

Article

Study on Water Imbibition and Wettability Characteristics of Marine Shale: A Novel Method for Macro-Scale Wettability Evaluation Based on Micro-Scale Water Distribution

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Abstract

Accurate assessment of shale wettability is crucial for optimizing fracturing design and enhancing shale gas recovery. However, conventional evaluation methods are often unreliable due to shale's complex mineral composition and heterogeneous pore structure. This study investigated marine shale from the Sichuan Basin by establishing a multi-scale research framework that integrates macro-scale spontaneous imbibition evolution, micro-scale dynamic video observation, and interfacial property characterization. Using techniques including X-ray diffraction (XRD), nuclear magnetic resonance (NMR), and deep-field microscopy, we investigated the water distribution patterns and imbibition mechanisms. The results indicate that the mixed-wettability characteristics of shale are governed by the synergistic effects of mineral composition and pore structure. Specifically, hydrophilic surfaces facilitate stable adsorbed water film formation via hydrogen bonding and van der Waals forces, whereas hydrophobic surfaces inhibit water spreading. At the macro-scale, a distinctive “water ring” was observed immediately upon immersion. This phenomenon reveals a physical correlation between the mass per unit length of the water ring and the contact angle at the gas–solid–liquid interface. Based on this correlation, an innovative standard curve method was developed to evaluate rock wettability. This method allows for the inversion of the apparent contact angle by simply measuring the mass per unit length of the water ring, thereby overcoming the limitations of traditional optical methods that are constrained by surface roughness and pore structure. Consequently, a logical chain of “wettability → occurrence characteristics → imbibition patterns” was established. This work provides new insights and theoretical support for understanding fluid dynamics and optimizing fracturing fluids in unconventional reservoirs.



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Keywords: shale; imbibition characteristics; wettability; water ring mass; standard curve

1. Introduction

Against the backdrop of ever-increasing global energy demand, shale oil and gas, as a critical component of unconventional energy resources, have made their efficient development crucial for ensuring national energy security [1]. However, the complex pore structure and multiscale transport properties of shale reservoirs pose significant challenges to their production and development [2]. Among the numerous physicochemical properties influencing shale hydrocarbon migration and recovery efficiency, wettability plays a pivotal

role, as it directly governs the distribution of fluids within nanopores and their relative permeability characteristics [3]. Yet, accurately characterizing shale wettability remains difficult due to the rock's complex mineral composition and pronounced heterogeneity. This limitation hinders the ability of current techniques to effectively guide complex fracturing operations and production enhancement evaluations [4]. Therefore, in-depth research on the wettability evolution mechanisms in shale and their impact on fluid transport is not only at the forefront of current scientific inquiry but also constitutes an urgent need for enhancing shale hydrocarbon recovery.

Shale reservoirs exhibit significant mixed-wettability characteristics due to their complex mineral composition and pore structure. This heterogeneity arises fundamentally from the contrasting inherent wettability of different components: organic matter (kerogen) is typically oil-wet, while inorganic minerals such as quartz and clay are generally water-wet [5]. Furthermore, the local wettability can be further altered by physicochemical interactions, influenced by factors like the thermal maturity of organic matter and the adsorption of crude oil components onto pore walls [6,7].

This mixed-wettability fundamentally governs fluid distribution within shale pores. At the micro-scale, the wetting-phase fluid tends to occupy smaller pores or adhere to pore walls, while the non-wetting phase predominantly resides in the centers of larger pores, creating complex fluid occupancy patterns [8]. This configuration directly governs the multiphase flow mechanism, leading to significant resistance differences during the migration of phases such as gas–water or oil–water, which causes the relative permeability curves to exhibit pronounced nonlinear characteristics and obvious hysteresis effects [9,10]. Investigating the impact of mixed-wettability on seepage laws is, therefore, of significant theoretical importance for accurately evaluating recoverable shale hydrocarbon resources and optimizing development strategies.

The wettability of shale reservoirs is co-regulated by mineral composition and organic matter characteristics. Clay minerals typically exhibit strong hydrophilicity due to their large specific surface area and complex pore structure [11]. However, significant differences exist in the fluid adsorption capacity among different types of clay minerals, and their surface charge properties can alter pore surface wettability through ion exchange processes [12]. Simultaneously, organic matter is also a key factor influencing wettability. With increasing thermal maturity, changes in the chemical composition and functional groups of organic matter often lead to a more oil-wet reservoir [13]. Furthermore, the commonly formed organic-inorganic composites between organic matter and clay minerals can further enhance the spatial heterogeneity of wettability through hydrophobic interactions and hydrogen bonding [14]. Therefore, a thorough investigation into the synergistic control mechanisms of clay minerals and organic matter on wettability is of great significance for accurately evaluating the occurrence state of shale hydrocarbons and enhancing recovery efficiency [15].

The pore structure of porous media is a fundamental factor determining its wettability and imbibition behavior. The complex morphology of pores not only alters the distribution of local contact angles but also significantly influences the capillary driving force through scale effects [16]. At the micro- to nanoscale, pore size and connectivity govern the evolution path of the imbibition front and the displacement efficiency. Studies have shown that well-connected pore networks can effectively mitigate the hindrance caused by the Jamin effect, thereby promoting coordinated fluid flow within fine pores. Furthermore, the inherent heterogeneity of the pore structure leads to distinct non-uniform characteristics during imbibition, resulting in significant anisotropy in macroscopic fluid flow [17]. By thoroughly investigating the mechanisms through which pore geometry and connectivity influence

imbibition dynamics, the transport laws of fluids within complex microscopic spaces can be described more accurately [18].

Current methods for characterizing shale wettability are mainly divided into two categories: qualitative and quantitative. The contact angle method, as the most intuitive approach, determines wettability by measuring the geometric morphology of a droplet on the rock surface [2–4,19]; however, it suffers from poor local representativeness for highly heterogeneous materials such as shale. The Amott-Harvey method and the USBM method are commonly used quantitative evaluation techniques in industry [1,20], both relying on volumetric changes during fluid displacement. Nevertheless, when dealing with ultra-low-permeability samples like shale, these methods often encounter challenges such as prolonged experimental durations and difficulties in determining fluid equilibrium. In recent years, the combined spontaneous imbibition and nuclear magnetic resonance (NMR) technique has gained prominence. This method can dynamically characterize fluid migration processes within micro- and nano-pores [21,22]. Nevertheless, its computational models often involve significant simplifications of pore geometry, which still limits evaluation accuracy. In summary, the complex pore structure and mineral composition of shale make it difficult for any single measurement technique to achieve comprehensive and accurate wettability assessment. There is a pressing need to establish a multi-scale, physics-coupled evaluation framework.

