



Article Permeability Evaluation of Clay-quartz Mixtures Based on Low-Field NMR and Fractal Analysis

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Abstract: Nuclear magnetic resonance (NMR) technology has been widely used for predicting permeability coefficients of porous medium, such as shales, sandstones, and coals. However, there have been limited studies on the prediction model of clay-quartz mixtures based on NMR technology. In this study, evaporation tests at 40 °C and NMR tests were simultaneously performed on eight clay-quartz mixtures with different mineral compositions. The results show that during the evaporation process, the decay rate of T_2 total signal amplitudes was constant at first, and then decreased to 0 after a period of time. Based on the decay rate, the evaporation process was divided into two stages: the constant rate stage and the falling rate stage. Based on the two stages, the T_2 cut-offs of eight mixtures were determined. The water in the mixture was divided into two parts by the T_2 cut-off: the free water and the bound water. The prediction model of permeability coefficients of clay-quartz mixtures was established based on the Timur-Coates model. In order to simplify the process of predicting the permeability coefficient, fractal analysis was used to develop the relationship between the T_2 cut-off and fractal dimension of the T_2 spectrum of saturated mixture. A simplified method for predicting permeability coefficients of clay-quartz mixtures based on NMR technology without centrifugal and evaporation experiments was also proposed.

Keywords: clay-quartz mixture; nuclear magnetic resonance; permeability coefficient; *T*₂ cut-off; fractal analysis

1. Introduction

To protect the environment surrounding waste landfill sites, especially nuclear waste landfill sites, the landfill site needs to be isolated from its surroundings by a barrier made of low-permeability materials [1]. Expansive clays such as montmorillonite and kaolinite are materials commonly used to make barriers because of their low permeability coefficient [2–4]. The permeability coefficients of montmorillonite and kaolinite are in the range of 10^{-11} to 10^{-12} m/s [5]. Nevertheless, there is one unavoidable shortcoming in using these two materials. Both montmorillonite and kaolinite are sensitive to water, especially montmorillonite. When the moisture content of clay changes, the strength and volume of clay also change sharply. In particular, the dehydration of clay always causes shrinkage cracks, which could damage the integrity of the barrier [6–8]. Many studies have shown that adding quartz to clay can solve this problem. The addition of quartz can reduce the water sensitivity and enhance the strength of clay while maintaining a low permeability coefficient [9–11]. Clay-quartz mixtures are suitable materials for building barriers of waste landfill sites.

The traditional method used to determine permeability coefficients of clay-quartz mixtures is the variable head permeability test. Because of the low permeability coefficients of clay-quartz mixtures, the variable head permeability test is effort- and time-consuming. Many scholars use consolidation test data to calculate the permeability coefficients of mixtures based on Terzaghi's one-dimensional

consolidation theory [9,12]. This method is also time-consuming and there is a considerable gap between the measured and predicted permeability coefficients. It is therefore necessary to establish a simple, nondestructive, and accurate method for determining the permeability coefficients of clay-quartz mixtures.

As a fast, convenient, and nondestructive tool, nuclear magnetic resonance (NMR) technology has been widely used in petroleum engineering, coal engineering, and geological engineering [13]. The transverse relaxation time (T_2) distribution can reflect the pore characteristics of porous media [14–16]. Previous studies have proposed prediction models of permeability coefficients for sandstones, coals, and shales based on NMR technology [17–20]. These models were proposed based on the Schlumberger Doll Research model (SDR model) and Timur-Coates model (TC model) [21–23]. Almost no studies have been performed to confirm the applicability of these two models in predicting the permeability coefficients of clay-quartz mixtures with different mineral compositions.

In the TC model, which is also called the free fluid model, the volumes of free water and bound water in porous media are used to predict the permeability coefficient. In the T_2 spectrum, the T_2 cut-off is used to discriminate between the free water and the bound water. The traditional method for determining T_2 cut-offs of sandstones, coals, and shales is the centrifugal method [24–26]. It has been verified by experiments that there are two problems in applying this method to clay-quartz mixtures: (1) Compared with sandstones, coals, and shales, clay-quartz mixtures have a lower strength, so they might be damaged during centrifugation, and (2) the pore size of the mixture is very small, so little water can be removed by centrifuging at the maximum centrifugal velocity. Some scholars have calculated T_2 cut-offs of shales based on the evaporation tests at increasing temperatures [27–29]. According to Tang, most water in clayey soil evaporates, even at room temperature [30,31]. It is unreasonable to determine the T_2 cut-off directly by an evaporation test at increasing temperatures. An improved method based on evaporation tests to determine T_2 cut-offs of clay-quartz mixtures needs to be proposed.

To simplify the determination process of the T_2 cut-off, previous studies have proposed several models to predict the T_2 cut-offs of sandstones, shales, and coals. In these methods, fractal analysis was verified to be a useful tool for predicting the T_2 cut-offs of sandstones, shales, and coals [25,32–37]. Fractal analysis has also become a commonly used method for evaluating the particle and pore distribution characteristics of soil [38–41]. Nevertheless, almost no studies have established the relationship between the fractal dimension and T_2 cut-off because of the complex structure and pore characteristics of clay-quartz mixtures.

