

Review

Key Points and Current Studies on Seepage Theories of Marine Natural Gas Hydrate-Bearing Sediments: A Narrative Review

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Abstract: The internal fluid flow capacity of hydrate-bearing sediment (HBS) is one of the important factors affecting the efficiency of natural gas exploitation. This paper focuses on seepage studies on gas hydrates with the following contents: scope of theories' application, normalized permeability (K_t) models, extension combined with new technology, and development. No review has elucidated the prediction of original permeability (K_0) of sediments without hydrates. Moreover, there are few studies on seepage theories with new technologies, such as Computed Tomography (CT), Nuclear Magnetic Resonance (NMR), Magnetic Resonance Imaging (MRI), and resistivity. However, this review summarizes the prospects, evolution, and application of HBS seepage theories from the perspectives of experiments, numerical simulation, and microscopic visualization. Finally, we discuss the current limitations and directions of the seepage theories of HBS.

Keywords: natural gas hydrate; permeability; pore characteristics; porous media; multiphase flow; challenges and prospects



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1. Introduction

Natural gas hydrates (NGHs), which are widely found in oceanic sediments and permafrost regions, are ice-like non-stoichiometric crystalline compounds [1,2] composed of gas (methane, ethane, carbon dioxide) and water molecules, in low-temperature and high-pressure environments [3,4]. NGHs are generally viewed as a new energy source due to their abundance and zero environmental implications after combustion [5–10]. Therefore, the efficient exploitation of NGHs is of great importance to ensure energy security and social stability. Many countries, such as China, Japan, the United States, India, and South Korea, have carried out hydrate exploration and trial exploitation [11–14]. In 2017, China completed its first trial production in the Shenhu area of the South China Sea and set a record of 60 consecutive days with a cumulative methane output of more than $3 \times 10^5 \text{ m}^3$ [15]. Based on the first trial production, the second trial production was carried out in 2020, using the horizontal well-depressurization production technology. An average daily output of $2.87 \times 10^4 \text{ m}^3$ was achieved within 30 days, which was 5.57-times higher than the first trial production [16].

Since NGHs were discovered in the last century [17,18], several basic production methods have been gradually proposed, such as thermal stimulation, depressurization, inhibitor injection, replacement with CO_2 , and a combination of these methods [19–23]. The essence of these production methods is to decompose NGHs into gas and water by endothermic reaction in the reservoirs in situ, collect the gas–liquid fluid through

the wellbore, and transport it to the ocean surface. The research experiences and trial production indicated that seepage of gas–liquid fluid significantly impacts production efficiency during the exploitation [24–26]. Low permeability is a key factor restricting production efficiency, especially in clayey-silt NGHs. The seepage ability of HBS directly affects the flow velocity and spread distance during depressurization production, which also determines the decomposition rate of hydrates. At the same time, the seepage ability significantly impacts the gas–liquid fluid collection. During thermal stimulation, inhibitor injection and the replacement with CO₂ production method involve the collection of gas–liquid fluid after the decomposition of NGHs, and the seepage process of injecting thermal fluid, chemical agent and CO₂ fluid in HBS. Besides, the fluid flow in HBS is also closely related to the heat transfer process, which also affects the hydrate decomposition and recovery rate. Therefore, it is necessary to study the seepage characteristics and mechanisms of gas–liquid fluid in HBS and establish suitable flow models to accurately describe the HBS seepage properties and changing laws.

Permeability is a commonly used critical parameter to quantitatively describe the macroscopic seepage capacity of fluid in HBS [27–29]. On the one hand, the effect of exploitation is mainly evaluated by the final gas production. On the other hand, permeability is a straight evaluation index to predict the gas recovery from HBS. Permeability data in the field are often difficult to obtain directly. Temperature and pressure preservation measures should be taken after coring. Such measures require sophisticated equipment and are costly. However, the permeability of sediments without hydrates is easily measured, and each reservoir has a specific absolute permeability value. Therefore, permeability measurement of HBS is transformed into the calculation of the ratio for the permeability of HBS to that of sediments without hydrates. This ratio is generally defined as normalized permeability [30,31]. At present, many normalized permeability models have been established by scholars and evaluated at different levels [32–40]. The results indicate that macroscopic flow characteristics can be measured, but the effect of pore-throat thickness and particle arrangement on permeability remains unclear. Therefore, Lv [41] summarized the developments of micro-computed tomography (CT) technology in pore habits and flow characteristics. Similarly, Yang [42] comprehensively analyzed the advances of nuclear magnetic resonance (NMR) and magnetic resonance imaging (MRI) techniques in hydrate phase transformation, displacement exploitation, heat transfer and multiphase flow. Ren [43] reviewed the progress in theoretical analysis, numerical simulation, experimental measurement and field test of permeability in HBS. None of the above reviews summarize the permeability prediction model of sediments without hydrates. In addition, resistivity technology has developed rapidly in recent years, which can calculate permeability from the resistance value. Therefore, this paper focuses on the application and development of HBS seepage theories, including the research progress driven by traditional and new technologies.

In this review, normalized permeability models are first introduced. Moreover, theoretical expansion under new technology is reviewed. These theories are verified by classical experiments, simulation, microcosmic technology and a combination of these methods. Finally, the challenges and prospects of seepage theories are addressed. The two main aims of this review are: (1) to summarize the permeability models of the current theories in an organized way and analyze the parameters and influencing factors of each model; (2) to classify the current limitations and challenges in the seepage theories in NGHs and propose development directions in the future to achieve high production in HBS.

2. Application of Seepage Law in NGHs

The flow capacity in HBS determines the exploitation effect. On the one hand, there is a huge pressure difference between the interior and exterior of the wellbore. On the other hand, the pressure difference increases the fluid velocity in the area near the production well. Inertia and turbulence effects become obvious and Forcheimer's equation is used to compensate for Darcy's law and Bernoulli's law for high-speed flow. Apart from the rapid gas–water flow rate, temperature and pressure changes in the production well are more

likely to reform and plug the wellbore. Consequently, the flow state at the production well is different from that in HBS.