In summary, the accurate evaluation of shale wettability is essential for unraveling fluid occurrence mechanisms and optimizing fracturing design [1]. However, the strong heterogeneity and complex pore structure of shale pose significant challenges to the applicability and accuracy of conventional wettability assessment methods [2,3,19,22]. Therefore, there is an urgent need to develop novel evaluation techniques capable of characterization at the micro-scale and under in situ conditions, thereby advancing the shale reservoir characterization framework [23]. Establishing a scientific and systematic new methodology for wettability evaluation will not only provide theoretical support for research on shale hydrocarbon seepage laws but also offer crucial guidance for engineering practices aimed at enhancing recovery and formulating differentiated development strategies [24,25].

2. Materials and Methods

2.1. Sample Collection and Preparation

The Sichuan Basin represents the region with the most promising shale gas exploration potential in China. It is a typical intracratonic basin, situated within a complex tectonic transition zone between the Paleo-Pacific and Tethys-Himalayan tectonic domains [26–28]. The Longmaxi Shale was deposited in a deep-water shelf environment in the southern part of the Sichuan Basin. The core samples used in the experiment were collected from outcrops of the marine Longmaxi Formation black shale in South China, exhibiting extremely low permeability with an average value of 0.007 mD. This interval exhibits typical black shale characteristics, including well-developed laminations and enrichment of organic matter, indicating excellent regional geological representativeness. The total organic carbon (TOC) content of the samples was determined by Rock-Eval pyrolysis, yielding values ranging from 2.5% to 4.5%, which corresponds to moderate organic matter richness. The presence of organic matter provides an oleophilic component to the shale, serving as one of the key factors contributing to the formation of mixed wettability. Following collection, the samples were cut and mechanically ground according to experimental requirements. They were processed into standard cores with a diameter of 25 mm, and several thin sections with a thickness of 1.5 mm were prepared. To mitigate the influence of residual moisture and impurities on pore structure characterization and mechanical testing, the samples were cleaned with a 3% sodium chloride solution and subsequently dried in a constant-

temperature oven at 105 °C until a constant weight was achieved, as illustrated in Figure 1. Using a 3% NaCl solution for cleaning may slightly alter the chemical properties of clay mineral surfaces through cation exchange, thereby introducing some bias into wettability measurements. To mitigate this effect, a unified cleaning and drying procedure was applied to all samples in this study to ensure consistent experimental conditions.



Figure 1. Sampling and Preparation of Rock Samples.

2.2. Methods

2.2.1. Mineralogical Composition Analysis

The mineralogical composition was quantitatively analyzed using X-ray diffraction (XRD) (Shanghai Erdi Instrument Technology Co., Ltd., Shanghai, China). Powder samples with a particle size of less than 200 mesh were analyzed using a Bruker X-ray diffractometer (Shanghai Erdi Instrument Technology Co., Ltd., Shanghai, China). The weight percentage of each mineral phase present was quantified based on the semi-quantitative area of its primary diffraction peak following Lorentz-polarization correction [29].

2.2.2. Porosity Analysis

Porosity is a critical parameter for evaluating the physical properties of shale reservoirs, shale gas accumulation, and reserve estimation. In this study, porosity was primarily measured using the pressure-saturation method with three distinct fluids: deionized water, formation water (3% KCl solution), and 0.05% slickwater. Porosity measurement was performed using a BH-3 core vacuum-pressurization saturation apparatus (Hai'an Core Petroleum Instrument Co., Ltd., Hai'an, Jiangsu, China). First, the core sample was placed in the saturation chamber and evacuated to 0.095 MPa for 4 h. Then, the saturating fluid was injected, and the pressure was increased to 30 MPa and maintained for 48 h to achieve forced saturation. After saturation, the core was removed, and excess liquid on its surface was wiped off with a moist filter paper. The sample was weighed every 30 min until the difference between two consecutive weighings did not exceed 0.01 g, which was considered constant weight. The average core porosity of the shale was then calculated based on the mass difference of the cores before and after saturation with each fluid, according to Equation (1).

$$\phi = \frac{4 \times (M_2 - M_1)}{\rho \pi h_0 D_0^2} \times 100\% \quad (1)$$

where ϕ [%] is shale porosity measured by the saturation method, dimensionless, M_2 [g] is mass of the shale sample after saturation, M_1 [g] is mass of the shale sample before saturation, h_0 [mm] is height of the core sample, D_0 [mm] is diameter of the core sample, ρ is density of the saturation fluid. The density of deionized water is taken as $1.0 \times 10^3 \text{ kg/m}^3$, the density of the 3% KCl solution (formation water) is $1.02 \times 10^3 \text{ kg/m}^3$, and the density of the 0.05% slickwater solution is $1.0 \times 10^3 \text{ kg/m}^3$.

2.2.3. Pore Size Distribution

The pore size distribution of the shale was measured using a MicroMR12-025V bench-top nuclear magnetic resonance (NMR) analyzer (Suzhou Niumag Analytical Instrument Co., Ltd., Suzhou, Jiangsu, China). The NMR T_2 relaxation time reflects the chemical

environment of hydrogen protons within the sample, which is related to the constraining forces on the protons and their degree of freedom. The degree of proton constraint, in turn, is intrinsically linked to the internal structure of the sample. For fluids in pores, three distinct relaxation mechanisms contribute to the T_2 spectrum: free relaxation, surface relaxation, and diffusion relaxation. Excluding the effects of free and diffusion relaxation, the T_2 distribution correlates with pore size. The pore size was calculated by combining the water relaxation time in the porous medium with Equation (2).

$$1/T_2 = 1/T_{2free} + 1/T_{2surface} + 1/T_{2diffusion} \quad (2)$$

where T_2 is the transverse relaxation time of the pore fluid, acquired using the CPMG pulse sequence, T_{2free} is the transverse relaxation time of the pore fluid in a sufficiently large container (where boundary effects are negligible), $T_{2surface}$ is the transverse relaxation time contributed by surface relaxation, $T_{2diffusion}$ is the transverse relaxation time of the pore fluid caused by diffusion under a magnetic field gradient. The conversion of T_2 relaxation time to pore size was performed using a surface relaxivity coefficient of $\rho_2 = 0.01 \mu\text{m/ms}$, which was derived from a combined NMR and MICP calibration study on Longmaxi Formation shale [30,31]. Although this parameter affects the absolute calibration of pore size values, this study primarily focuses on the relative characteristics and qualitative trends of the pore size distribution; therefore, this choice does not affect the core conclusions.