In this study, evaporation tests at 40 °C and NMR tests were performed on eight clay-quartz mixtures with different mineral compositions. The water in the mixtures was divided into two parts, according to the different decay rates of the T_2 total signal amplitude during evaporation. A prediction model for the permeability coefficients of clay-quartz mixtures was proposed based on the TC model. We also established a method for determining the T_2 cut-offs of mixtures by combining the NMR tests and fractal analysis. Based on the prediction model and novel method for determination of the T_2 cut-off, a simplified method for determining the permeability coefficients of clay-quartz mixtures without centrifugal and evaporation tests was established.

2. Materials and Methods

2.1. Theoretical Basis

2.1.1. NMR Theory

According to the NMR relaxation mechanism, transverse relaxation consists of three parts: bulk relaxation, surface relaxation, and diffusion relaxation [21]:

$$\frac{1}{T_2} = \frac{1}{T_{2B}} + \frac{1}{T_{2S}} + \frac{1}{T_{2D}}$$
(1)

$$T_{2D} = \frac{C_{md}(\gamma G T_E)}{12} \tag{2}$$

where T_2 is the transverse relaxation time, T_{2B} is the transverse bulk relaxation time, T_{2S} is the transverse surface relaxation time, T_{2D} is the transverse diffusion relaxation time, C_{md} is the molecular diffusion coefficient, G is the gyromagnetic ratio of a proton, and T_E is the inter-echo spacing. When the magnetic field is uniform (G is very small) and T_E is short enough, the T_{2D} can be ignored. For porous media saturated with distilled water, the T_{2B} is much bigger than T_{2S} , and the $1/T_{2B}$ is also usually negligible. Equation (1) can be simplified as follows [13,42,43]:

$$\frac{1}{T_2} = \frac{1}{T_{2S}} \approx C_r \left(\frac{S}{V}\right) = F_s \frac{C_r}{r_c}$$
(3)

where C_r is the relaxation coefficient which is mainly affected by the mineral composition and surface properties of clay mineral, *S* is the surface area of pores, *V* is the volume of pores, r_c is the diameter of pores, and F_s is the geometric shape factor (3 for spherical pores and 2 for columnar pores) [44].

2.1.2. Fractal Theory

According to previous studies, the fractal dimension can be calculated by Equation (4) [45–48]. The present fractal dimension can be applied to evaluate the pore characteristics of geomaterials such as rock and soil. According to [45–48], it was testified that the fractal behavior of a pore-size distribution of clayey soil suits the fractal model. All of the eight clay-quartz mixtures in this study can be classified as clayey soil:

$$V(>r) = V_a \left[1 - \left(\frac{r}{L}\right)^{3-D} \right]$$
(4)

where V(>r) is the cumulative volume of pores with a size bigger than r, V_a is the total volume of the mixture, and L is the range of the pore size distribution. L can be expressed by Equation (5):

$$L = r_{\rm max} - r_{\rm min} \tag{5}$$

where r_{max} is the maximum pore size and r_{min} is the minimum pore size. Based on Equation (3), Equations (4) and (5) can be converted into one Equation, as follows:

$$V_a - V(>r) = \frac{V_a}{\left(T_{2\max} - T_{2\min}\right)^{3-D}} (T_2)^{3-D}$$
(6)

where T_{2max} is the maximum transverse relaxation time and T_{2min} is the minimum transverse relaxation time. The porosity of the mixture was defined as

$$\varphi = \frac{V_v}{V_a} \tag{7}$$

where V_v is the cumulative volume of pores. V_a is assumed to be 1, and the cumulative volume of pores with a size smaller than *r* and equal to *r* can be expressed by

$$V(\le r) = \varphi - V(>r) \tag{8}$$

Based on Equation (8), Equation (6) can be revised as

$$1 - \varphi + V(\leq r) = \frac{1}{\left(T_{2\max} - T_{2\min}\right)^{3-D}} (T_2)^{3-D}$$
(9)

When logarithms are used in Equation (9), Equation (9) is converted into Equation (10):

$$lg[1 - \varphi + V(\le r)] = (3 - D)lgT_2 + (D - 3)lg(T_{2max} - T_{2min})$$
(10)

The value of *D* can be determined from the curve of $[1 - \varphi + V(\leq r)]$ versus T_2 in the double logarithmic plot. The relationship between *D* and the slope of this curve can be expressed as follows:

$$D = 3 - H \tag{11}$$

where *H* is the slope of the curve of $lg[1 - \varphi + V(\leq r)]$ versus $lg(T_2)$.

It is noteworthy that the present fractal dimension is treated for space. This fractal model was established based on the pore size distribution of the soil. According to Equation (3), the transverse relaxation time (T_2) is proportional to the pore size (r_c). Therefore, the fractal dimension can be determined by the T_2 spectrum from the result of the NMR test.