Although many seepage theories can be directly applied to HBS, these theories are generally based on Darcy's law. Therefore, the scope of seepage theories should be clearly defined. According to the seepage velocity, HBS can be divided into three zones:

- (1) The exploitation area near the production well: Because the pressure at the bottom of the production well is less than that in HBS, NGHs transition into methane and water. Under the pressure difference between the front and the back, the fluid velocity is too fast to satisfy the linear relationship between flow velocity and pressure drop. This phenomenon belongs to high-speed non-Darcy flow. Three kinds of non-Darcy flow (up warping, down bending and compound) will appear due to the obvious change in the pressure drop. For some areas with large pore size or decomposition, the influence of velocity with pressure drop is small, and the trend of down bending appears easily. Conversely, if the pore size of the area is small, a small amount of hydrate decomposes and there is no obvious dominant channel. When the pressure breaks through the starting pressure gradient, the flow rate and pressure drop show an obvious upward trend. Similarly, complex piecewise non-Darcy flows also exist.
- (2) Stability zone of HBS: This region is far away from the production well. HBS is relatively stable and does not decompose. However, this area determines the final effect of exploitation because the decomposition front is continuously spreading to the HBS stability zone to achieve continuous mining. In this process, permeability is a crucial parameter for evaluating the exploitation efficiency.
- (3) Boundary of HBS: This is often an unexploited area where the pressure drop does not propagate. In this region, there is no pressure difference driving without reaching the starting pressure gradient, the fluids in an ultralow velocity. Low-velocity non-Darcy flow will happen, which belongs to the down-bending curve. According to the flow characteristics, we should attach more importance to describe flow capacity in the stability zone.

To further study the exploitation principle of HBS, this paper focused on the undecomposed area of HBS and used permeability to characterize the ability of fluid to pass through porous media (as shown in Figure 1). Furthermore, the interior of HBS is a low-speed flow area, which conforms to the linear relation between pressure gradient and flow velocity. Therefore, the flow in porous media can be analyzed by Darcy's law.

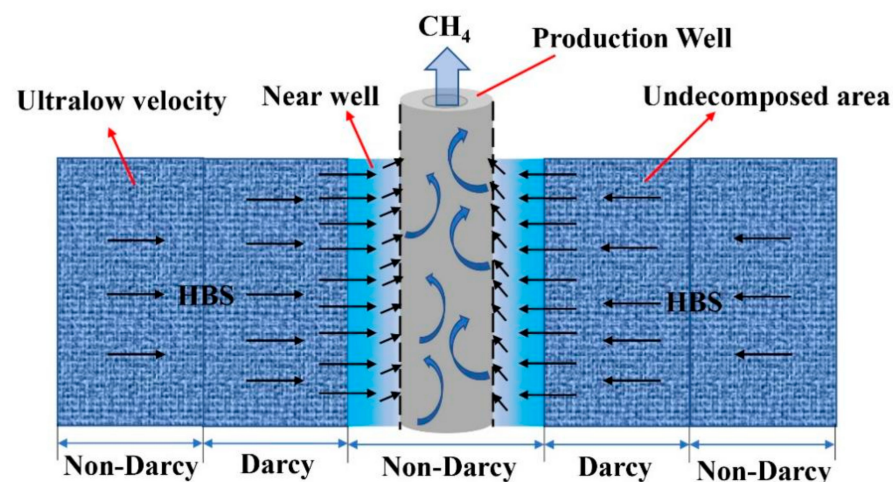


Figure 1. The distribution of flow characteristics in hydrate exploitation.

The existence morphology and saturation of hydrates in HBS are essential parameters that control permeability and flow process [44–46]. From the morphology perspective, the shape and arrangement of NGHs are determined by the effective stress of formation and the host sediments [47]. In the actual site, hydrates occur in the sediment layers in the form

of lenses, nodules, blocks and meridians [12,48,49]. Hydrate samples were obtained from actual exploitation in the South China Sea [50,51], as shown in Figure 2.

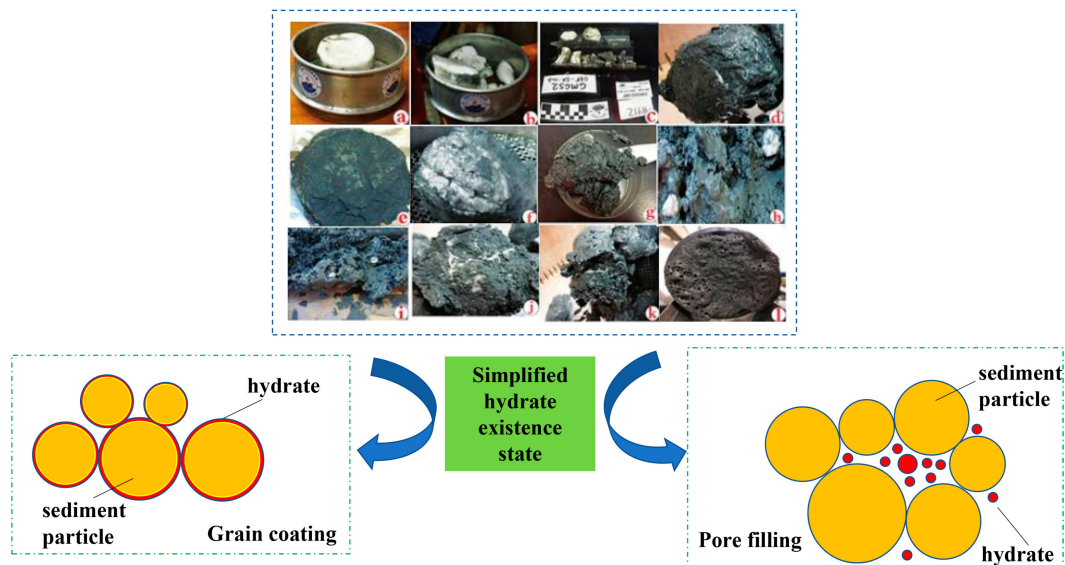


Figure 2. The natural samples and simplified modes of NGHs. (a–c) Massive hydrate; (d,e) thin layers of hydrate; (f) nodular hydrate; (g–i) concretion hydrate; (j,k) vein hydrate; (l) disperse hydrate.