2.2.4. Microscopic Dynamic Observation of Water

The distribution and imbibition characteristics of water on shale surfaces were dynamically observed using a Keyence VHX-5000 deep-field microscope (KEYENCE (China) Co., Ltd., Guangzhou, China). First, the surface morphology of the shale was examined under the high-resolution deep-field microscope. Formation water was then dropped onto the surface. After allowing sufficient time for adsorption, the distribution pattern of the water on the shale surface was observed again. Subsequently, a new core thin section was used. A droplet of red ink (used to enhance visual contrast) was placed on its surface. The microscopic process of water flow on the shale thin section was then recorded in video format using a $900\times$ objective lens. Observations were conducted on two types of thin sections with distinct pore structures: one without apparent fractures and one containing visible fractures. Based on these observations, the dynamic imbibition behavior of water on shale surfaces was summarized. The experimental procedure is illustrated in Figure 2. Red ink may contain trace amounts of surfactants, which could potentially affect fluid wettability. However, dye tracing is a common experimental technique for visualizing flow fronts in porous media and fractures [32]. In this study, the red ink was diluted to approximately 1:100 and used solely for qualitatively tracing preferential flow paths; it was not involved in any quantitative wettability calculations.

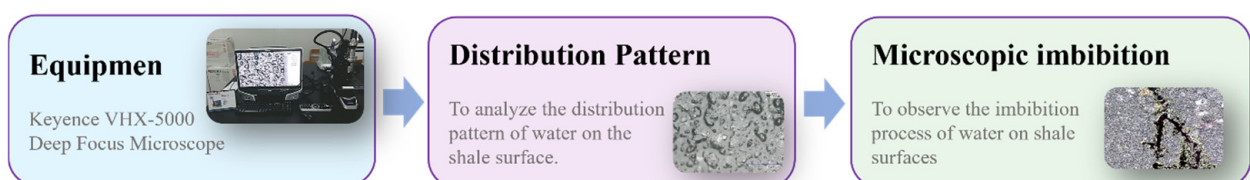


Figure 2. Microscopic dynamic observation of water imbibition in shale.

2.2.5. Spontaneous Water Imbibition Experiment

To further investigate the water imbibition behavior in shale, a macro-scale water uptake experiment was designed. Twelve core thin sections without apparent fractures were selected, and their dimensions were measured using a vernier caliper. Each shale thin

section was then suspended from the bottom of an electronic balance. After the reading stabilized, the balance was tared. Subsequently, the thin section was immersed 3 mm into water without applying any external pressure, and the change in mass recorded by the balance was monitored. The experimental setup is shown in Figure 3. After immersion, the net effect of gravity and buoyancy influences the mass change recorded by the balance, as described by Equation (3).

$$\Delta F = \Delta G - F_f \quad (3)$$

where ΔF [N] is change in the force measured by the balance, ΔG [N] is change in the gravitational force due to water uptake by the shale, F_f [N] is buoyant force.

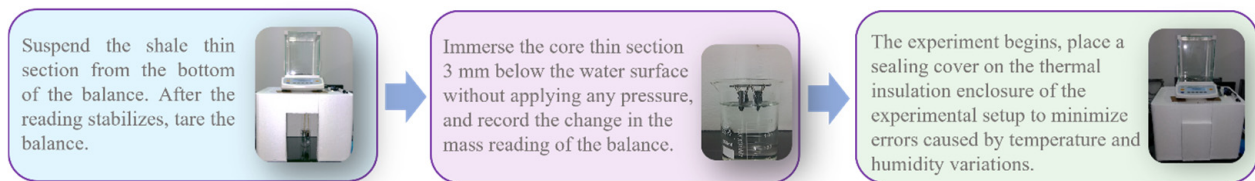


Figure 3. Macroscopic imbibition experiment.

Three sets of parallel tests were conducted, each containing four shale core thin sections with comparable thickness. The detailed parameters of the thin sections are listed in Table 1. The data recording interval (in minutes) was determined based on the experimental progress. Specifically, the interval was kept shorter at the initial stage of imbibition and was progressively lengthened at later stages.

Table 1. Parameters of the core thin sections.

No.	1	2	3	4	5	6	7	8	9	10	11	12	Average
Thickness/mm	1.42	1.44	1.45	1.47	1.52	1.52	1.53	1.53	1.54	1.54	1.56	1.57	1.515
Diameter/mm	25.22	25.44	25.22	25.08	25.27	25.32	25.17	25.10	24.97	25.17	25.20	25.12	25.19
Mass/g	1.72	1.822	1.79	1.807	1.81	1.91	1.91	1.91	1.74	1.94	1.89	1.84	1.84
Volume/mm ³	709.00	731.59	723.98	725.84	761.95	764.96	755.93	756.67	753.75	765.87	777.67	777.70	753.80

2.2.6. Wettability Measurement

The complex pore structure of shale surfaces renders traditional wettability evaluation methods, such as optical contact angle goniometry, inadequate for accurately assessing shale wettability. A new measurement method was therefore designed based on the principle that a liquid annulus forms at the solid surface due to wettability when gas, liquid, and solid phases come into contact. By measuring the apparent mass increment and subtracting the buoyancy contribution, a quantitative relationship was established between the “water ring mass” and the material’s contact angle.

First, the contact angles of non-porous, smooth materials (Glass Slide 1, Glass Slide 2, an iron sheet, and a copper sheet; detailed parameters are listed in Table 2) were measured using an optical contact angle goniometer. Subsequently, the water uptake mass for these materials was determined using the experimental setup described in Section 2.2.5. A standard curve correlating the “mass per unit length of the water ring” to the contact angle was established. This calibration allows for the inversion of the macroscopic contact angle from measurements of the mass per unit length of the water ring.

Table 2. Parameters of materials for contact angle experiments.

Experimental Materials	Length/mm	Width/mm	Thickness/mm	Volume/mm ³	Mass/g	Contact Angle/°
Iron	37.08	25.1	1.09	1014.472	1.0536	82.83
Copper	35.43	25.3	1.05	941.198	0.9412	109.42

Table 2. Cont.

Experimental Materials	Length/mm	Width/mm	Thickness/mm	Volume/mm ³	Mass/g	Contact Angle/°
Glass Slide 1	50.69	25.29	1.08	1384.506	1.3845	26.48
Glass Slide 2	48.15	25.13	1.14	1379.411	1.3794	58.71

3. Results and Discussion

3.1. Influence of Petrophysical Properties on Wettability

The mineralogical composition of the shale was analyzed using X-ray diffraction (XRD), as shown in Figure 4a. The composition is consistent with the characteristics of typical Longmaxi Formation shale in the Sichuan Basin, where quartz and clay minerals are dominant [33–35]. Quartz (siliceous minerals) exhibits strong hydrophilicity (contact angle $\theta < 90^\circ$), promoting water-wet imbibition. In contrast, clay and carbonate minerals, due to their relatively weaker hydrophilicity and higher affinity for hydrocarbons (following the trend: ferruginous minerals > carbonate > clay > siliceous minerals [2]), contribute to mixed-wettability. Compared to silica-rich shale, the relatively high content of clay (37%) and carbonate (27.3%) in the samples likely reduces the overall hydrophilicity, which aligns with the negative correlation observed in contact angle studies [2,36]. The high content of brittle minerals (63%) enhances fracture propagation capability, which is beneficial for subsequent reservoir stimulation and hydraulic fracturing operations. This mineral assemblage underscores the wettability heterogeneity—from the microscale water distribution within clay interlayer pores to the macroscale imbibition process [2,37].

