristics (Hosseinalipoor et al., 2019; Vamerzani et al., 2021). As shown in Figures 7 and 8, comparing samples, the heterogeneity and anisotropy of pore networks in Samples #5 and #8 were significantly higher in the saturated state. The higher heterogeneity of Sample #8, which showed a unimodal

distribution with the broadest T_2 distribution, is highly conducive to the occurrence of the tonguing phenomenon. As shown in Figure 9, the viscosity ratio (M) is defined as the ratio of the viscosities of the displacing (non-wetting) and displaced (wetting) fluids (Lenormand et al., 1988). Under the experimental conditions, the density and viscosity of CO_2 were found to be lower than that of deionized water, due to which CO_2 protruded along the upper part of Sample #8 (Figure 7). The displacement front of Sample #5 gradually evolved into the fingering phenomenon, which can be explained by the abovementioned reasons, including viscosity, density and pore structure characteristics. Sample #5 is a nonuniform core with dual porosity behavior and a wide distribution of pore size (Figure 4), resulting in higher heterogeneity than Sample #8. However, for Sample #3, the heterogeneous pore structure with bimodal T_2 distribution did not lead to unstable displacement, which can be mainly attributed to its higher permeability (Table 1). Significant differences in gas flow rate cannot develop in widely connected high-permeability channels. In this study, compared with the viscosity ratio and density difference, the heterogeneity and anisotropy of pore structure are the main factors causing the unstable displacement front, while high-permeability channels inhibit the occurrence of the fingering phenomenon.

4.3 Capillary displacement pressure and effective permeability

CO_2-water displacement experiments have been performed to obtain information on both capillary displacement pressure (P_d) and effective gas permeability (k_{eff}) after gas breakthrough. The pressure gradient and volumetric flow rate of the gas was monitored as a function of time (Figure 10). As the back pressure was set at the outlet of the core holder, the downstream pressure (P_2) increased from 20 MPa and gradually approached the upstream pressure (P_1). When the downstream pressure tends to be constant, a stable pressure difference (ΔP) can develop between the upstream and downstream, which is regarded as the capillary displacement pressure (Hildenbrand et al., 2002). The displacement experiments were completed after obtaining the stable pressure difference. In this study, the re-imbibition of the wetting phase was not applied because the fluctuation of NMR signals was very weak (Figures 5, 7).

The effective gas permeability (k_{eff}) of the sample varies with time as a function of the gas phase saturation (Hildenbrand et al., 2002), as well as the water saturation (Zhao and Yu, 2017a). It is calculated from the pressure change using Darcy's law for compressible media:

$$k_{\text{eff}} = \frac{2P_a \text{Q L}}{A(P_1^2 - P_2^2)} \times 10^3 \quad (3)$$

where P_a is the standard atmospheric pressure, 0.1 MPa; Q is the volumetric flow rate of gas, cm^3/s; is the gas dynamic viscosity under experimental conditions, mPas; P_1 and P_2 are the pressures at inlet and outlet of the core holder, 0.1 MPa; and L (cm) and A (cm^2) are the length and cross-sectional area of the core, respectively.

The water saturation (S_w) in the region of interest can be obtained by analyzing

the signal intensity of the images through the following equation (Ying et al., 2018):

$S_w = \frac{I_i S_0}{I_0}$ (4)

where S_0 is the original displaced-phase saturation, whose value is 1, I_0 is the image intensity at time zero, and I_i is the signal intensity at time i.

The saturation of CO_2 is defined as follows:

$S_{CO_2} = 1 - S_w$ (5)

The results of the two-phase displacement experiments are shown in Figures 10 and 11. The values of effective gas permeability reported in Figure 11 are the maximum values recorded in the corresponding displacement experiments, and the capillary displacement pressure in Figure 10 represents the residual pressure difference at the end of the experiments. The P_d values ranged from 0.5 to 3.2 MPa, and the effective permeability coefficients of Samples #1, #2, and #9 were one to three orders of magnitude lower than those of the other three samples. This is directly related to the pore size distribution because samples with high micropore ratio have significantly higher capillary displacement pressure and lower effective permeability. The variation trend of effective gas permeability with water saturation is shown in Figure 11. The k_{eff} values increased with decreasing water saturation. In other words, further increases of gas saturation will enhance effective gas permeability by generating new fluid flow pathways.

5. Discussion

5.1 Displacement properties and flow patterns

The displacement of the six cores can be generally divided into two types: stable piston-like displacement (Samples #1, #2, #3 and #9) and unstable displacement with the tonguing and fingering phenomena (Samples #5 and #8). Differences in lithology do not yield notable difference in the displacement characteristics of porous media. The displacement property is more closely related to the pore structure and appears to be independent of mineral compositions. Samples #1, #2, and #9 (representing shale, sandstone, and carbonate), with unimodal T_2 distributions and more than 98% micropores, resulted in compact gas flow pattern and stable piston-like displacement. Unstable displacement is more likely to occur in samples with higher heterogeneity and anisotropy, such as Samples #5 and #8, which have a bimodal pore structure or broader T_2 distribution. However, displacement in Sample #3 exhibited a stable piston-like pattern although its pore size distribution presents the typical characteristic of double peaks.