According to the theoretical analysis, the growth modes of hydrates in sediment pores are divided into two modes [34,52–54]: (1) grain coating, hydrates form around sediments, accumulate and enclose the sediment particles (they are often formed in this way in the laboratory and reduce the formation time); (2) pore filling, hydrates are freely occupied in the pores of sediments without connecting two or more particles. In addition, the distribution of hydrates is extremely uneven. Permeability of HBS is anisotropic due to the difference in hydrate arrangement and the existence of fractures in sediments. It is undoubtedly complicated and difficult to accurately describe the flow capacity of HBS directly by absolute permeability.

As for the saturation of hydrates, which profoundly impacts the permeability of HBS, the presence of hydrates changes the pore space inside porous media and reduces the size of the pore-throat channels. With an increase in the saturation, the connected channels of fluid flow are blocked, and the flow capacity in HBS is reduced, leading to a decrease in permeability. Decomposition of NGHs is a phase transformation that involves the decomposition of solid hydrate in situ into gas and water before extraction. Therefore, the influence of the relative flow capacity of different phases in the microscopic pores of sediments should be viewed from the point of relative permeability. The relative permeability of the gas phase and the water phase is negatively correlated, indicating that the relative permeability of the water phase increases with an increase in the saturation, and the relative permeability curve of the gas phase decreases accordingly. Due to the increase in the saturation of the aqueous phase, the flow space of water in porous media increases. When the water phase occupies the flow space of the gas phase, the gas phase easily loses its original shape due to the resistance effect (Jamin effect). This effect plays a vital role in gas–water flow. The gas phase will gradually lose its continuity and distribute in the water phase, leading to a gradual decrease in the relative permeability of the gas phase and remaining in the pores at last. Hydrates in porous media will occupy the pores used for fluid flow, resulting in a decrease in the pore-throat radius and a significant increase in capillary force in porous media to hinder the flow of the water phase.

Besides, when hydrates are decomposed into gas and water, three-phase migration of gas–water–hydrate particles occurs, resulting in a constant change in absolute permeability of HBS. In turn, decomposition leads to a drop in environment temperature, resulting in

the secondary formation of hydrates or rearrangement of hydrates during the three-phase migration. Hence, it is still a difficult point to directly express the absolute permeability of each phase of HBS at the present stage.

3. Traditional Seepage Theories in NGHs

The traditional seepage theories of NGHs regard saturation as the only variable in HBS permeability. The advantage of these theories is that they only need to find the relation between saturation and existence morphology to build models. In this paper, five widely accepted models were summarized, respectively, from the perspectives of grain coating and pore-filling type. The development and evolution of the models are shown in Figure 3.

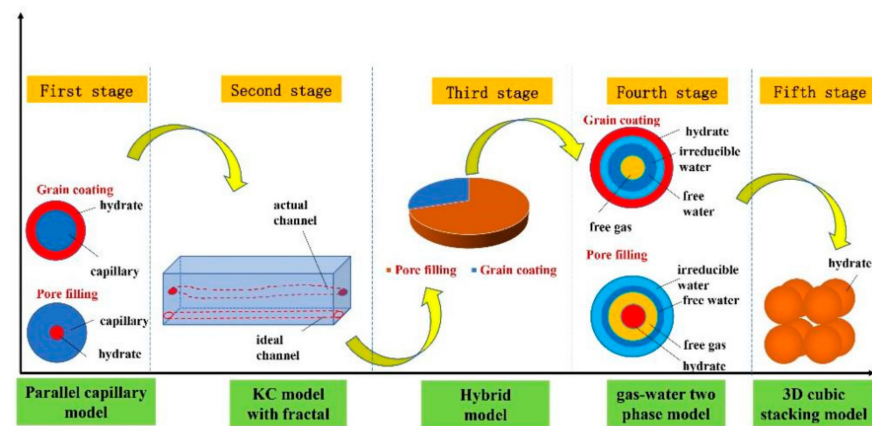


Figure 3. Evolution of normalized permeability models in HBS.

3.1. Parallel Capillary Model

It is assumed that pore configuration in sediments is made up of many equal-diameter parallel capillaries [55] with the cross-sectional area consisting of X capillaries. When fluid flows through a capillary of length L (m) and inner radius r (m), the flow rate is q (m³/s). According to Poiseuille's theory, the total flow in the cross-sectional area of the capillaries can be expressed as follows:

$$Q = xq = \frac{x\pi r^4 \Delta p}{8\mu L} \quad (1)$$

where μ (MPa·s) is liquid viscosity and ΔP (MPa) is the pressure difference on both ends.