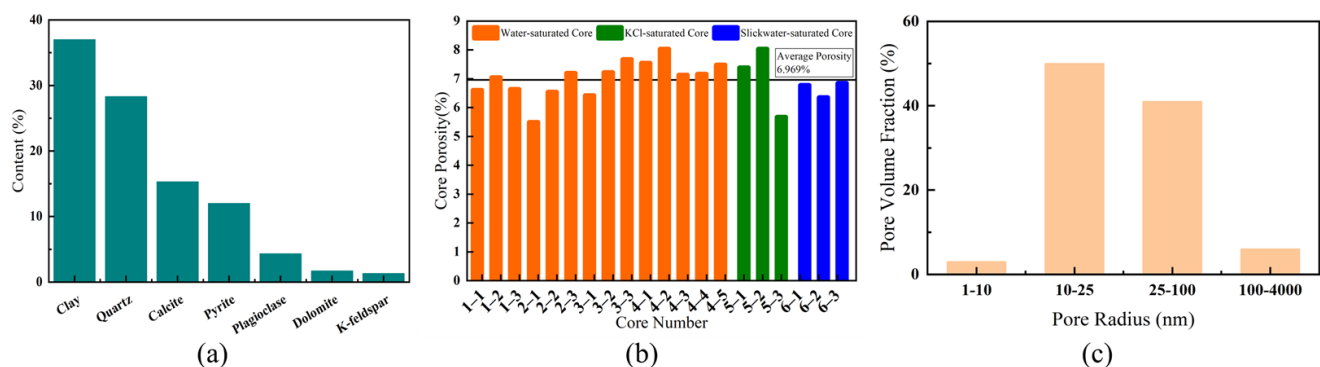


Figure 4. Physical properties of shale. (a) Composition, (b) Porosity, (c) Pore size distribution.

The average porosity of the core samples measured by the water saturation method is 6.97%, as shown in Figure 4b. The porosity differences among different saturating media (deionized water, formation water, and slickwater) are small ($<0.5\%$), indicating limited clay hydration swelling and good connectivity of inorganic pores. It should be noted that porosity itself does not directly characterize wettability; the latter depends on interfacial interactions between mineral surfaces and fluids [38,39]. Under conditions of low porosity ($\sim 7\%$), the small difference observed between saturation media implies limited hydration expansion of clay minerals, with the hydrophilic nature of inorganic pores being dominant. This mechanism helps avoid significant pore compression [2,40].

Based on nuclear magnetic resonance (NMR) analysis, as shown in Figure 4c, pores with a radius within 100 nm account for 95% of the total pore volume, while pores around 1 μm contribute minimally. Notably, the primary peak lies within the 10–25 nm range, representing 53–61% of the volume fraction. Surface tension effects are significant in these nano-scale pores. The pores within this dominant peak range are primarily organic matter-hosted, exhibiting oil-wet or strongly oil-wet characteristics, which facilitates hydro-

carbon adsorption but inhibits water-phase imbibition. In contrast, inorganic intergranular pores are hydrophilic, where water films readily form, thereby reducing the effective flow radius [2,36,41]. Porosity and pore size synergistically regulate wettability. The low porosity reinforces the dominance of small pores, reflecting an overall water-wet tendency. However, the substantial proportion of oil-wet pores in the primary peak region leads to mixed-wettability (oil-wet in small pores, water-wet in large pores), which is favorable for shale hydrocarbon desorption [40,42].

3.2. Microscopic Occurrence and Dynamic Imbibition Characteristics of Water

The distribution characteristics of water on the shale surface before and after water uptake were observed under a deep-field microscope, as shown in Figure 5. The observations indicate that the static adsorbed water primarily exists in the forms of continuous water films and adsorbed water films. The continuous water films display various morphologies, including mountain-ridge-valley, spread-sheet, and isolated-island patterns. Wettability governs both the spreading capability and adsorption strength of water on mineral surfaces. Hydrophilic surfaces (e.g., inorganic intergranular pores and micro-fractures) readily form continuous water films, facilitating film extension along the surface. In contrast, hydrophobic surfaces (e.g., organic matter pores) result in water distribution as isolated islands or droplets, thereby limiting connectivity [43–45]. Wettability is therefore not only the intrinsic controlling factor for water occurrence morphology but also a key bridge linking microscopic distribution (e.g., water film morphology) to macroscopic imbibition behavior (e.g., spontaneous imbibition rate and permeability variation) [44].

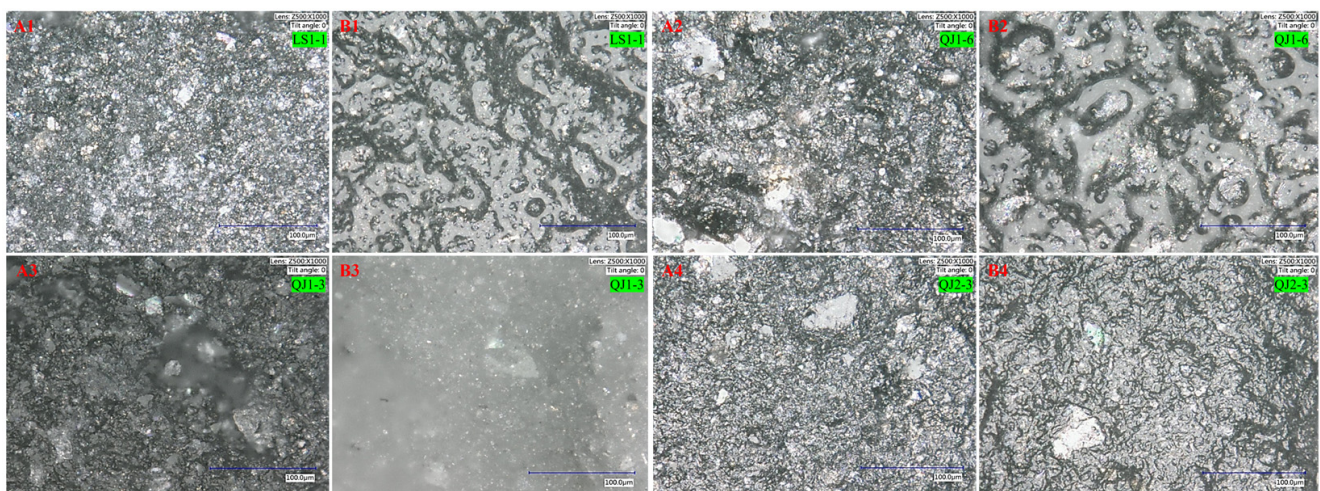


Figure 5. Shale microphotograph of before and after the flooding: (A1–A4): Before the flooding, (B1–B4): After the flooding. (LS1-1) Form continuous water film, mountain ravine appearance, (QJ1-6) Form continuous water film, the island features, (QJ1-3) Form continuous water film, tile, (QJ2-3) Forming a adsorption water film.