Regardless of the gravitational forces, two-phase displacement in horizontal micromodels can be characterized by the capillary number (Zhang et al., 2011). Saffman and Taylor (1958) used the capillary number to interpret the fingering

geometry of air in experiments of air displacing glycerin in a Hele-Shaw cell. The original form of capillary number can be expressed as:

$Ca = \mu \times \overline{u}/\sigma$ (5)

where is the viscosity of the resident fluid, *Pas*; $\overline{u}$ is the average Darcy velocity of the injected fluid, ms^{-1}; and is the interfacial tension between the injected and resident fluid, Nm^{-1}.

The average Darcy velocity ($\overline{u}$) of the injected gas can be calculated by dividing the volumetric flow rate (Q) by the cross-sectional area (A) of the core. In addition, interfacial tension ( ) can be calculated according to the following equation (Sutton, 2009):

$$\sigma = \left[\frac{1.58(\rho_w - \rho_g)+1.76}{T_r^{0.3125}}\right]^4 \times 10^{-3} \quad (6)$$

where $_w$ and $_g$ are the density of water and gas, respectively, g/cm^3. T_r is the reduced temperature of gas (dimensionless).

CO_2 saturations in the two samples with imposed *log*Ca values from -2.78 to 1.64 are compared in Figure 12. As shown in the graph, the CO_2 saturation of all samples increased monotonically with Ca. However, the MRI images show wide differences in gas flow behaviors and displacement patterns. For Sample #5, two displacement patterns with varying gas flow rates can be observed (Figure 5a). At low flow rate (*log*Ca < -1.88), within the first 30 min of displacement, the displacement process was dominated by high capillary pressure. Consequently, $scCO_2$ intruded high-permeability channels and their adjacent pores simultaneously through randomly distributed forward and lateral flow paths (indicated by red solid line in Figure 12a, II). Such a displacement pattern can be attributed to capillary fingering (Zhang et al., 2011; Wang et al., 2012; Chang et al., 2019). After 30 min, the NMR signal intensity in the high permeability channel tended to stabilize, and the displacement front with relatively smooth boundary further invaded more flow paths, as clearly observable in Figure 12a (VI). Carruthers (1998) pointed out that the fluid flow regime changes from capillary dominated to viscous-fingering dominated and the new flow paths will become less focused. The displacements were dominated by viscous fingering because with the stronger viscous force, CO_2 can invade additional small pores. As capillary fingering drives gas to flow mainly in a few pathways in the middle of the core, the displacement efficiency during this stage is lower than that of viscous fingering. In addition, unlike the piston-like displacement, the movement rate at the displacement end (indicated by dotted line) is obviously inconsistent with that at the displacement front during viscous fingering. Finally, after the displacement front reached the outlet end of the core, residual water (marked by red dashed irregular box) could be clearly observed in some pores.

The gas flow rate (*log*Ca) of Sample #8 was much lower than that of Sample #5. As a result, the displacement front of Sample #8 exhibited a weak unstable tonguing phenomenon during the displacement process, rather than

developing into a distinct viscous fingering. When *log*Ca < -2.76 within the first 15 min of displacement, water in high-permeability channels, which have good connectivity with their neighboring pores (marked by red solid box), was displaced first, and relatively high displacement efficiency was observed at this stage. Thereafter, the occur of the tonguing phenomenon with increased *log*Ca caused a decline of displacement efficiency. Comparing the two images in Figure 12, with increasing gas flow rate (*log*Ca), the two-phase displacement instability appears to gradually evolve from tounging (*log*Ca > -2.76) to capillary fingering (*log*Ca < -1.85), and then further evolve into the most complex viscous fingering (*log*Ca > -1.85).

As mentioned before, the NMR T_2 spectra of Sample #3 presented a bimodal and broad distribution, indicating large difference in pore size and strong heterogeneity, but its displacement characteristics differed from those of Samples #5 and #8. As shown in Figure 4, Sample #3 is the only core dominated by macropores (nearly 50%), because of which it exhibited the maximum porosity and permeability (Table 1). The water distribution in MRI images (Figures 8 and 9) also confirms its good pore connectivity, as well as slight anisotropy. The absolute gas permeability of Sample #3 was almost 30–55 times that of the other two samples, whereas the maximum effective gas permeability was higher by approximately 3.6–37 times. In other words, even if the $log C_a$ of Sample #3 is in the range of -2.61 to -1.64 (in the region of interest in Figure 12), its good pore connectivity, slight anisotropy, and high-permeability channels restrain the occurrence of an unstable displacement front.