The relationship between porosity ϕ and the number X of capillaries per unit cross-sectional area is

$$\phi = x\pi r^2 \quad (2)$$

The real fluid flow in HBS can be expressed by Darcy's formula as follows:

$$Q = \frac{KA\Delta P}{\mu L} \quad (3)$$

Assuming the total cross-sectional area is A (m²) and substituting Equations (1) and (2) into Equation (3), the absolute permeability K_0 in the sediments without hydrates can be obtained:

$$K_0 = \frac{\phi r^2}{8} \quad (4)$$

If the hydrate particles grow uniformly on the surface of the sediment particles, the thickness of the hydrate is d (m), so the radius of the capillary decreases from r to $r-d$. Combined with the above theories, the absolute permeability of HBS is

$$K_H = \frac{\phi r_H^4}{8r^2} \quad (5)$$

According to the geometric relation in Figure 4a, the relationship between capillary radius and hydrate saturation S_H can be expressed as

$$(r - d)^2 = r^2(1 - S_H) \quad (6)$$

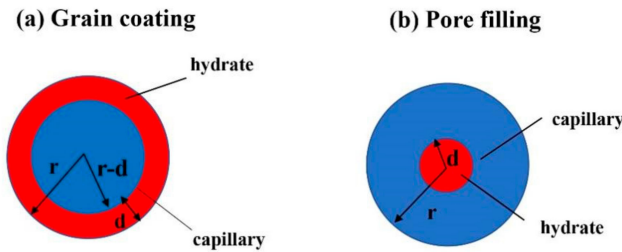


Figure 4. Two filling modes of parallel capillary.

Hence, when saturation is S_H , the normalized permeability in HBS is

$$k_t = \frac{K_H}{K_0} = \frac{r^2 \varphi (1 - S_H)^2}{8} / \frac{\varphi r^2}{8} = (1 - S_H)^2 \quad (7)$$

In particular, Masuda [33] further concluded that the normalized permeability of HBS is

$$k_t = (1 - S_H)^n \quad (8)$$

Based on the above-mentioned results, this index model was also known as the Tokyo model. However, the adjustable parameter n lacks a physical basis and its value varies with different pore habits in HBS. Dai [39] found that n ranged from 1.25 to 25 and many researchers also gave different values, so a piecewise function with varying different values of n for different filling of hydrates in HBS was put forward [56].

Similarly, according to Figure 4b, the parallel capillary model of pore filling can be expressed as

$$k_t = 1 - S_H^2 + \frac{2(1 - S_H)^2}{\ln S_H} \quad (9)$$

The parallel capillary model [32] is the simplest model for normalized permeability prediction, which has no empirical parameters and simple mathematical form. However, the pores in the actual sediments are not uniform and different in diameter. Besides, the migration route of fluid through the pores is not a straight line. Therefore, the application of this theory still has a lot of limitations.

3.2. Kozeny–Carman Model with Fractal Theory

The internal structure of porous media is very complicated in the actual environment. Therefore, some scholars proposed the fractal theories [57–59] that porous media was constructed by parallel capillaries with unequal diameters. The absolute permeability, porosity, and specific surface can be expressed as, respectively

$$K_0 = \frac{\pi \alpha D}{8\tau(4 - D)} r_{\max}^{4-D} \quad (10)$$

$$\varphi = \frac{\alpha \pi \tau D}{2 - D} r_{\max}^{2-D} \quad (11)$$

$$\sigma = \frac{2\alpha \pi \tau D}{D - 1} r_{\min}^{1-D} \quad (12)$$

where α , D , τ , $r_{\max}$, φ , and σ represent fractal parameter, fractal dimension, tortuosity, maximum capillary radius (m), porosity, and specific surface (cm^2/cm^3), respectively.

Equations (10)–(12) can be transformed into the following from the Kozeny–Carman equation (KC equation for short), as follows:

$$K_0 = \frac{\varphi^3}{C\sigma^2} \quad (13)$$

$$C = \frac{2\tau^2(4-D)(D-1)^2}{(2-D)^3\alpha^{2(1-D)}} \quad (14)$$

Equation (13) is the KC equation with fractal characteristics, which shows that permeability is a function of the fractal dimension of pore structure, macroscopic physical and microscopic pore structure parameters of porous media. This formula has no empirical parameters and each parameter has a specific physical meaning. Compared with the classical KC equation, it can be seen that C is a new KC constant, and its value is related to the fractal dimension D and microscopic pore structure parameters of porous media.

However, the actual HBS skeleton is composed of particles, and the actual flow path of fluid is longer than the geometrical length of HBS due to the irregularity of pore space. To deal with the problem, the concept of tortuosity is introduced [60].

3.2.1. Development of Tortuosity in Fractal Theory

Tortuosity in sediments is difficult to observe directly due to the diversity and randomness of the flow path. In order to better analyze the influence of tortuosity on flow, Yu [61] summarized the models of porous media without hydrates. In addition, some scholars proposed relative tortuosity to represent the relative change in HBS to sediments without hydrates, as shown in Table 1, below.

Table 1. Tortuosity models of sediments without/with hydrates.

	Type	Model	Literature
Without hydrates	Cube & Sphericity	$\tau = 1 + \nu \ln(1/\varphi)$ (ν is shape factor)	Yu [61]
	Fine Particles	$\tau = \sqrt{1 - \ln(\varphi)^2}$	Boundreau [62]
	Sphericity	$\tau = 1/\sqrt{\varphi}$	Sen [63]
	Square	$\tau = \frac{1}{2} \left\{ 1 + \frac{1}{2} \sqrt{1 - \varphi} + \frac{\sqrt{(1-\varphi) \left[\left(\frac{1}{\sqrt{1-\varphi}} - 1 \right)^2 + \frac{1}{4} \right]}}{1 - \sqrt{1-\varphi}} \right\}$	Yu [61]
Contain hydrates	Sphericity	$\tau_H = \sqrt{1 + 2[1 - \varphi_0(1 - S_H)]}$	Iversen [64]
		$\tau_H = 1 + 0.41 \ln(1/[\varphi_0(1 - S_H)])$	Liu [65]
		$(\tau \times A/V) = 1 + 2S_H(A/V)$ is specific surface	Dai [39]

Zhang [66] used X-ray CT to propose a fractal model for predicting flow capacity in HBS. The fractal-theory-based model included extracted parameters, such as tortuosity dimension, pore-size dimensions, and maximal pore diameter. It is suitable for the model to detect the physics of saturated water permeability reduction in HBS during formation.

$$k_t = \frac{D_{f,h}}{D_{f,0}} \frac{3 + D_{\tau,0} - D_{f,0}}{3 + D_{\tau,h} - D_{f,h}} \left(\frac{\lambda_{\max,h}}{\lambda_{\max,0}} \right)^{3+D_{\tau,0}} \quad (15)$$

where D_f , D_τ , and $\lambda_{\max}$ represent pore-size dimension, tortuosity dimension, and normalized maximal area pore diameter, respectively. The parameters with the subscripts “0” and “H” are without hydrates and completely full of hydrates.