Figure 6 shows video snapshots of water imbibition on a shale surface without apparent fractures. It can be observed that on such a shale thin section, the ink preferentially diffuses into larger pores first, and then gradually imbibes into smaller pores. This sequence reflects the controlling effect of pore scale on fluid distribution under mixed-wettability conditions [46,47]. Based on pore size and mineral composition analyses, the shale sample exhibits mixed-wettability characteristics, where inorganic mineral pores (e.g., quartz, calcite) are hydrophilic, while organic pores are oil-wet [48]. Consequently, this microscopic wettability heterogeneity leads to variations in the preferential flow paths of water through different pores.

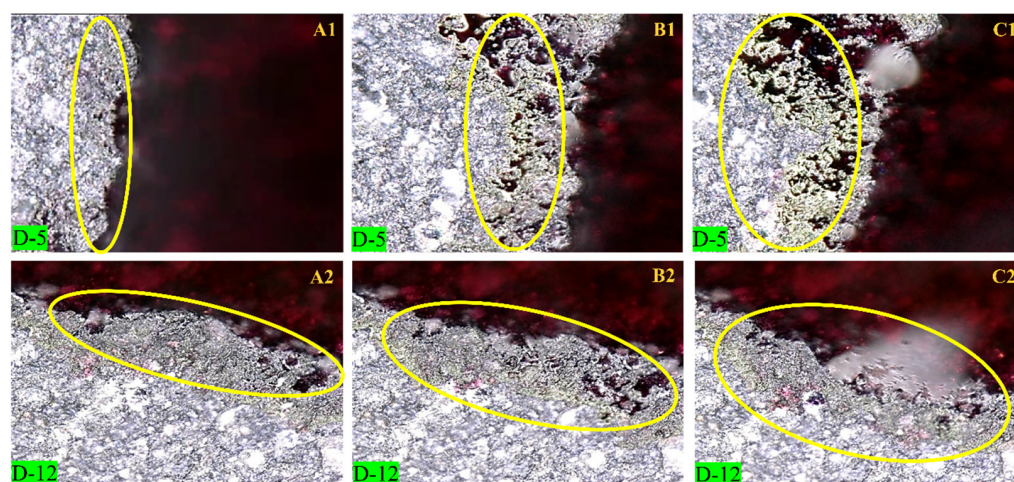


Figure 6. Screenshots from the imbibition video for an unfractured shale thin section at different stages: (A1,A2) initial stage, (B1,B2) intermediate stage, (C1,C2) late stage. The yellow circle indicates the edge of water flow on the shale surface at different times.

Figure 7 presents video snapshots of water imbibition on a shale surface containing visible fractures. It can be seen that in the fractured shale sample, the ink rapidly propagates along the major fractures, indicating the dominant role of fractures as preferential flow pathways in controlling fluid movement [49,50]. The persistent swirling motion observed at the edges of the ink suggests that the fluid maintains a dynamic flow state within the fractures, which is closely associated with capillary pressure gradients at pore throats. Research indicates that under mixed-wettability conditions, hydrophilic pore throats promote cooperative pore filling, whereas hydrophobic pore throats lead to burst-type pore filling. The coexistence of these two mechanisms results in complex spatiotemporal distribution characteristics of fluid movement [48].

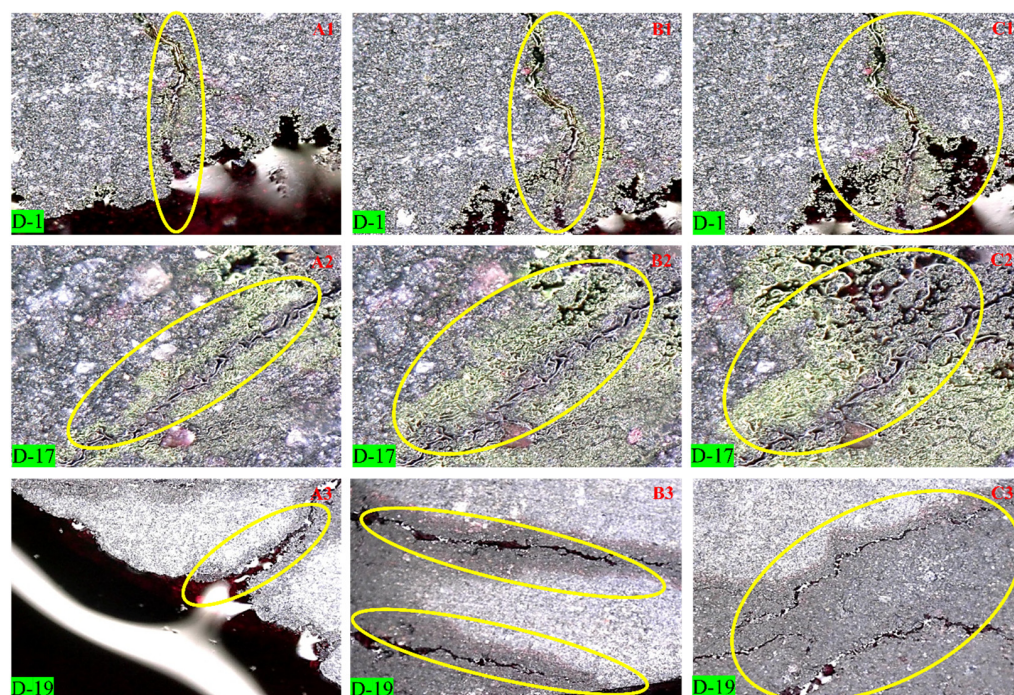


Figure 7. Screenshots from the imbibition video for a fractured shale thin section at different stages: (A1–A3) initial stage, (B1–B3) intermediate stage, (C1–C3) late stage. The yellow circle indicates the advancing edge of water flow within shale fractures at different times.

3.3. Macroscopic Imbibition Dynamics

The macroscopic water imbibition experiments in shale were conducted over approximately 15 days. The cumulative mass changes for the first, second, and third sets (lasting 16, 14, and 15 days, respectively) were 1.184 g, 1.277 g, and 1.489 g. The average water uptake mass change per shale thin section, after buoyancy correction, was calculated to be 0.33 g.