5.2 Capillary sealing and displacement efficiency

It has been confirmed that samples with different pore structures show different displacement characteristics, leading to different values of capillary displacement pressure, effective gas permeability, and residual water saturation (Figures 10, 11). According to Hildenbrand et al. (2002), the capillary sealing efficiency of a porous medium with a given pore size distribution is characterized by the capillary displacement pressure and effective permeability to the gas phase after breakthrough. The k_{eff} value after gas breakthrough corresponds to the maximum effective gas permeability marked in Figure 11. Accordingly, high displacement pressure is often accompanied by very low effective gas permeability, and the maximum effective gas permeability is significantly lower than the absolute gas permeability of the dry samples. As shown in Figure 13, double logarithm linear relationships were established between (a) the maximum effective gas permeability coefficients and capillary displacement pressure and (b) the absolute permeability coefficients and capillary displacement pressure. The correlations were consistent with the previous correlation established by Hildenbrand et al. (2002). The double logarithm linear relationships in our study can be written as:

$$\log P_d = -0.44 log k_{\text{eff}} - 1.39 \ (\text{R}^2\text{=}0.95) \quad (7)$$

$$\log P_d = -0.36 log k_{\text{abs}} - 0.45 \ (\text{R}^2\text{=}0.96) \ (8)$$

The P_d values of Samples #1, #2, and #9 were one order of magnitude higher than those of the other three samples, whereas their k_{eff} values were 1–3 orders of magnitude lower. For tight rock cores of shale and carbonate (Samples #1 and #9) and a sandstone core with low permeability (Sample #2), the piston-like displacement pattern was maintained owing to the relatively low gas flow rate, and their displacement process consumed more than five hours. As caprocks, these three samples are likely to have high sealing efficiency, and their stable displacement pattern with uniform displacement front will reduce the probability of premature breakthrough of CO_2. Certainly, the capillary sealing efficiency is closely related to the pore structure, especially for small pores (Zhao and Yu, 2017b). Dominated by micropores, Samples #1, #2, and #9 have much higher sealing efficiency. The remaining three samples feature variable displacement processes, attributable to the heterogeneity and anisotropy of the pore structure. Dominated by macropores, Sample #3 showed the minimum capillary displacement pressure and the shortest displacement time, as well as the maximum effective permeability after gas breakthrough, resulting in the lowest sealing efficiency. With a wide distribution of pore size, Samples #5 and #8 exhibited higher sealing efficiency than Sample #3, but lower than Samples #1, #2 and #9. In addition, the unstable displacement front caused by the tounging or fingering phenomenon may further reduce their sealing efficiency.

From the perspective of caprock optimization, Samples #3, #5, and #8 do not completely satisfy the requirements for CO_2 storage security. Sample #3, with the lowest residual water saturation of 17.03%, can be regarded as a favorable target reservoir for GCS. The stable piston-like displacement pattern reflects high displacement efficiency. However, Samples #5 and #8 are less favorable owing to the occurrence of the fingering and tounging phenomena, which are of considerable importance in determining displacement efficiency. These phenomena may lead to the premature breakthrough of CO_2 and hence decrease the displacement efficiency of water. The displacement efficiency can be estimated using the following equation (Song et al. 2012).

$$E = \left(1 - \frac{S_{\text{wr}}}{S_0}\right) \times 100\% \ (9)$$

where E is the displacement efficiency, and S_{wr} is the final residual water saturation at the end of displacement. The final residual water saturation under different displacement processes is presented in Figure 11b. The calculated values of displacement efficiency were 82.97%, 78.87%, and 79.92% for Samples #3, #5, and #8, respectively.

Displacement efficiency is closely related to the pore structure. Samples with high porosity and permeability also show relatively large displacement efficiency. The distribution of water saturation in different pores can be calculated with Eq. (4) using the signal intensity measured in each pore. Then the real-time displacement efficiency corresponding to different types of pores can be calculated by replacing S_{wr} with S_w in Eq. (9). For Sample #3 with the piston-like displacement

pattern, the displacement efficiency in macropores, mesopores, and micropores essentially remained the same during the entire displacement process (Figure 14a), resulting in the highest E value. For Sample #5 (Figure 14b), negative E values were recorded in most micropores in the first 30 min of displacement, which was dominated by capillary fingering. Even in some micropores marked by the black dashed circle, the displacement efficiency decreased with increasing displacement time, indicating that the high capillary force pushed a small part of water to smaller pores. Moreover, the displacement efficiency in mesopores and macropores did not increase monotonically with increasing pore size because of the irregularly advancing displacement front during this period. Particularly in macropores with T_2 exceeding 350 ms, the displacement efficiency even showed a negative value. This may be attributable to the movement of water being mainly concentrated in some high-permeability channels, which induces a temporary increase in NMR signals in some macropores. In the subsequent viscous fingering process with a relatively smooth displacement front, the displacement efficiency increased gradually in the three types of pores. The average E values exceeded 96% after 70 min in the mesopores and macropores, but it was only 36% in micropores. By the end of displacement, the E values in mesopores and macropores increased to 98% and 71%, respectively. For Sample #8 (Figure 14c), the displacement efficiency presented an obvious ladder shape caused by the tonguing phenomenon. Except in some micropores marked by the black dashed circle, the displacement efficiency showed a negative correlation with time, but the correlation was positive in other pores. With the increase of pore size, the displacement efficiency presented a ladder-shaped rise. On the whole, the pore size distribution can be concluded to have a significant impact on the displacement efficiency under unstable displacement patterns, but the influence can be ignored under stable piston-like displacement patterns.