2.2. Materials

The mineral powders used in this study were montmorillonite, kaolinite, and quartz. These three kinds of mineral powders were bought from Guangzhou Jialiang Mineral Products Co., Ltd. (Guangzhou, China); Guangzhou Yifeng Chemical Technology Co., Ltd. (Guangzhou, China); and Inner Mongolia Ningcheng Tianyu Chemical Co., Ltd. (Chifeng, China), respectively. The grain size distributions of these three kinds of mineral powders were measured by the Mastersizer 2000 laser particle analyzer. The grain size distributions of the three mineral powders are shown in Figure 1. The maximum particle sizes of the montmorillonite, kaolinite, and quartz were 0.01, 0.04, and 0.55 mm, respectively. The clay (<0.005 mm), silt (0.005–0.075 mm), and sand (>0.075 mm) contents of the three kinds of mineral powders are shown in Table 1. Particles finer than 0.005 mm in montmorillonite, kaolinite, and quartz represented 70.23%, 84.10%, and 1.63% of the samples, respectively. Additionally, 15.9%, 29.77%, and 4.15% of the particles in the montmorillonite, kaolinite, and quartz were between 0.005 and 0.0075 mm. Only the quartz had particles bigger than 0.075 mm; 94.22% of the particles in the quartz were bigger than 0.075 mm.



Figure 1. The grain size distributions of quartz, kaolinite, and montmorillonite. From left to right, the red curve, black curve, and blue curve indicate grain size distributions of kaolinite, montmorillonite, and curve, respectively. The particle size of quartz mineral powder is the largest among the three kinds of mineral powder.

Property	Materials		
	Quartz	Kaolinite	Montmorillonite
Atterberg limits			
Plastic limit (%)	_	32.00	61.34
Liquid limit (%)	_	68.99	178.65
Plasticity index	_	36.99	117.31
Grain size distribution			
Clay (%;<0.005 mm)	1.63	70.23	84.10
Silt (%; 0.005–0.075 mm)	4.15	29.77	15.90
Sand (%; >0.075 mm)	94.22	0	0
Chemical composition			
SiO ₂ (%)	98.85	57.82	66.63
Al ₂ O ₃ (%)	0.57	35.24	16.07
K ₂ O (%)	_	3.89	_
Fe ₂ O ₃ (%)	0.08	1.86	6.50
CaO (%)	0.18	_	3.99
MgO (%)	_	0.37	5.32
Specific gravity	2.68	2.76	2.61
Classification	_	CH	CH

Table 1. Basic properties of quartz, kaolinite, and montmorillonite used in this study.

Table 1 presents the basic properties of the quartz, kaolinite, and montmorillonite used in this study. The Atterberg limits were measured by the method presented in ASTM D4318. The plastic limit, liquid limit, and plasticity index of the kaolinite were 32.00%, 68.99%, and 36.99%, respectively. The plastic limit, liquid limit, and plasticity index of the montmorillonite were 61.34%, 178.65%, and 117.31%, respectively. According to ASTM D2487, the kaolinite and montmorillonite used in this study can be classified as high plastic clay (CH). The chemical compositions of minerals were determined by the X-ray fluorescence method. The main chemical composition of quartz used in this study was SiO₂, and its proportion was 98.85%. The montmorillonite used in this study was mainly composed of SiO₂, Al₂O₃, Fe₂O₃, CaO, and MgO. The proportions of these chemical compositions were 62.76%, 17.13%, 8.46%, 5.80%, and 4.49%, respectively. The main chemical compositions of kaolinite were SiO₂, Al₂O₃, K₂O, and Fe₂O₃, and the proportions of these chemical compositions of a kaolinite were SiO₂, Al₂O₃, K₂O, and Fe₂O₃, and the proportions of these chemical compositions of a compositions were form and the proportions of these chemical compositions of a composition was 98.85%, and 1.86%, respectively. According to ASTM D7263, the specific gravity values of quartz, kaolinite, and montmorillonite were determined to be 2.68, 2.76, and 2.61, respectively.

The distilled water used in this study had a pH of 6.7 and the electrical conductivity of the distilled water was below 1 ms/m.

2.3. Sample Preparation

All the mineral powders were dried in an oven at 250 °C to constant weight for 24 h. In this procedure, almost all of the water was removed. Then, the mineral powders were mixed at the fixed proportions based on the dry weight. Eight clay-quartz mixtures were prepared in the laboratory. All the mixtures consisted of montmorillonite and quartz or kaolinite and quartz. The clay mineral (montmorillonite or kaolinite) contents in the mixtures increased from 40% to 100% with the increment of 20%. The mixtures were named after the kind of clay mineral and clay mineral content. As an example, K60 consisted of kaolinite and quartz and the kaolinite fraction was 60%. Next, distilled water was added to the mixtures until the moisture content reached the plastic limit. Afterward, all the eight mixtures were put into plastic sealing bags for two days to reach a full hydration state. Following the hydration period, the mixtures were put into the hollow cylinder with the inner diameter and height of 31.9 mm and 80 mm respectively, and a jack was used to shape the mixtures under static pressure. All the formed mixtures had reached the maximum dry density at the plastic limit. Finally, all the mixtures were saturated with distilled water by the vacuum method. The mixtures were taken

6 of 23

out from distilled water once the weight has reached maximum limit. NMR and evaporation tests were carried out on the eight mixtures after surface water was erased.