3.2.2. Electrical Tortuosity in HBS

In HBS, Archie’s first formula [67] is most widely used to solve tortuosity, which can be obtained:

$$\tau = \left(\frac{L_a}{L} \right)^2 = \frac{R_o}{R_w} \varphi = F\varphi \quad (16)$$

where L_a (m), L (m), R_o ($\Omega \cdot m$), R_W ($\Omega \cdot m$), and F represent the actual flow length inside HBS, the geometric length of HBS, the resistivity of the sediments completely saturated with water, the resistivity of formation water, and formation factor, respectively. In some studies, tortuosity is defined as the ratio of the path length for flow in the streamline to the straight-line distance of the sediments [58]. In fact, in anisotropic media, tortuosity is a second-order tensor, so in this paper, tortuosity is defined as the square value.

In order to get closer to the actual flow capacity in the HBS, Kleinberg [32] revised the model based on the KC equation [68–71], as follows:

$$K_0 = \frac{\varphi}{\nu\tau(A/V)^2} = \frac{\varphi}{\nu\tau\sigma^2} \quad (17)$$

where ν , τ , σ (cm^2/cm^3), K_0 (D), and φ represent shape factor, tortuosity, the specific surface of the particles, the absolute permeability of the HBS, and porosity, respectively.

Substituting Equation (16) into Equation (17) to obtain the effective permeability of water phase under HBS with different saturation (only hydrate and water are in HBS, $S_W + S_H = 1$) leads to:

$$K_H = \frac{1}{\nu F_H \left(\frac{A_H}{V_H} \right)^2} \quad (18)$$

As for further comments about the idea of normalized permeability, the effective permeability of the aqueous phase in HBS can be compared with the absolute permeability of the sediment saturated with water:

$$k_t = \frac{K_H}{K_0} = \frac{F_0}{F_H} \left(\frac{V_H}{V_0} \right)^2 \left(\frac{A_0}{A_H} \right)^2 \quad (19)$$

where K_H (D), K_0 (D), F_H , F_0 , V_H/A_H (cm^2/cm^3), and V_0/A_0 (cm^2/cm^3) represent effective permeability of water phase in HBS, absolute permeability of sediments completely saturated with water, formation factor of HBS, formation factor without hydrates, volume/surface area of HBS, and volume/surface area without hydrate, respectively.

Many empirical data verified that Archie's second formula could be described as:

$$\frac{R_H}{R_0} = \frac{z}{S_W^n} \quad (20)$$

In the above formula, z is the parameter, close to 1 (it can be directly equal to 1 in practical application); n is the saturation index, which is influenced by rock wettability and pore structure, but mainly by wettability. In many experiments, it is found that the n of oil-wet rock is significantly higher than that of water-wet rock [59,72,73].

It is worth noting that (V_H/V_0) is the ratio of the volume of water in HBS pores (partially hydrates, $S_W + S_H = 1$) to the total pore volume filled with water in HBS, so Equation (19) can be transformed as

$$k_t = \frac{K_H}{K_0} = S_W^{n+2} \left(\frac{A_0}{A_H} \right)^2 \quad (21)$$

(1) Grain coating

If hydrate particles grow uniformly on the surface of sediment particles, the radius of the capillary decreases from r to $r-d$. Combining with the geometric relation in Figure 4a, the relationship between the ratio of area and saturation can be linked, and the normalized permeability of HBS can be obtained as

$$k_t = \frac{K_H}{K_0} = (1 - S_H)^{n+1} \quad (22)$$

Note: For Equation (22), when $0 < S_H < 0.8$, $n = 1.5$. When $S_H > 0.8$, n is very small, it has little influence on the permeability prediction model under the low-permeability condition [74].

(2) Pore filling

It is assumed that hydrates grow in the center of the sediment particles and are distributed in cylindrical form. The capillary radius is r and the thickness of hydrate is d , so

$$k_t = \frac{K_H}{K_0} = \frac{(1 - S_H)^{n+2}}{(1 + S_H^{0.5})^2} \quad (23)$$

Note: In Equation (23), $n = 0.7 S_H + 0.3$.

3.3. Hybrid Model

It is generally accepted that the two filling modes in HBS are determined by the degree of saturation, and the permeability of HBS is dependent on the value of hydrate saturation. Because the distribution of hydrates in the sediment is heterogeneous, it is not very accurate to use the saturation alone to estimate which filling method exists. For this reason, Delli [37] put forward a new theoretical model based on the weighting idea, as

$$k_t = S_H^N k_t^{PF} + (1 - S_H)^M k_t^{GC} \quad (24)$$

where K_t^{PF} , K_t^{GC} , N and M represent normalized permeability of pore filling obtained from Equation (9), normalized permeability of grain coating obtained from Equation (7), and weight index, respectively. Particularly, when $S_H = 1$, it is pore filling; when $S_H = 0$, it is basically grain coating.

3.4. Gas–Water Two-Phase Seepage Model

The above capillary models assumed only a single phase, but there is a complex system of gas–water–hydrate coexistence in the actual pores of HBS. Singh [52] derived a new analytical model based on the Navier–Stokes equation of gas–water two-phase flow and the concept of tortuosity. In this analytical model, the absolute permeability is the variable of HBS, which will change with the hydrate's saturation. The concept of relative permeability is introduced to better characterize the flow of two fluids in the pores. The two filling modes are shown in Figure 5 and satisfy $S_W + S_{wr} + S_g + S_H = 1$.