6. Conclusions

This study characterized the effect of different displacement behaviors between immiscible two phases in porous media on displacement efficiency and sealing efficiency. CO_2-water displacement experiments were performed on six different samples with various pore structures. The fluid distribution was characterized and displacement patterns were determined using NMR and MRI techniques.

Our experimental observations indicate that the displacement property is more closely related to the pore structure and appears to be independent of mineral compositions. More specifically, the heterogeneity and anisotropy of the pore structure have significant effects on the displacement characteristics. Samples with narrow unimodal T_2 distribution exhibited compact gas flow pattern and stable piston-like displacement, whereas samples with higher heterogeneity and anisotropy tended to exhibit unstable displacement. The capillary number can be used to improve the characterization of flow patterns and properties under unstable displacement. With increasing logCa, the two-phase displacement instability gradually evolved from tounging (logCa > -2.76) to capillary fingering

(logCa < -1.85), and then further evolved into viscous fingering (logCa > -1.85). However, rocks with good pore connectivity and high-permeability channels will restrain the occurrence of unstable displacement, even if logCa is within the range of unstable displacement.

For rocks with high sealing efficiency that can be considered as caprocks, their pore structures are often dominated by micropores, resulting in higher capillary displacement pressure and lower effective gas permeability. Their displacement pattern is more likely to correspond to time-consuming piston-like displacement, which will reduce the potential of CO_2 leakage (probability of premature CO_2 breakthrough). For rocks with lower residual water saturation that can be regarded as favorable reservoirs for GCS, various fluid saturation distribution characteristics attributable to different displacement patterns have a significant impact on their displacement efficiency. Rocks with good pore connectivity, high-permeability channels, and stable piston-like displacement exhibit the highest displacement efficiency. Nevertheless, the influence of pore structure on displacement efficiency cannot be ignored for rocks with unstable displacement patterns. With increasing pore size of core samples, the displacement efficiency presented an obvious ladder-shaped rise, which is attributable to the tonguing phenomenon. In the capillary fingering process, the two-phase displacement was mainly concentrated in high-permeability channels and their neighboring pores, which may induce a temporary increase in the NMR signal in some macropores, decreasing the corresponding displacement efficiency. Under a high capillary force, the movement of water to smaller pores leads to decreases in the displacement efficiency in micropores with increasing displacement time. In the subsequent viscous fingering process, the relatively smooth displacement front induced a gradual increase in displacement efficiency in the three types of pores, and the E values of mesopores and macropores were much higher than that of micropores.

The results of this study provide deeper insight into two-phase displacements in relation to the storage efficiency and security of GCS. Moreover, it provides an effective means for the optimization of caprocks and reservoirs. The full two-phase drainage and imbibition cycle should be performed on more heterogeneous rocks to improve the observations made in this study.

Conflicts of interest

The authors declare no competing financial interest.

Data Availability Statement

Data are deposited in the Dryad repository with DOI: 10.5061/dryad.fxpnvx0vb, and available through the follow link: https://datadryad.org/stash/share/mts7tkk823g9OgCZM8Uhcaye2d4lt73AHHr1gnDOOGk.

Acknowledgements

We are very grateful for the relevant researchers who provided help during the experiment. This paper was funded by the National Natural Sciences Foundation of China (Grant No. 42007174), Natural Science Basic Research Program of Shaanxi (Grant No. 2020JQ-352) and China Postdoctoral Science Foundation (Grant No. 2021M692736).

References

Allen, D., et al. (2000), Trends in NMR logging. *Oilfield Rev*, *12*(3), 2–19.

Bachu, S. (2000). Sequestration of CO_2 in geological media: criteria and approach for site selection in response to climate change. *Energy Conversion and Management*, *41*(9), 953-970. https://doi.org/10.1016/s0196-8904(99)00149-1

Bachu, S. (2013). Drainage and imbibition CO_2/brine relative permeability curves at in situ conditions for sandstone formations in western Canada. *Energy Proc*, *37*, 4428–4436. https://doi.org/10.1016/j.egypro.2013.07.001

Bachu, S., & Bennion, B. (2007). Effects of in-situ conditions on relative permeability characteristics of CO_2-brine systems. *Environ. Geol*, *54*(8), 1707–1722. https://doi.org/10.1007/s00254-007-0946-9

Baldwin, B.A., & Yamanashi, W. S. (1989). Detecting fluid movement and isolation in reservoir core with medical nmr imaging techniques. *Spe Reservoir Engineering*, *4:2*(02), 207-212. https://doi.org/10.2118/14884-pa

Bennion, D.B., Bachu, S. (2010). Drainage and Imbibition CO_2/brine Relative Per-Meability Curves at Reservoir Conditions for Carbonate Formations. *SPE Paper*, 134028. https://doi.org/10.2118/134028-ms

Berg, S., Ott, H. (2012). Stability of CO_2–brine immiscible displacement. *Int. J. Greenhouse Gas Control*, *11*, 188–203. https://doi.org/10.1016/j.ijggc.2012.07.001