2.4. Methods

The NMR instrument used in this study was the MesoMR12-150H-I NMR analyzer produced by NIUMAG Co., Ltd., Suzhou, China. The magnetic induction, resonant frequency, diameter of coil, and magnetic field temperature were 0.55T, 12 MHZ, 60 mm, and 30 °C, respectively. According to a review [13], the free induction decay (FID) could not be used to determined the value of T_2 because of the effect of magnetic field inhomogeneities on NMR signal. The value of T_2 measured by FID was less than the actual value. To minimize the effect of magnetic field inhomogeneities on NMR signal, the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence was used in NMR tests [49,50]. According to literatures [51,52], refocusing flip angle had great influence on the value of T_2 . When the refocusing angle was π (180°), the T_2 estimated from the echo trains was accurate because no longitudinal magnetization was introduced in the transverse plane. So the refocusing angle of CMPG pulse sequence in this study was 180°. The CPMG pulse began with the application of a 90° pulse and followed by a series of 180° pulses. The time interval between application of two 180° pulses were 2τ and the first 180° pulse were applied at a time τ after the 90° pulse. The time τ was equal to half of echo time. The CPMG pulse sequence used in this study was same as that in previously studies [43,53–55]. It was testified the CPMG pulse sequence could be used to determine the value of T_2 of soil samples. The 90° pulse width, 180° pulse width, and sampling points were set as 20 µs, 30.48 µs, and 208,018, respectively. The sampling frequency ratio, frequency delay, analog gain, and digital gain were set as 200 kHz, 8 µs, 20, and 3, respectively. The repeated sampling waiting time, accumulated sampling times, echo time, and echo number were set as 8000 ms, 4260 µs, and 4000, respectively. The NMR tests were performed on the saturated mixtures. Then, the mixtures were put into an oven at 40 °C to simulate the highest temperature under natural conditions. In the evaporation procedure, the NMR tests were carried out on mixtures per hour. In order to be consistent with the temperature of the magnetic field, mixtures needed to be cooled to 30 °C before each NMR test. After NMR tests, the T_2 spectra were obtained automatically by the software provided by NIUMAG Co., Ltd. (Suzhou, China) The inversion software was developed based on inverse Laplace transform [56] and the simultaneous iterative reconstruction technique (SIRT) [57].

3. Results

3.1. T₂ Spectra of Saturated Mixtures

The T_2 spectra of kaolinite-quartz and montmorillonite-quartz saturated mixtures are shown in Figure 2. The T_2 values corresponding to the peak signal amplitude (T_{2P}) of kaolinite-quartz and montmorillonite-quartz saturated mixtures were different. The T_{2P} of kaolinite-quartz mixtures and montmorillonite-quartz mixtures ranged from 7.84 to 11.89 ms and 1.20 to 2.25 ms, respectively. Based on this, the dominant clay mineral could be roughly inferred from the T_2 spectrum of saturated mixtures. Besides T_{2P} , the whole T_2 spectrum, including the maximum and minimum T_2 , shifted to the left as the clay content increased. According to Equation (3), the reason why T_2 shifted to the left may have been due to the increases in the relaxation coefficient or decreases in the pore diameter of mixtures with increased clay contents. The peak signal amplitude increased as the clay contents increased in mixtures.



Figure 2. The T_2 spectra of kaolinite-quartz and montmorillonite-quartz saturated mixtures. From left to right, curves with different colors and symbols with different shapes indicate T_2 spectra of M100, M80, M60, M40, K100, K80, K60, and K40, respectively. According to T_{2p} , T_2 spectra could be divided into two groups. The group on the left and right are the T_2 spectra of montmorillonite-quartz and kaolinite-quartz saturated mixtures, respectively.

According to NMR theory, the total area of the T_2 spectrum, which is equal to the T_2 total signal amplitude (A_t), is proportional to the weight of distilled water in mixtures. The distilled water was used to verify and determine this relationship. The relationship between A_t and the weight of distilled water can be expressed by Equation (12).



$$A_t = 302.6 \text{ m}$$
 (12)

Figure 3. The relationship between the T_2 total signal amplitude and weight of distilled water. The line is the fitting line of the points. The Equation in the box is the Equation of the line. R^2 indicates the correlation coefficient of the Equation.

Here, *m* is the weight of distilled water and the correlation coefficient R^2 of Equation (12) was 0.996. This indicated that the water content of mixture can be expressed by the T_2 total signal amplitude of the T_2 spectrum.