Based on the temporal evolution curve of mass change shown in Figure 8a, the shale imbibition process can be divided into three characteristic stages, each significantly influenced by wettability. (1) Burst-like imbibition stage: The instant the shale thin section contacts the liquid, water rapidly fills surface-exposed micro-fractures and large pores driven by both gravitational and physicochemical forces. In this stage, wettability governs the spreading velocity of water on fracture surfaces and the initial mass of the water ring. Stronger hydrophilicity leads to faster water ring formation and a higher initial water uptake rate. (2) Decelerating imbibition stage: After approximately 1 min, as the larger channels become saturated, the liquid phase begins to migrate into the nano-scale pores deeper within the matrix. Wettability affects the subsequent water penetration rate by regulating the adsorption capacity and flow resistance at the pore walls. (3) Quasi-equilibrium stage: After about 5 days, the imbibition process nears its end, with the driving force for water uptake and the internal pressure tending towards equilibrium. In this stage, wettability determines the final water saturation and the form of water occurrence—water exists stably as bound water films in hydrophilic pores, whereas isolated water droplets or gas channels may remain in hydrophobic pores.

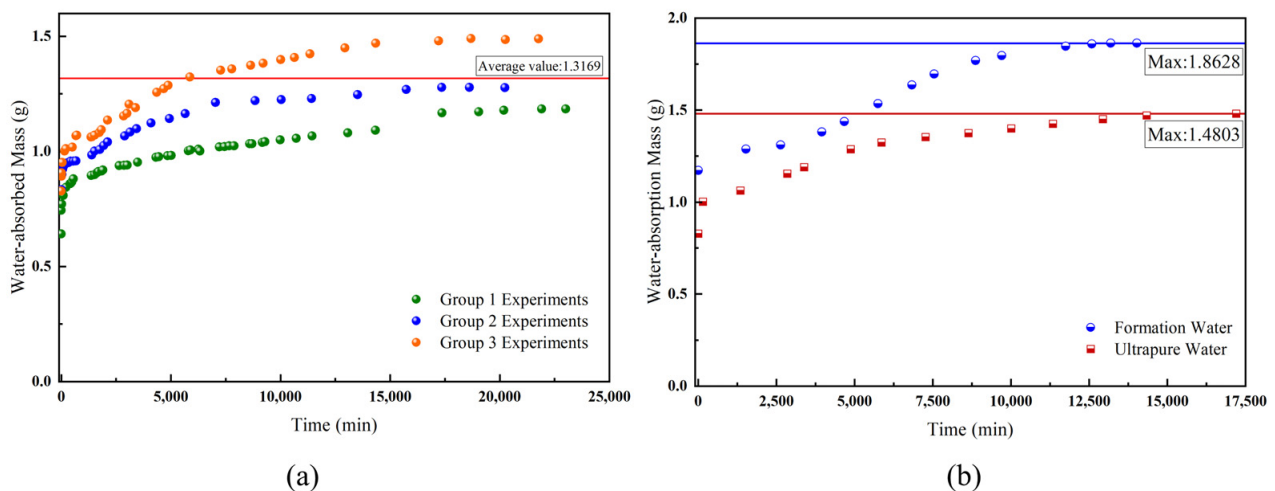


Figure 8. Water uptake versus time for shale thin sections: (a) for three different sets of samples, (b) in different imbibition fluids.

Since the formation water (3% KCl solution, density 1.02 g/cm^3) and ultra-pure water (density 1.00 g/cm^3) contain different minerals, a comparative experiment was designed to further investigate whether the formation water exhibits similar imbibition behavior in shale. The results show that the water uptake mass of formation water and ultra-pure water follows a highly consistent trend over time, as illustrated in Figure 8b. However, under identical experimental conditions, K^+ ions enter the interlayer spaces of clay minerals, generating osmotic water uptake that draws more water into the interlayer structure, whereas ultra-pure water lacks such ion-driven mechanisms. Furthermore, K^+ exhibits strong intercalation ability into illite/montmorillonite-type clays, further enhancing the water uptake capacity. The superposition of these two effects results in a higher long-term cumulative water uptake for formation water compared to ultra-pure water. Electrical

double layer compression plays a secondary role in this system, and its effect of reducing water film thickness opposes the osmotic pressure effect, with the net outcome being dominated by osmotic pressure. Consequently, a higher cumulative water uptake is achieved during the long-term imbibition process [51], and the imbibition mass of formation water is significantly greater than that of ultra-pure water.

Based on the results of macroscopic imbibition experiments, the balance recorded an average imbibition mass of (in grams) for the shale wafer. To accurately interpret the physical origin of this mass variation, a complete force model incorporating pore water uptake, water-ring formation, and buoyancy effects must be established.

When a shale wafer is partially submerged in water, the following forces act upon it: the gravitational increment due to pore water absorption and water-ring formation, $(m_{\text{pore}} + m_{\text{ring}})g$ (directed downward), and the buoyant force caused by the displacement of water by the submerged portion, $\rho V_{\text{imm}}g$ (directed upward). The net force change sensed by the balance is the difference between the gravitational increment and the buoyant force:

$$\Delta F = (m_{\text{pore}} + m_{\text{ring}})g - \rho V_{\text{imm}}g \quad (4)$$

The mass change M displayed by the balance satisfies $\Delta F = Mg$; therefore:

$$M = m_{\text{pore}} + m_{\text{ring}} - \rho V_{\text{imm}} \quad (5)$$

where M is the real-time mass change displayed by the balance (g), m_{pore} is the mass of water absorbed into the pores of the shale (g), m_{ring} is the mass of the water ring adhering to the periphery of the wafer (g), V_{imm} is the volume of the shale wafer immersed in water (cm^3), and ρ is the density of water (taken as 1.0 g/cm^3).

The immersed volume of the shale wafer is V_{imm} , within which the pore volume is ϕV_{imm} (where ϕ is the porosity, taken as 7%). Assuming that the pores in the immersed portion are fully saturated with water, the mass of water absorbed into the pores is:

$$m_{\text{pore}} = \rho \phi V_{\text{imm}} \quad (6)$$

Thus, the calculation formula for the water-ring mass is obtained as follows:

$$m_{\text{ring}} = M + \rho V_{\text{imm}}(1 - \phi) \quad (7)$$

The experimentally measured apparent water uptake mass (0.33 g) is significantly higher than the theoretical pore water absorption mass (0.0633 g), with the excess amount corresponding to the water-ring mass (0.3147 g). This result confirms that, during the early stage of partial immersion imbibition, the formation of a water ring is the key factor responsible for the overestimation of the apparent water uptake.

To verify the validity of this hypothesis, the following two different experiments were designed: (1) comparing the water uptake mass of shale thin sections at different immersion depths; and (2) measuring the water uptake mass using non-porous materials to observe if any water uptake still occurs.