Brownstein KR, Tarr CE. (1979). Importance of classical diffusion in NMR studies of water in biological cells. *Phys Rev A*, *19*(6):2446–53. https://doi.org/10.1103/physreva.19.2446

Callaghan, P. T. (1991), Principles of Nuclear Magnetic Resonance Microscopy, vol. *XVII*, *492 pp.*, *Clarendon*, *Oxford*, *U. K.* https://doi.org/10.1002/ange.19931050256

Carruthers, D.J.F. (1998). Transport modelling of secondary oil migration using gradient-driven inversion percolation techniques. *PhD Thesis Heriot-Watt University*, *Edinburgh: 289 pp.* http://hdl.handle.net/10399/1250

Chang, C. , Kneafsey, T. J. , Zhou, Q. , Oostrom, M. , & Ju, Y. (2019). Scaling the impacts of pore-scale characteristics on unstable supercritical co2 -water

drainage using a complete capillary number. *International Journal of Greenhouse Gas Control*, *86*, 11-21. https://doi.org/10.1016/j.ijggc.2019.04.010

Chang, C., Kneafsey, T. J., Tokunaga, T. K., Wan, J., & Nakagawa, S. (2021). Impacts of pore network-scale wettability heterogeneity on immiscible fluid displacement: A micromodel study. *Water Resources Research*, *57*, e2021WR030302.

Chang, C., Kneafsey, T. J., Zhou, Q., Oostrom, M., & Ju, Y. (2019). Scaling the impacts of pore-scale characteristics on unstable supercritical co2 -water drainage using a complete capillary number. *International Journal of Greenhouse Gas Control*, *86*, 11-21. https://doi.org/10.1016/j.ijggc.2019.04.010

Chang, C., Zhou, Q., Xia, L., Li, X., Yu, Q. (2013). Dynamic displacement and non-equilibrium dissolution of supercritical CO_2 in low-permeability sandstone: an experimental study. *Int. J. Greenhouse Gas Control*, *14*, 1–14. https://doi.org/10.1016/j.ijggc.2012.12.025

Chen, S., Kim, K. H., Qin, F., & Watson, A. T. (1992). Quantitative nmr imaging of multiphase flow in porous media. *Magnetic Resonance Imaging*, *10*(5), 815-26. https://doi.org/10.1016/0730-725x(92)90417-x

Coates GR, Xiao L, Prammer G. (1999). NMR logging principles and applications. *Haliburton Energy Services*, *Houston*.

Cottin, C.; Bodiguel, H.; Colin, A. (2010). Drainage in two-dimensional porous media: From capillary fingering to viscous flow. Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. *Interdiscip. Top. 82*(4), No. 046315. https://doi.org/10.1103/physreve.82.046315

Doughty, C. (2010). Investigation of CO_2 Plume Behavior for a Large-Scale Pilot Test of Geologic Carbon Storage in a Saline Formation. *Transp. Porous Media, 82*(1), 49-76. https://doi.org/10.1007/s11242-009-9396-z

Dunn KJ, Bergman DJ, Latorraca GA. (2002). Nuclear magnetic resonance petrophysical and logging applications. *Elsevier Science, Kidligton*, *pp* 1-30. https://doi.org/10.1016/s0950-1401(02)80001-5

Dunn, K.J., D. J. Bergman, and G. A. Latorraca (2002), Nuclear Magnetic Resonance: Petrophysical and Logging Applications, in Handbook of Geophysical Exploration: Seismic Exploration, vol. *Pergamon, New York, pp 32*, 293. https://doi.org/10.1016/s0950-1401(02)80001-5

Ferer, M., Anna, S.L., Tortora, P., Kadambi, J.R., Oliver, M., Bromhal, G.S., Smith, D.H. (2011). Two-phase flow in porous media: predicting its dependence on capillary number and viscosity ratio. *Transp. Porous Med. 86* (1), 243–259. https://doi.org/10.1007/s11242-010-9619-3

Ferer, M., Brohmal, G.S., Smith, D.H. (2005). Two phase flow in porous media: crossover from capillary fingering to compact invasion for drainage. *Phys. Rev. E 71*, 026303. https://doi.org/10.1103/physreve.71.026303

Ferer, M., Bromhal, G.S., Smith, D.H. (2007). Crossover from capillary fingering to compact invasion for two-phase drainage with stable viscosity ratios. *Adv. Water Resour. 30*(2), 284–299. https://doi.org/10.1016/j.advwatres.2005.10.016

Ferer, M., Ji, C., Bromhal, G.S., Cook, J., Ahmadi, G., Smith, D.H. (2004). Crossover from capillary fingering to viscous fingering for immiscible unstable flow: experiment and modeling. *Phys. Rev. E 70*(1), 016303. https://doi.org/10.1103/physreve.70.016303

Gallé, C. (2000). Gas breakthrough pressure in compacted Fo-Ca clay and interfacial gas overpressure in waste disposal context. *Applied Clay Science*, *17*: 85-97. https://doi.org/10.1016/s0169-1317(00)00007-7