The relationship between the T_2 signal amplitude per unit weight of dry soil particles (A_{uw}) and clay content is shown in Figure 4. The T_2 signal amplitude per unit weight of dry soil particles can represent the water content of per unit weight of dry soil (m_{uw}). The m_{uw} increased with an increase in clay content. The m_{uw} of montmorillonite-quartz was much bigger than in kaolinite-quartz mixtures. This is mainly because the double-layer structure of montmorillonite can hold more water. The relationships between A_{uw} and clay contents of kaolinite-quartz mixtures and montmorillonite-quartz mixtures can be expressed by Equations (13) and (14), and the R^2 values of Equations (13) and (14) were 0.997 and 0.982.

$$A_{um} = 0.606CC + 35.22 \tag{13}$$

$$A_{um} = 1.581CC + 25.98\tag{14}$$



Figure 4. The relationship between the T_2 signal amplitude per unit weight of dry soil particles (A_{um}) and clay content (*CC*). The lines at the top and bottom indicate the relationships between the A_{um} and *CC* of montmorillonite-quartz and kaolinite-quartz mixtures, respectively. The Equations in the two boxes are the Equations of the two lines. R^2 indicates the correlation coefficient of the Equation.

The geometric mean of T_2 (T_{2gm}) was defined by Equation (15):

$$T_{2gm} = \exp\left(\sum_{T_{2s}}^{T_{2e}} \frac{A_i}{A_t} \ln(T_{2i})\right)$$
(15)

where T_{2s} and T_{2e} were the start and ending points of T_2 spectra, respectively, which were $T_{2s} = 0.01$ ms and $T_{2e} = 10,000$ ms in this study; T_{2i} represents the individual values of T_2 ; A_i is the cumulative signal amplitude at T_{2i} ; and A_t is the total signal amplitude of the T_2 spectrum. The T_{2gm} values of mixtures in the initial saturated state are shown in Figure 5. The T_{2gm} decreased as the clay content increased. For mixtures with the same clay content, the T_{2gm} of montmorillonite-quartz mixtures was much smaller than kaolinite-quartz mixtures. The T_{2gm} of montmorillonite-quartz mixtures and kaolinite-quartz mixtures ranged from 0.978 to 1.797 ms and 7.139 to 11.60 ms, respectively.



Figure 5. The relationship between T_{2gm} and the clay content (*CC*). The lines at the top and bottom indicate the relationships between the T_{2gm} and *CC* of kaolinite-quartz (K-Q) and montmorillonite-quartz (M-Q) mixtures, respectively. The Equations in the two boxes are the Equations of the two lines. R^2 indicates the correlation coefficient of the Equation.

What is worth noting here is that the T_{2gm} cannot be used to compare the diameters of pores of mixtures directly. According to Equation (3), the mean value of pore size (r_m) is proportional to T_{2gm} , so the relationship between r_m and T_{2gm} can be expressed by

$$\frac{1}{T_{2gm}} = F_s \frac{\rho}{r_m} \tag{16}$$

According to previous studies, the relaxation coefficients of soil with different mineral compositions vary greatly [58,59].

3.2. Variation of T₂ Spectra During Evaporation

The variations of T_2 spectra of montmorillonite-quartz and kaolinite-quartz mixtures during the evaporation process are shown in Figures 6 and 7, respectively. All the T_2 spectra were single peaks, which meant that the pores in mixtures were distributed continuously. The peak signal amplitude kept decreasing during evaporation. The decay rate of the peak signal amplitude reduced gradually. All the T_2 spectra of mixtures shifted to the left during the evaporation process. This meant that the pore sizes of the mixture decreased due to volume shrinkage during evaporation.

The variations of the T_2 total signal amplitude with respect to the heating time are shown in Figure 8. For the same heating time, the mixtures with a higher clay content had a bigger T_2 total signal amplitude. With the same clay content, the T_2 total signal amplitude of montmorillonite-quartz mixtures was bigger than that of kaolinite-quartz mixtures. The A_t kept decreasing during evaporation and the decay rate reduced gradually, until it reached 0.

500 -

400

300

200

100

0.

600

500

400

300

200

100

0

60h heating 65h heatin

0.1

 T_2 signal amplitude

 T_2 signal amplitude



200

100

0. 0.01 60h heati 65h heati

0.1

Figure 6. The variation of T_2 spectra of montmorillonite-quartz mixtures: (a) M40; (b) M60; (c) M80; (d) M100. In (a-d), from top to bottom, curves with different colors and symbols with different shapes indicate T_2 spectra of montmorillonite-quartz mixtures after heating at different times. The T_2 spectra in the box were enlarged and placed in the upper right corner of (a-d).

(c)

1000

100

10

Transverse relaxation time T, (ms)

(d)

1000

100

10

Transverse relaxation time T_2 (ms)



Figure 7. The variation of T_2 spectra of kaolinite-quartz mixtures: (**a**) K40; (**b**) K60; (**c**) K80; (**d**) K100. In (**a–d**), from top to bottom, curves with different colors and symbols with different shapes indicate T_2 spectra of kaolinite-quartz mixtures after heating at different times. The T_2 spectra in the box were enlarged and placed in the upper left corner of (**a–d**).



Figure 8. Variation of the T_2 total signal amplitude (A_t) with respect to the heating time. From top to bottom, curves with different colors and symbols with different shapes indicate variation of M40, M60, M80, M100, K40, K60, K80, and K100, respectively. The scales of the Y axes of the upper and lower parts of the figure are different.