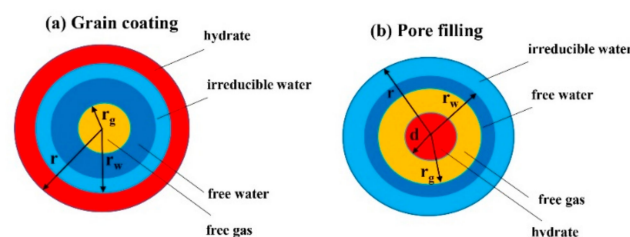


Figure 5. Two filling modes under gas–liquid flow.

(1) Grain coating

In the mobile phase, gas and liquid can flow in the pores, and water occupies the walls of the pores during the wetting phase. Gas, a non-wetting phase, is adjacent to water, so the relative permeability of gas and liquid must be considered separately.

$$\begin{cases} k_{rg} = \left(\frac{r_g}{r}\right)^2 \times \left[2\psi\left(1 - \frac{r_w^2}{r_g^2}\right) - 1\right] \times \left[\frac{\tau(\varphi, 1 - S_H - S_{wr})}{\tau(\varphi, S_g)}\right] \\ k_{rw} = \left[\frac{(r_w^2 - r_g^2)^2}{r^2(r_w^2 - r_g^2)}\right] \times \left[\frac{\tau(\varphi, 1 - S_H - S_{wr})}{\tau(\varphi, S_w)}\right] \end{cases} \quad (25)$$

where $\psi = (\mu_g/\mu_w)$ and $\tau(\varphi, 1 - S_H - S_{wr})$ represent the viscosity ratio of gas to liquid and tortuosity of a mobile phase in a medium, respectively.

Note: $\tau(\varphi, 1 - S_i)$ represents the tortuosity of each mobile phase ($i = g, w$) as a function of each phase saturation and the porosity of HBS. Meanwhile, the porosity of HBS decreases linearly with hydrate saturation. The formulas are expressed as follows

$$\begin{cases} \varphi(S_H) = \varphi_i \times (1 - S_H) \\ \tau(\varphi, S_i) = \left(\frac{S_i}{\varphi}\right)^{-2} \times (S_i)^{\frac{-4}{3}} \end{cases} \quad (26)$$

(2) Pore filling

The growth pattern of most hydrates is that hydrates gather in the middle of pores [49,52]. As shown in Figure 5b, water is close to the wall of pores in the wetting phase, while gas is close to the middle of pores in the non-wetting phase. The final relative permeability is

$$k_{rg} = \left[\frac{1}{r^2(r_g^2 - d^2)} \right] \times \left\{ \begin{aligned} &-(r_g^4 - d^4) + 4 \left[\frac{r_g^2(1-\psi) + \psi r^2 - d^2}{(1-\psi)\ln(r_g) + \psi\ln(r) - \ln(d)} \right] \times \left[\frac{r_g^2 \ln(r_g) - r_w^2 \ln(r_w)}{2} - \frac{(r_g^2 - d^2)}{4} \right] \\ &+ 2 \left\{ \frac{(1-\psi)[d^2 \ln(r_g) - r_g^2 \ln(d)] + \psi[r_H^2 \ln(r) - r^2 \ln(d)]}{(1-\psi)\ln(r_g) + \psi\ln(r) - \ln(d)} \right\} \times (r_g^2 - d^2) \end{aligned} \right\} \quad (27)$$

$$k_{rw} = \left[\frac{1}{r^2(r_w^2 - r_g^2)} \right] \times \left\{ \begin{aligned} &-(r^4 - r_g^4) + 4 \left[\frac{r_g^2(1-\psi) + \psi r^2 - d^2}{(1-\psi)\ln(r_g) + \psi\ln(r) - \ln(d)} \right] \times \left[\frac{r^2 \ln(r) - r_g^2 \ln(r_g)}{2} - \frac{(r^2 - r_g^2)}{4} \right] \\ &+ 2 \left\{ \frac{(1-\psi)[r^2 \ln(r_g) - r_g^2 \ln(r)] - [r^2 \ln(d) - r_H^2 \ln(r)]}{(1-\psi)\ln(r_g) + \psi\ln(r) - \ln(d)} \right\} \times (r^2 - r_g^2) \end{aligned} \right\} \quad (28)$$

3.5. Three-Dimensional Cubic Stacking Model

In the actual HBS pores, hydrate particles are not all stacked in a parallel disjoint way, so capillary models are extended to a three-dimensional space, based on Section 3.1, and the traditional models are modified by cylindrical, spherical, and random accumulation, respectively.

3.5.1. Cylindrical Accumulation

(a) Grain coating

Assuming that the pores consist of hydrates and free water, as shown in Figure 6a, the relationship between saturation and radius is as follows:

$$\left. \begin{aligned} S_H &= \frac{V_H}{V_{pore}} \\ V_{pore} &= (4 - \pi)r^2L \\ \pi(r + d)^2 &= \pi r^2 + V_H \end{aligned} \right\} \Rightarrow \frac{r + d}{r} = \left(\frac{4 - (4 - \pi) \times (1 - S_H)}{\pi} \right)^{0.5} \quad (29)$$