Goodman, A., Hakala, A., Bromhal, G., Deel, D., Rodosta, T., Frailey, S., Small, M., Allen, D., Romanov, V., Fazio, J., et al. (2011). U.S. DOE methodology for the development of geologic storage potential for carbon dioxide at the national and regional scal Int. J. *Greenhouse Gas Control*, *5*(4), 952−965. https://doi.org/10.1016/j.ijggc.2011.03.010

Hildenbrand, A., Schlömer, S., Krooss, B.M. (2002). Gas breakthrough experiments on fine-grained sedimentary rocks. *Geofluids*, *2*(1), 3–23. https://doi.org/10.1046/j.1468-8123.2002.00031.x

Homsy, G.M. (1987). Viscous fingering in porous media. *Annu Rev Fluid Mech*, *19*(1):271–311. https://doi.org/10.1146/annurev.fl.19.010187.001415

Horseman, S.T., Harrington, J.F. & Sellin, P. (1999). Gas migration in clay barriers. *Engineering Geology 54*: 139-149. https://doi.org/10.1016/s0013-7952(99)00069-1

Hosseinalipoor SM, Nemati A, Zare Vamerzani B, Saffari H. (2019). Experimental study of finger behavior due to miscible viscous and gravity contrast in a porous model. *Energy Sources Part A Recover Util Environ Eff*. https://doi.org/10.1080/15567036.2019.1607943

Hurlimann, M. D., M. Flaum, L. Venkataramanan, C. Flaum, R. Freedman, and G. J. Hirasaki (2003). Diffusion-relaxation distribution functions of sedimentary rocks in different saturation states. *Magn. Reson. Imaging*, *21*(3–4), 305–310. https://doi.org/10.1016/s0730-725x(03)00159-0

Ibrahim, M.A., Tek, M.R. & Katz, D.L. (1970). Threshold pressure in gas storage, Pipeline Research Committee American Gas Association at the University of Michigan. *Michigan: 309 pp.*

IPCC. (2005). Special Report on CO_2 Capture and Storage. *Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.*

Jorand, R., A. Fehr, A. Koch, and C. Clauser. (2011). Study of the variation of thermal conductivity with water saturation using nuclear magnetic resonance. *J. Geophys. Res.*, *116*, B08208. https://doi.org/10.1029/2010jb007734

Juanes, R., MacMinn, C. W., & Szulczewski, M. L. (2010). The footprint of the CO2 plume during carbon dioxide storage in saline aquifers: Storage efficiency for capillary trapping at the basin scale. *Transp. Porous Media*, *82*(1), 19-30. https://doi.org/10.1007/s11242-009-9420-3

Juanes, R., Spiteri, E. J., Orr, F. M., & Blunt, M. J. (2006). Impact of relative permeability hysteresis on geological CO_2 storage. *Water Resources Research*, *42*(12), 395-397. https://doi.org/10.1029/2005wr004806

Kleinberg, R. and Vinegar, H. (1996). NMR Properties of Reservoir Fluids. *The Log Analyst*, *37*(6), November-December.

Kleinberg, R. L. (1996). Utility of NMR T_2 distributions, connection with capillary pressure, clay effect, and determination of the surface relaxivity parameter $_2$, *Magnetic Resonance Imaging*, *14*(7–8), 761–767. https://doi.org/10.1016/S0730-725x(96)00161-0

Lenormand, R., Touboul, E., & Zarcone, C. (1988). Numerical models and experiments on immiscible displacements in porous media. *Journal of Fluid Mechanics*, *189*, 165-187. https://doi.org/10.1017/s0022112088000953

Levitt MH (2001). Spin dynamics: basics of nuclear magnetic resonance. Wiley, Chichester. https://doi.org/10.1002/mrc.1092

Li Q., Liu G, Liu X., et al. (2013). Application of a Health, Safety, and Environmental Screening and Ranking Framework to the Shenhua CCS Project. *International Journal of Greenhouse Gas Control*, *17*(5):504-514. https://doi.org/10.1016/j.ijggc.2013.06.005

Li, S., Wang, C., Zhang, X., Zou, L., & Dai, Z. (2019). Classification and characterization of bound water in marine mucky silty clay. *Journal of Soils and Sediments*, *19*(5), 2509–2519. https://doi.org/10.1007/s11368-019-02242-5

Li, Y., Di, Q., Hua, S., Jia, X., & Chen, H. (2020). Visualization of foam migration characteristics and displacement mechanism in heterogeneous cores. *Colloids and Surfaces A Physicochemical and Engineering Aspects*, *607*, 125336. https://doi.org/10.1016/j.colsurfa.2020.125336

Liu, Y., Y. Zhao, J. Zhao, and Y. Song (2011), Magnetic resonance imaging on CO_2 miscible and immiscible displacement in oil-saturated glass beads pack. *Magnetic Resonance Imaging*, *29*(8), 1110–1118. https://doi.org/10.1016/j.mri.2011.05.009

MacMinn, C. W., Szulczewski, M. L., & Juanes, R. (2010). CO_2 migration in saline aquifers. Part 1. Capillary trapping under slope and groundwater flow. *Journal of Fluid Mechanics*, *662*, 329-351. https://doi.org/10.1017/s0022112010003319