Figure 9 shows the variations of the decay rate with respect to the heating time. According to the decay rate, the evaporation process could be divided into two stages: the constant rate stage and the falling rate stage. The time when the decay rate started to fall was defined as the falling rate critical time (T_f). The T_f values of the montmorillonite-quartz mixtures and kaolinite-quartz mixtures were 6 and 20 h, respectively.



Figure 9. Variation of the *At* decay rate with respect to the heating time. From top to bottom, curves with different colors and symbols with different shapes indicate variation of M40, M60, M80, M100, K40, K60, K80, and K100, respectively. The scales of the Y axes of the upper and lower parts of the figure are different. Red and olive vertical line indicate 20 and 6 h, respectively. T_f is the time when the decay rate started to fall.

4. Discussion

4.1. Novel Method for Determining the T_2 Cut-Off

In previous studies, the T_{2c} values were determined from the T_2 spectra of saturated and centrifugal samples. This method assumed that centrifugation could remove all free water in samples. There are two problems when this method is used to measure the T_{2c} of clay-quartz mixtures: (1) The strength of the clay-quartz mixtures is much lower than that of coal, sandstone, and shale, so the centrifugal force may damage the samples, and (2) because of the complexity of the structure, the water in mixtures is hardly removed by the centrifugal method. Even at the maximum rotational speeds, little water is extracted from samples by centrifuging. Therefore, a new method needs to be proposed for determining the T_{2c} of clay-quartz mixtures.

According to the results of NMR and evaporation tests, the evaporation process can be divided into two stages. The water that evaporated easily corresponded to a larger signal decay rate and the water that evaporated with more difficultly corresponded to a smaller decay rate. Based on this, the water in mixtures can divided into two types: the free water and the bound water. In this study, the water that evaporated during the constant rate stage and falling rate stage was defined as the free water and the bound water, respectively. The T_{2c} was used to discriminate between the free water and the bound water in the T_2 spectrum. The T_{2c} divides the T_2 spectrum of initial saturated mixtures into two parts. The cumulative signal amplitude from T_{2min} to T_{2c} corresponded to free water. Therefore, the T_{2c} could be determined from the T_2 spectra of mixtures under two saturated states: an initial state and a falling rate state. The mixture under the initial state and falling rate state were the saturated mixture before evaporation and the mixture at the beginning of the falling rate stage, respectively. Based on the two T_2 spectra, the cumulative signal amplitude curves of mixtures under two states could be obtained. A line parallel to the T_2 axis can be drawn from the maximum cumulative signal amplitude of the falling rate state, which intersects with the cumulative signal amplitude of the initial state. The T_{2i} of the intersect point was the T_2 cut-off value. Figure 10 shows the T_{2c} of all eight mixtures.



Figure 10. Cont.



Figure 10. T_2 cut-offs (T_{2c}) of the eight mixtures: (**a**) K40; (**b**) K60; (**c**) K80; (**d**) K100; (**e**) M40; (**f**) M60; (**g**) M80; (**h**) M100. The black curve with a solid square and red curve with solid circle indicate T_2 spectra of the saturated mixture before evaporation and the mixture at the beginning of the falling rate stage, respectively. The curves with an open square and open circle indicate the cumulative signal amplitude of T_2 spectra with the same color. The intersection of the black curve with the open square and the red curve with the open circle was enlarged and placed in the upper left corner of (**a**–**d**).

The relationships between T_{2c} and the clay content of mixtures are shown in Figure 11, which reveals that the T_{2c} decreased as the clay content increased. The relationships between T_{2c} and the clay content of K-Q mixtures and M-Q mixtures can be expressed by Equations (17) and (18), for which the R^2 values were 0.987 and 0.912, respectively.

$$T_{2c} = -0.012CC + 6.626 \tag{17}$$

$$T_{2c} = -0.016CC + 3.322 \tag{18}$$



Figure 11. The relationships between T_{2c} and the clay content (CC). The lines at the top and bottom indicate the relationships between the T_{2c} and CC of kaolinite-quartz (K-Q) and montmorillonite-quartz (M-Q) mixtures, respectively. The Equations in the two boxes are the Equations of the two lines. R^2 indicates the correlation coefficient of the Equation.

4.2. TC Permeability Coefficient Prediction Model

The variable head permeability test is the traditional method used to measure the permeability coefficients of clay-quartz mixtures. The method is time- and effort-consuming. NMR technology has

gradually become a commonly used method for determining the permeability of porous media. For shales, coals, and sandstones, it has been proved that the Schlumberger Doll Research (SDR) model and Timur-Coates model (TC model) can be used to predict permeability. Because of the complexity of the structures, whether these two models are suitable for predicting the permeability of clay-quartz mixtures with different mineral compositions has not been previously verified. The SDR model can be expressed by Equation (19):

$$k_{SDR} = a\varphi_{NMR}{}^m \left(T_{2gm}\right)^n \tag{19}$$

where k_{SDR} is the permeability predicted by the SDR model and φ_{NMR} is the porosity measured by the NMR test. The empirical constants *a*, *m*, and *n* are related to the basic properties of porous media. This model used the average pore size to predict permeability. However, because the surface relaxivity of mixtures with different mineral compositions varied greatly, the T_{2gm} could not be used directly to compare the average pore size. It is unreasonable to use the SDR model to predict the permeability of clay-quartz mixtures with different mineral compositions.