The comparative experimental results indicate that under identical experimental conditions, the water uptake mass of a fully immersed shale thin section is significantly lower than that of a partially immersed one. In the partial immersion scenario, water not only enters the internal pores of the rock but also forms a significant liquid annulus (water ring) at the gas–liquid–solid three-phase contact line on the non-immersed surface. This leads to a total mass gain exceeding that attributable solely to pore-filling imbibition, as shown in Figure 9a. Furthermore, as seen in Figure 9b, the curve fitted for the buoyancy-induced mass change and the mass displayed by the balance are nearly parallel. This indicates that as immersion depth increases, a mass increment attributable to wettability—specifically,

the water ring mass—still occurs on the material surface, and its magnitude remains constant. These two sets of comparative experiments rigorously validate the primary hypothesis from both positive and negative perspectives: during the initial stage of partial immersion imbibition, the formation of the water ring is the core factor leading to the overestimation of apparent water uptake. This finding provides a critical basis for the accurate characterization of shale imbibition behavior.

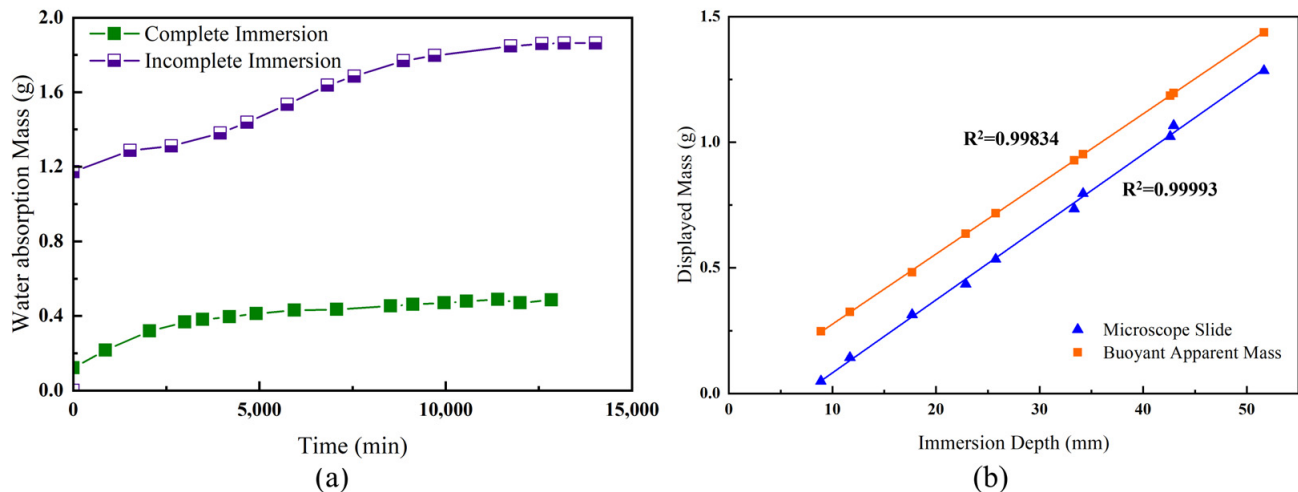


Figure 9. Validation of water-ring measurements: (a) water uptake of shale at different immersion depths; (b) water uptake of a non-porous material.

To quantitatively describe the kinetic behavior of shale imbibition, a power-law model and an exponential decay model were employed for piecewise fitting of the experimental curves. The power-law model fitting results show that the mean initial imbibition exponent of the three experimental samples is 0.7675, which is higher than the value of 0.5 predicted by ideal capillary imbibition, reflecting additional contributions from surface adsorption and clay swelling in shale. The exponential decay model fitting results indicate that the mean equilibrium water uptake mass of the three parallel experiments is 0.3297 g, with a deviation from the theoretically calculated value falling within a reasonable range. The dispersion of parameters among different samples originates from the inherent heterogeneity of shale; nevertheless, the three-stage imbibition behavior exhibits consistent characteristics across all samples.

3.4. A Novel Wettability Evaluation Model

When a wafer is partially immersed in a liquid, the liquid surface tension σ acts on the solid surface along the tangent direction of the liquid surface at the three-phase contact line (gas–liquid–solid). According to Young’s equation, the contact angle θ is determined by the interfacial tensions of the solid–gas, solid–liquid, and liquid–gas interfaces. In the vertical direction, the vertical component of surface tension per unit length of the contact line is $\sigma \cos\theta$. For a wafer with perimeter L , the total vertical force generated by surface tension is:

$$F_{\text{cap}} = \sigma L \cos\theta \quad (8)$$

This force is transmitted to the solid via the meniscus, appearing as an extra apparent mass (the water-ring mass) on the balance. With gravitational acceleration g , the water-ring mass m_{ring} is related to the capillary force by:

$$m_{\text{ring}} = F_{\text{cap}} / g = \sigma L \cos\theta / g \quad (9)$$

Therefore, the water-ring mass per unit length $\omega = m_{\text{ring}} / L$ satisfies:

$$\omega = m_{\text{ring}}/L = \sigma \cos\theta / g \quad (10)$$

This equation indicates that the water-ring mass per unit length, ω , is proportional to the cosine of the contact angle θ . Since $\cos\theta$ decreases monotonically with increasing θ over the range $0^\circ \leq \theta \leq 180^\circ$, ω exhibits a monotonic negative correlation with θ —the smaller the contact angle (i.e., the more hydrophilic the surface), the larger the water-ring mass; conversely, the larger the contact angle (i.e., the more hydrophobic the surface), the smaller the water-ring mass. This derivation is based on the classical Wilhelmy plate principle and is independent of specific materials or pore structures, thus possessing general physical applicability.

In shale imbibition tests, a subtle but physically significant “water ring” was observed to form rapidly at the liquid–rock contact upon specimen immersion. To determine whether a well-defined functional relationship exists between water-ring mass and intrinsic wettability, four non-porous reference materials with representative contact angles—two glass slides, an iron sheet, and a copper sheet—were tested comparatively (Figure 10a). The results show a strong negative correlation: water-ring mass increases linearly with decreasing contact angle. Notably, the copper sheet, being strongly oleophilic, exhibited poor water spreading and yielded the smallest water-ring mass.