Thus, the relationship between hydrate saturation and permeability can be further deduced by combination with Equation (21) to give:

$$k_t = \frac{\pi(1 - S_H)^{n+2}}{4 - (4 - \pi)(1 - S_H)} \quad (30)$$

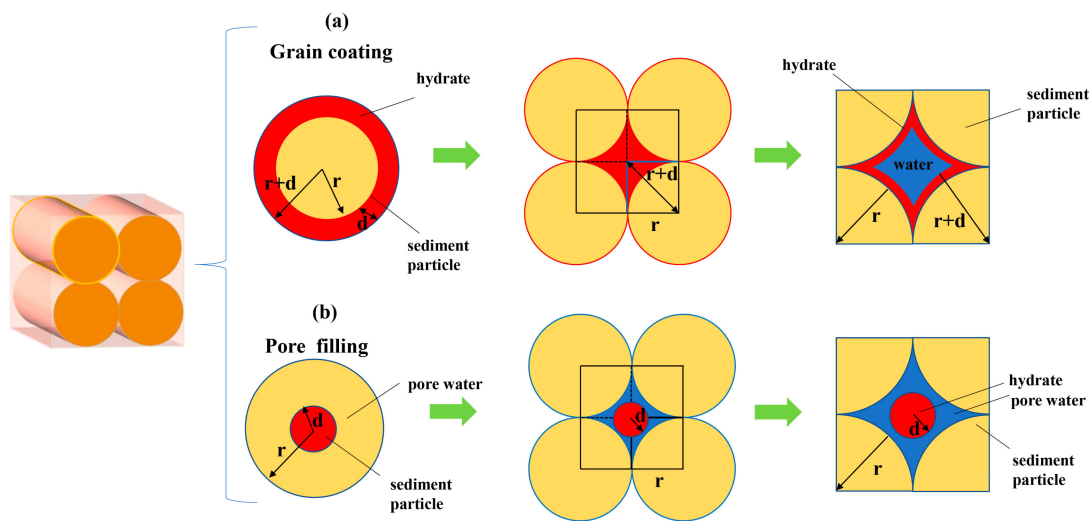


Figure 6. Two filling modes of cubic cylinder.

(b) Pore filling

Assuming that the pores are composed of hydrates and free water, as shown in Figure 6b, the relationship between saturation and radius is as follows:

$$\left. \begin{aligned} S_H &= \frac{V_H}{V_{pore}} \\ V_{pore} &= (4 - \pi)r^2L \\ V_H &= \pi d^2 \end{aligned} \right\} \Rightarrow \frac{d}{r} = \left(\frac{(4 - \pi) \times S_H}{\pi} \right)^{0.5} \quad (31)$$

Thus, the relationship between hydrate saturation and normalized permeability can be given by combining with Equation (21):

$$k_t = \frac{(1 - S_H)^{n+2}}{\left[1 + \left(\frac{(4 - \pi)S_H}{\pi} \right)^{0.5} \right]^2} \quad (32)$$

Note: In order to make permeability only dependent on saturation, the above formulas do not consider the overlap between particles. In particular, Equation (30) applies to saturation less than 0.6238 and $d/r < 0.732$ [34].

3.5.2. Spherical Accumulation

(1) Grain coating

By referring to Figure 7a, saturation, pore volume, and hydrate volume can be obtained as follows:

$$\left\{ \begin{aligned} S_H &= \frac{V_H}{V_{pore}} \\ V_{pore} &= \left(8 - \frac{4\pi}{3} \right) d^3 \\ V_H &= \frac{4\pi}{3} \left[(r + d)^3 - r^3 \right] \end{aligned} \right. \quad (33)$$

Thus, the relationship between hydrate saturation and normalized permeability can be further deduced by combining with Equation (28):

$$k_t = \frac{(1 - S_H)^{n+2}}{\left[1 + \left(\frac{6}{\pi} - 1 \right) S_H \right]^{\frac{4}{3}}} \quad (34)$$

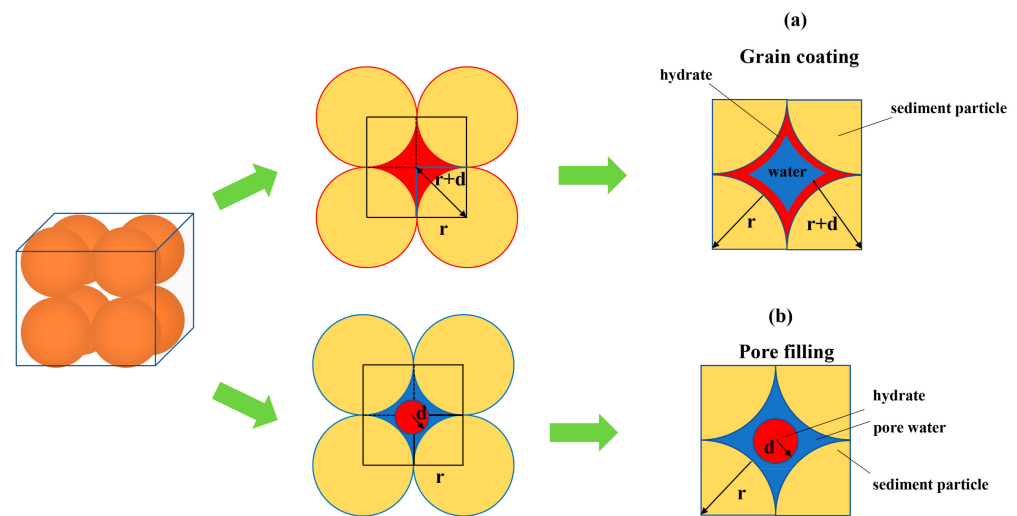


Figure 7. Two filling models of Cubic Sphere.