The TC model can be expressed by Equation (20):

$$k_{TC} = a\varphi_{NMR}^{m} \left(\frac{FFV}{BFV}\right)^{n}$$
(20)

where k_{TC} is the permeability predicted by the TC model, *FFV* is the volume of free fluid, and *BFV* is the volume of bound fluid. The TC model is also called the free fluid model. In NMR tests, *FFV* corresponded to the cumulative T_2 signal amplitude between T_{2c} and T_{2max} (A_{FF}), and *BFV* corresponded to the cumulative T_2 signal amplitude between T_{2min} and T_{2c} (A_{BF}). Equation (21) can be revised to form:

$$k_{TC} = a\varphi_{NMR}^{m} \left(\frac{A_{FF}}{A_{BF}}\right)^{n}$$
(21)

To verify the applicability of the TC model, variable head permeability tests were used to measure the permeability coefficients of the eight mixtures. What is worth noting is that the permeability coefficient (K) determined from variable head permeability tests is not the permeability (k) in Equation (21). The k reflects the inherent permeability of porous media, independent of fluid properties. The K is not only affected by the properties of porous media, but also by the properties of fluids. The relationship between K and k is shown in the following Equation:

$$K = \frac{\rho g}{\eta} k \tag{22}$$

where φ , *g*, and η are the density, gravitational acceleration, and dynamic viscosity coefficient of the fluid, respectively. For the distilled water used in this study, these three parameters were fixed values. Equation (22) can be simplified as follows:

$$K = bk \tag{23}$$

By combining Equations (21) and (23), the TC model can be expressed by Equation (24):

$$K_{TC} = b \bullet a \varphi_{NMR}^{m} \left(\frac{A_{FF}}{A_{BF}}\right)^{n} = B \varphi_{NMR}^{m} \left(\frac{A_{FF}}{A_{BF}}\right)^{n}$$
(24)

After regression fitting, the three constants *B*, *m*, and *n* were 1.527, -3.353, and 0.662, respectively. The R^2 of Equation (24) was 0.957. Figure 12 presents the predicted permeability coefficients versus the measured permeability coefficients. The points of the curve were close to the line y = x. This indicated that the accuracy of the TC model met the requirements. The TC model can thus be used to predict the permeability coefficients of clay-quartz mixtures.



Figure 12. The predicted permeability coefficients versus the measured permeability coefficients. Red solid line indicates a slope of 1:1. The closer the black point is to the line, the smaller the difference between the predicted and measured permeability coefficient is.

4.3. Determination Method of T_{2c} Based on Fractal Analysis

Before using the TC model to predict the permeability of mixtures, it is necessary to determine T_{2c} . In this study, the T_{2c} was determined by an evaporation test, which is time-consuming. A simple method is thus needed to determine the T_{2c} . According to previous studies, fractal dimensions can be used to determine the T_{2c} because fractal dimensions can reflect the characteristics of the pore distribution in mixtures. The fractal dimensions were determined based on the fractal theory presented in Section 2.1.2. According to Equation (10), there is a liner relationship between $lg[1 - \varphi + V(\leq r)]$ and $\lg T_2$. The slope of the curve of $lg[1 - \varphi + V(\leq r)]$ versus lgT_2 was obtained by linear regression. The linearity of the points at the beginning and end of the curves was relatively poor because of the scale dependency of the fractal dimension. The fractal dimensions calculated with different length scales are different. To achieve accurate fractal dimensions, we adopted a unified standard for the eight mixtures: maximize the length scale under the condition of the correlation coefficient reaching 0.99. Available length scales (red points in Figure 13) of K40, K60, K80, and K100 were 4.199–25.53, 3.409–19.34, 3.181–16.83, and 2.967–14.65 ms, respectively. Available length scales of M40, M60, M80, and M100 were 0.370-5.543, 0.280-3.917, 0.227-3.181, and 0.185-2.768 ms, respectively. After the slopes of the curves were determined, the fractal dimensions were determined by Equation (11). The fractal dimensions of the eight mixtures are shown in Figure 13.



Figure 13. Cont.



Figure 13. The fractal dimensions (*D*) of the eight mixtures: (**a**) K40; (**b**) K60; (**c**) K80; (**d**) K100; (**e**) M40; (**f**) M60; (**g**) M80; (**h**) M100. The red solid line is the fitting line of the red circular point. The Equation in the box is the Equation of the line. R^2 indicates the correlation coefficient of the Equation. *D* was calculated by Equation (11).