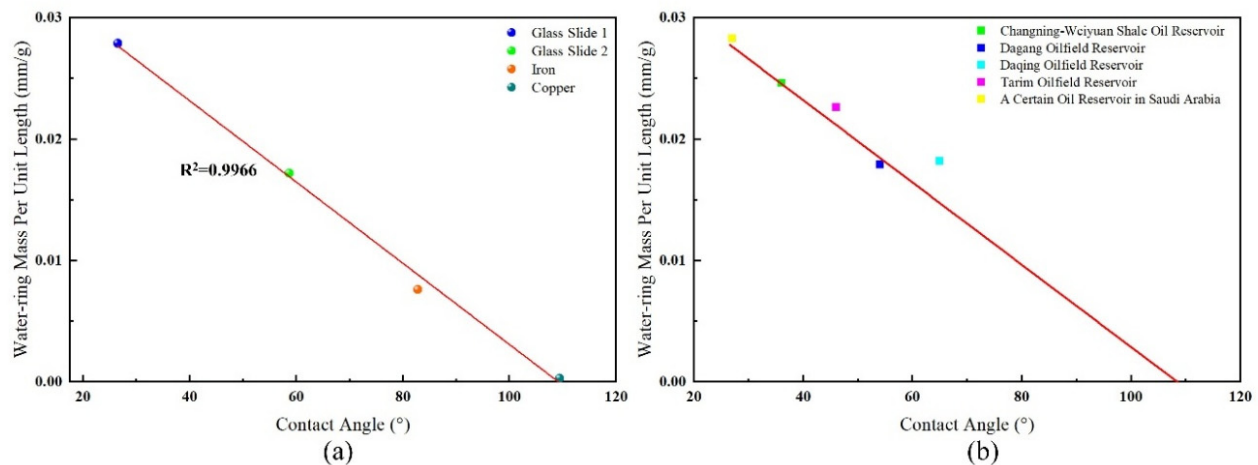


Figure 10. The mass of different contact angle material unit water-ring: (a) Non-porous material; (b) Different reservoir rocks.

From the perspective of statistical rigor, the limited sample size ($N = 4$) currently used to establish the preliminary calibration curve may lead to an overestimated coefficient of determination (R^2) for the linear fit. Although the current standard curve is based on only four non-porous materials, we further conducted a statistical evaluation. By calculating the 95% prediction interval of the linear regression, we found that even under the most unfavorable conditions (when the contact angle approaches extreme values), the error in the contact angle inverted from the water-ring mass per unit length remains within $\pm 5^\circ$. A leave-one-out cross-validation was also performed: each data point was sequentially removed, and the remaining three points were used for fitting to predict the contact angle of the omitted point. The results show that the maximum prediction deviation is only 3.2° , indicating good interpolation stability of this linear relationship within the current data range. We fully acknowledge that, due to the small sample size, the reliability of this prediction interval when extrapolated to a broader range of contact angles still requires verification. Therefore, the current fitting results should be regarded as a preliminary trend validation. The robustness of the quantitative assessment model linking water-ring

mass and wettability needs to be further refined and supported by introducing more gradient-varying sample data in subsequent studies.

To further validate the universality and accuracy of the proposed method, rock samples from different oil reservoirs were selected, and their wettability was evaluated using both the conventional optical contact angle measurement method and the water-ring mass method proposed in this study. The comparison results show that the contact angle values obtained by the two methods are highly consistent, with a relative error within $\pm 2\%$ (Figure 10b). The contact angles of all rock samples were independently determined by the conventional optical contact angle measurement method. For each sample, no fewer than three measurement points were selected on the polished cross-section, and the average value was taken as the apparent contact angle. These results confirm the reliability of the water-ring mass method for characterizing the wettability of complex porous media and provide direct experimental evidence for its potential to replace the traditional optical method. By measuring the water-ring mass per unit length of an unknown rock under specific conditions, its apparent contact angle can be retrieved using this calibration curve. This method overcomes the limitations of conventional optical contact angle measurements imposed by surface roughness and mineral heterogeneity, thereby laying an experimental and theoretical foundation for rapid and accurate characterization of shale reservoir wettability.

4. Conclusions

This study, by establishing a tripartite research framework integrating “macro-scale spontaneous imbibition evolution, micro-scale dynamic video observation, and interfacial property characterization,” has achieved significant breakthroughs in understanding the water-phase imbibition mechanisms and quantitative wettability evaluation of shale. The main conclusions are as follows:

(1) The influence of fundamental rock properties on surface wettability is elucidated. The shale’s wettability is co-governed by its mineral composition, porosity, and pore size distribution. Clay and carbonate minerals contribute to mixed-wettability due to their relatively weaker hydrophilicity and higher affinity for hydrocarbons (following the trend: ferruginous minerals > carbonate > clay > siliceous minerals). The low porosity reinforces the dominance of small pores, reflecting an overall water-wet tendency. However, the substantial proportion of oil-wet pores with diameters less than 100 nm results in overall mixed-wettability characteristics for the rock (oil-wet in small pores, water-wet in large pores).

(2) The interrelationship between wettability and imbibition is clarified. Wettability governs both the spreading capability and adsorption strength of water on mineral surfaces. Hydrophilic surfaces readily form continuous water films, whereas hydrophobic surfaces result in water distribution as isolated islands or droplets. Under mixed-wettability conditions, the controlling effect of pore scale on fluid distribution leads to a distinct hierarchical characteristic in the water imbibition process within shale. Fracturing fluid fully saturates hydrophilic pores and, under the coupled action of interfacial tension and wettability, becomes adsorbed within the pores, making it difficult to displace.

(3) A novel method for rock wettability evaluation based on water ring mass is established. Experiments revealed a significant negative correlation between the contact angles of different materials and their corresponding water ring mass. By developing a quantitative mathematical model relating the change in water ring mass under immersion conditions to wettability, a new standard curve method for rock wettability evaluation was established. This method enables the rapid assessment of wettability by inversely estimating the contact angle from the measured water ring mass, providing a new tool for the quick and accurate characterization of wettability in shale reservoirs.

Although this study has achieved significant progress in understanding the water imbibition mechanism of shale and quantitative wettability evaluation, the following two limitations remain to be addressed in future work:

(1) The samples used in this study are black shale outcrops from the Longmaxi Formation in the Sichuan Basin. Outcrop samples may have undergone late-stage diagenetic alteration, oxidation of organic matter, and partial hydrocarbon loss, leading to certain differences in mineral composition, pore structure, and wettability compared to subsurface in situ shale. In future work, downhole core samples will be employed for comparative validation with the proposed method to evaluate the degree of difference between outcrop and in situ samples.

(2) Due to the complexity of the reservoir environment, it is necessary to simulate the in situ pressure and temperature fields of deep shale reservoirs to systematically investigate the flow behavior of formation water/fracturing fluid under supercritical or high-temperature conditions. Furthermore, multiphase flow experiments should be conducted to explore the regulatory mechanism of wettability on gas–water displacement efficiency. For a more comprehensive and systematic improvement of rock wettability measurement methods, the sample database should be further expanded. Wettability evaluation under different temperature and pressure conditions should be refined under high-temperature and high-pressure conditions to eliminate the influence of sample heterogeneity on measurement results, ultimately establishing a rapid wettability measurement and standardized evaluation system applicable to engineering field operations.

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