MacMinn, C., Szulczewski, M., & Juanes, R. (2011). CO_2 migration in saline aquifers. Part 2. Capillary and solubility trapping. *Journal of Fluid Mechanics*, *688*, 321-351. https://doi.org/10.1017/jfm.2011.379

Majors, P. D., Ping, L., & Peters, E. J. (1995). NMR Imaging of Immiscible Displacements in Porous Media. *Spe Formation Evaluation*, *12*(3), 164-169. https://doi.org/10.2118/30557-pa

Mitchell, J., T. C. Chandrasekera, and L. F. Gladden. (2010), Obtaining true transverse relaxation time distributions in high-field NMR measurements of saturated porous media: Removing the influence of internal gradients. *The Journal of Chemical Physics*, *132*(24), 244705, https://doi.org/10.1063/1.3446805

Nordbotten, J.M., Celia, M.A., Bachu, S. (2005). Injection and storage of CO_2 in deep saline aquifers: analytical solution for CO_2 plume evolution during injection. *Transp.Porous Med. 58* (3), 339–360. https://doi.org/10.1007/s11242-004-0670-9

Prather, C. A., J. M. Bray, J. D. Seymour, and S. L. Codd. (2016). NMR study comparing capillary trapping in Berea sandstone of air, carbon dioxide, and supercritical carbon dioxide after imbibition of water. *Water Resources Research*, *52*, 713–724. https://doi.org/10.1002/ 2015WR017547

Qu Y, Dai Z, Li G, Wang S, Jia L, Zhang Q. Petroleum Industrial Standard of People Republic of China: practices for core analysis, SY/T 5336–2006. National Dev Reform Commission 2006:1–215.

Saffman, P. G., & Taylor, G. (1958). The Penetration of a Fluid into a Porous Medium or Hele-Shaw Cell Containing a More Viscous Liquid. Proceedings of the Royal Society A: Mathematical. *Physical and Engineering Sciences*, *245*(1242), 312–329. https://doi.org/10.1098/rspa.1958.0085

Schowalter, T.T. (1979). Mechanics of secondary hydrocarbon migration and entrapment. *AAPG Bulletin*, *63*(5): 723-760. https://doi.org/10.1306/2f9182ca-16ce-11d7-8645000102c1865d

Singer, P.M., Asthagiri, D., Chen, Z., Valiya Parambathu A, Hirasaki GJ, Chapman WG. (2018). Role of internal motions and molecular geometry on the NMR relaxation of hydrocarbons. *J Chem Phys.*, *148*(16). 164507,1-17. https://doi.org/10.1063/1.5023240

Song, Y. Q., H. Cho, T. Hopper, A. E. Pomerantz, and P. Z. Sun (2008), Magnetic resonance in porous media: Recent progress, *J. Chem. Phys.*, *128*(5), 052212. https://doi.org/10.1063/1.2833581

Song, Y., Jiang, L., Yu, L., Yang, M., Zhao, Y., & Zhu, N., et al. (2012). An experimental study on CO_2/water displacement in porous media using high-resolution magnetic resonance imaging. *International Journal of Greenhouse Gas Control*, 10(none).

https://doi.org/10.1016/j.ijggc.2012.07.017

Stingaciu, L. R., L. Weihermuller, S. Haber-Pohlmeier, S. Stapf, H. Vereecken, and A. Pohlmeier (2010), Determination of pore size distribution and hydraulic properties using nuclear magnetic resonance relaxometry: A comparative study

of laboratory methods, *Water Resources Research*, *46*, W11510. https://doi.org/10.1029/2009wr008686

Straley, C., D. Rossini, H. Vinegar, T. Pierre, and C. Morriss (1997), Core analysis by low-field NMR, Log Anal., 38(2), 84–93.

Sutton, R. P.. (2009). An Improved Model for Water-Hydrocarbon Surface Tension at Reservoir Conditions [R]. SPE 124968, 2009.

Tanino, Y., & Blunt, M. J. (2012). Capillary trapping in sandstones and carbonates: dependence on pore structure. *Water Resources Research*, *48*(8), 345-352. https://doi.org/10.1029/2011wr011712

Tsang, C. F., Birkholzer, J., Rutqvist, J. (2008). A comparative review of hydrologic issues involved in geologic storage of CO_2 and injection disposal of liquid waste, *Environ. Geol.*, *54*, 1723–1737, https://doi.org/10.1007/s00254-007-0949-6

Vamerzani, B. Z., Zadehkabir, A., Saffari, H., Hosseinalipoor, S. M., & Honari, P. (2021). Experimental analysis of fluid displacement and viscous fingering instability in fractured porous medium: effect of injection rate. *Journal of the Brazilian Society of Mechanical Sciences and Engineering*, *43*(2). https://doi.org/10.1007/s40430-020-02790-9

Wang, Y., Zhang, C., Wei, N., Oostrom, M., Wietsma, T.W., Li, X., Bonneville, A. (2012). Experimental study of crossover from capillary to viscous fingering for supercritical CO_2–water displacement in a homogeneous pore network. Environ. *Sci. Technol. 47*, 212–218. https://doi.org/10.1021/es3014503

Washburn, K. E., and P. T. Callaghan (2006), Tracking pore to pore exchange using relaxation exchange spectroscopy, *Phys. Rev. Lett., 97(17)*, 175502. https://doi:10.1103/PhysRevLett.97.175502.