As shown in Figure 13, the fractal dimensions of mixtures with the same kind of clay mineral decreased as the clay content increased. According to fractal theory [45,48], the more uniform the pore distribution of the mixture is, the smaller the fractal dimension of the mixture is. This indicates that the uniformity of the pore distribution increases as the clay content increases. For mixtures with the same clay content, the fractal dimensions of M-Q mixtures were larger than those of K-Q

mixtures. The reason why the M-Q mixture had larger fractal dimensions is that the uniformity of the pore distribution was worse. However, the microscopic mechanism of the difference among fractal dimensions of mixtures with different mineral compositions was not clear. The uniformity of pore distribution was determined by the pore size. The free water distributed in large pore and bound water distributed in small pore. There was a relationship between fractal dimension and bound water or free water. So, the fractal dimensions could be used to predict T_{2c} in this study. The microscopic mechanism of the close relationship between fractal dimension and bound water was also not clear. The two microscopic mechanisms will be explored in future work.

Figure 14 shows the relationships between T_{2c} and fractal dimensions. The relationships between T_{2c} and fractal dimensions of M-Q mixtures and K-Q mixtures are different, but T_{2c} increases with an increase in the fractal dimension. The relationship between T_{2c} and fractal dimensions of M-Q mixtures and K-Q mixtures and K-Q mixtures can be expressed by Equations (25) and (26), respectively:

$$T_{2c} = 9.511D - 22.10 \tag{25}$$

$$T_{2c} = 5.089D - 6.339 \tag{26}$$



Figure 14. The relationships between T_{2c} and fractal dimensions (*D*). The lines at the top and bottom indicate the relationships between T_{2c} and *D* of kaolinite-quartz (K-Q) and montmorillonite-quartz (M-Q) mixtures, respectively. The Equations in the two boxes are the Equations of the two lines. R^2 indicates the correlation coefficient of the Equation.

The R^2 values of Equations (25) and (26) are 0.912 and 0.982, respectively. The predicted T_{2c} versus measured T_{2c} is displayed in Figure 15. The points are close to the line y = x, so the Equations (25) and (26) can be used to predict the T_{2c} of mixtures.



Figure 15. The predicted T_{2c} versus the measured T_{2c} . Red solid line indicates a slope of 1:1. The closer the black point is to the line, the smaller the difference between the predicted and measured T_{2c} is.

In order to verify the accuracy of predicting the permeability coefficient by using T_{2c} which was predicted from fractal analysis, the T_{2c} values predicted from fractal analysis were used to calculate the A_{FF} and A_{BF} in Equation (24). The predicted permeability coefficients could also be obtained from Equation (24). The predicted permeability coefficients from fractal analysis versus the measured permeability coefficients are presented in Figure 16. According to Figure 16, all the points are close to the line y = x, so the accuracy of predicting the permeability coefficient by using T_{2c} which was predicted from fractal analysis was acceptable.



Figure 16. The predicted permeability coefficients from fractal analysis versus the measured permeability coefficients. Red solid line indicates a slope of 1:1. The closer the black point is to the line, the smaller the difference between the predicted and measured permeability coefficient is.

In order to simplify the prediction process of the permeability coefficient based on NMR technology, fractal analysis was used in this study. The following steps can be followed to predict the permeability coefficients of clay-quartz mixtures: (1) After sample saturation, the NMR test can be carried out on a sample to get the T_2 spectrum; (2) the fractal dimension can be determined by fractal analysis based on Equation (10); (3) according to the $T_2(T_{2p})$ corresponding to the peak signal amplitude, the type of clay mineral can be determined. The T_{2p} values of M-Q mixtures and K-Q mixtures are around 1 and 10 ms, respectively; (4) the T_{2c} of M-Q mixtures or K-Q mixtures can be determined by Equation (25) or (26). A_{FF} and A_{BF} can be calculated based on the T_2 spectrum; (5) the permeability coefficient can be calculated by Equation (24).

5. Conclusions

This paper mainly focused on the permeability evaluation of clay-quartz mixtures based on NMR tests and fractal analysis. The main conclusions that can be drawn are as follows:

- 1. The T_2 spectra of M-Q mixtures and K-Q mixtures are quite different. The T_{2p} of M-Q mixtures and K-Q mixtures ranged from 1.20 to 2.25 ms and 7.84 to 11.89 ms, respectively. The T_{2p} can be used to determine the kind of clay mineral in the clay-quartz mixture;
- 2. During evaporation, all the T_2 spectra of clay-quartz mixtures shifted to the left. This indicated that shrinkage of the mixture volume led to a decrease of the total pore radius;
- 3. According to the decay rate of the T_2 total signal amplitude, the evaporation process can be divided into two stages: the constant rate stage and the falling rate stage. The T_2 cut-offs can be determined from the T_2 spectra of the mixtures at the initial saturated state and the beginning of the falling rate stage;
- 4. A prediction model for permeability coefficients of clay-quartz mixtures based on the T-C model was established. The relationship between T_2 cut-offs and fractal dimensions of T_2 spectra of saturated mixtures was also proposed. Based on these, a simplified method for predicting permeability coefficients of clay-quartz mixtures by using only the T_2 spectrum of saturated samples without centrifugal and evaporation tests was established. Compared with the traditional method, which is effort- and time-consuming, the new prediction method proposed in this study can determine the permeability coefficients of clay-quartz mixtures rapidly, nondestructively, and accurately.

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