Washburn, K. E., Cheng, Y. (2017). Detection of intermolecular homonuclear dipolar coupling in organic rich shale by transverse relaxation exchange. *J Magn Reson.*, *278*:18–24. http://dx.doi.org/10.1016/j.jmr.2017.02.022

Westphal, H., I. Surholt, C. Kiesl, H. F. Thern, and T. Kruspe (2005). NMR measurements in carbonate rocks: problems and an approach to a solution. *Pure Appl. Geophys.*, *162*(3), 549–570. http s://doi.org/10.1007/s00024-004-2621-3

Yan, W., Sun, J., Golsanami, N., Li, M., Cui, L., Dong, H., Sun, Y. (2019). Evaluation of wettabilities and pores in tight oil reservoirs by a new experimental design. *Fuel 252*, 272–280. https://doi.org/10.1016/J.FUEL.2019.04.130.

Yang, S., & Yu, Q. (2020). Experimental investigation on the movability of water in shale nanopores: A case study of Carboniferous shale from the Qaidam Basin, China. *Water Resources Research*, *56*, e2019WR026973. https://doi.org/10.1029/2019wr026973

Ying Teng, Lanlan Jiang, et al. (2018). MRI study on CO_2 capillary trap and drainage behavior in sandstone cores under geological storage temperature

and pressure. *International Journal of Heat and Mass Transfer*, *119*: 678-687. https://doi.org/10.1016/j.ijheatmasstransfer.2017.12.013

Zeng L, Wang LS, Xu HX, Jiao YG, Cui SN, Han H, et al. (2010). Petroleum Industrial Standard of People Republic of China: analysis method for clay minerals and ordinary non-clay minerals in sedimentary rocks by the X-Ray diffraction, SY/T 5163–2010. National Energy Administration 2010:1–48.

Zhang, C., Oostrom, M., Wietsma, T.W., Grate, J.W., Warner, M.G.(2011). Influence of viscous and capillary forces on immiscible fluid displacement: pore-scale experimental study in a water-wet micromodel demonstrating viscous and capillary fingering. *Energy Fuel*, *25* (8), 3493–3505. https://doi.org/10.1021/ef101732k

Zhang, K., Xie, J., Li, C., Hu, L., Wu, X., & Wang, Y. (2016). A full chain CCS demonstration project in northeast Ordos Basin, China: Operational experience and challenges. *International Journal of Greenhouse Gas Control, 50*, 218-230. https://doi.org/10.1016/j.ijggc.2016.04.025

Zhao, Y., & Yu, Q. (2017a). CO_2 breakthrough pressure and permeability for unsaturated low-permeability sandstone of the Ordos Basin. *Journal of Hydrology, 550*, 331-342. https://doi.org/10.1016/j.jhydrol.2017.04.050

Zhao, Y., & Yu, Q.. (2017b). Effect of CH_4 on the CO_2 breakthrough pressure and permeability of partially saturated low-permeability sandstone in the ordos basin, china. *Journal of Hydrology*, *556*, 732-748. https://doi.org/10.1016/j.jhydrol.2017.11.030

Zhao, Y., Zhang Q., Chen X. (2021). Experimental investigation on effect of water film thickness in unsaturated sandstone cores on CO_2 transport during geologic storage. *Journal of Hydrology, 601.* https://doi.org/10.1016/j.jhydrol.2021.126595

Zheng, X., Mahabadi, N., Yun, T.S., Jang, J., 2017. Effect of capillary and viscous force on CO_2 saturation and invasion pattern in the microfluidic chip. *J. Geophys. Res. Solid Earth 122*, 1634–1647. https://doi.org/10.1002/2016JB013908

Table 1 Basic properties of core samples

Sample	**#1**	**#2**	**#3**	**#5**	**#8**	**#9**
Lithology	Shale	Sandstone	Sandstone	Sandstone	Sandstone	Carbonate
System	Triassic	Triassic	Jurassic	Permian	Carboniferous	Ordovician
Group	Yanchang	Yanchang	Yanchang	Shihezi	Shanxi	Majiagou
Diameter	25mm	25mm	25mm	25mm	25mm	25mm
Length	30.5mm	30.7mm	29.8mm	30.2mm	30.1mm	29.9mm
Porosity	<2.79	11.8	13.99	11.86	10.02	2.74
Permeability	0.001mD	0.018mD	7.964 mD	0.274 mD	0.145 mD	0.009 mD

Table 2 Minerals contents for six tight rock samples

Sample	Quartz (%)	Plagioclase (%)	K-feldspar (%)	Calcite (%)	Clay (%)	Plagioclase (%)	Dolomite %	Siderite (%)	Hematite (%)
#1						–	–		
#2						–	–		
#3						–	–	%	
#5		–	–			–	–		%
#8		–				–	–	%	
#9		–		–	–				

"–" indicates a negligible amount of the listed mineral.