(2) Pore filling

The relationship between normalized permeability and saturation can be obtained by referring to the above derivation, according to the geometric relation:

$$k_t = \frac{(1 - S_H)^{n+2}}{\left[1 + \left[\left(\frac{6}{\pi} - 1\right)S_H\right]^{\frac{2}{3}}\right]^2} \quad (35)$$

Li [75] considered the overlap between particles based on spherical cubic accumulation and derived the normalized permeability containing only the radius of sediment particles and hydrate particles.

$$\begin{cases} K_t = \left\{ \left[\frac{-\pi}{3} \left(\frac{r}{L}\right)^3 + \frac{3\pi}{4} \left(\frac{r}{L}\right)^2 - \frac{5\pi}{12} \right] / \left(1 - \frac{\pi}{6}\right) \right\}^{n+2} \left[\frac{3\sqrt{2}-4}{3\left(\frac{r}{L}\right)^2 - 2\left(\frac{r}{L}\right)} \right]^2 \\ 1 \leq \frac{r}{L} \leq \sqrt{2} \end{cases} \quad (36)$$

3.5.3. Random Accumulation

In the above cubic models, the particles are arranged in a spherical shape according to certain rules, but in HBS, the particle arrangement is quite irregular. Hence, we can imagine that the spherical particles are randomly distributed in a cube.

When hydrates grow on the surface of sediment particles, the normalized permeability can be expressed as [34]:

$$k_t = \frac{(1 - S_H)^{n+2}}{[1 + \varepsilon S_H]^{\frac{4}{3}}} \quad (37)$$

When hydrates grow in the center of pores, the normalized permeability can be expressed as [52]:

$$k_t = \frac{(1 - S_H)^{n+2}}{[1 + \varepsilon C_P S_H]^2} \quad (38)$$

where ε is the pore ratio and its value is $\varphi/(1 - \varphi)$; C_P is the ratio of sediment particle radius to hydrate particle radius.

3.6. Other Models

According to the self-developed EOSHYDR, from the Lawrence Berkeley National Laboratory in the United States: TOUGH2 simulator [35] coupled with the Genuchten [76] model, the normalized permeability of HBS can be obtained:

$$\begin{cases} k_{rw} = \sqrt{S_w} \left[1 - \left(1 - \sqrt[m]{S_w} \right)^m \right]^2 \\ k_{rg} = \sqrt{S_g} \left(1 - \sqrt[m]{S_w} \right)^{2m} \end{cases} \quad (39)$$

where $m = 1 - 1/l$, $\overline{S_w} = (S_w - S_{wr}) / (1 - S_{wr})$ and S_{wr} is the irreducible water saturation. In sandstone and other cores, m could be 0.46, S_{wr} as 0.09 [32]. Parker [77] reported l was 1.84 for sand and 1.86 for clay.

Singh [78] used empirical parameters to derive a gas–water two-phase flow model in HBS, where K_{ri} , K_{pm} , $(q_{i,pm}/A_i)$, μ_i , A_i , τ (φ , $1 - S_H - S_{wr}$), and r represent the relative permeability of gas/liquid, the absolute permeability of HBS (when the saturation is S_H), superficial velocity, viscosity of phase, the cross-sectional area of flow occupied by phase, tortuosity of a mobile phase in a porous media, and radius of cylindrical tubes, respectively. β_i and η_i are empirical parameters.

$$\begin{cases} k_{ri} = \frac{(q_{i,pm}/A_i)\mu_i}{K_{pm}[(\beta_i \times S_i^{\eta_i}) \times \Delta P]} \\ K_{pm} = \frac{r^2}{8} \frac{\varphi S_H}{\tau(\varphi, 1 - S_H - S_{wr})} \end{cases} \quad (40)$$

From the view of Singh, the parameter β_i is considered to be linked with constant properties, such as fluid densities, initial pore volume, and pore radius. The parameter η_i reflects petrophysical properties, such as the arrangement of specific properties in porous media. Therefore, the parameter β_i and η_i are independent of hydrate saturation. Only by fitting a curve of relative permeability for any hydrate saturation, two parameters can be estimated to predict relative permeability curves of HBS.

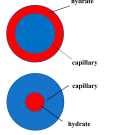
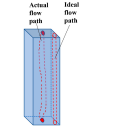
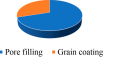
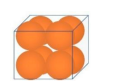
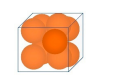
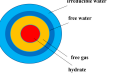
3.7. Overview of Permeability Models in HBS

Based on the above analysis and induction, the permeability prediction models of HBS are classified into single-phase flow and multi-phase flow, as shown in Table 2.

3.8. Permeability Prediction Model of Original Sediments

In the previous model derivation, the normalized permeability is the ratio of the absolute permeability of HBS to the absolute permeability of sediments without hydrates. The value of normalized permeability is only related to hydrate saturation. When the saturation increases, the value of normalized permeability decreases, reflecting the influence of hydrate formation on pore connectivity and pore-throat size. Because of the influence of hydrates on the internal permeability of sediments, it is difficult to directly evaluate the seepage in the reservoirs. In addition, in-situ measurement is the most direct method, but the cost is very high, and the numerical simulation also needs to be established based on suitable theories. Consequently, from the perspective of normalized permeability, establishing permeability models for sediments without hydrates can inversely drive the absolute permeability model of HBS to predict the seepage capacity of HBS. Although the prediction theories of permeability of sediments are still relatively small in the field of hydrates, a lot of research has been done in the traditional oil and gas field. These prediction theories mainly start from the relation between porosity, capillary pressure, pore-throat radius and permeability.

Table 2. Comparison of normalized permeability models of HBS and original permeability models of sediments without hydrate.

Schematic Diagram	Single Phase Flow	Equation	Highlights	Advantages	Disadvantages	Recommendations	Reference
	Parallel capillary	(4)	Equal-diameter capillaries	Easy to simulate and compare	Suitable for homogeneous system	Suitable as a basic model compared to other models due to its simple form	[32,56–59] [33]
		(7)	Simple form				
		(9)	Easy to calculation				
		(8)	Tokyo model				
	KC model Fractal theory	(17)	Formation factor replaces tortuosity	The solution of tortuosity is avoided and the value can be fitted flexibly by saturation index	The value range of saturation index varies greatly and has no physical sense	The influence of capillary diameter and microcosmic parameters on permeability is considered	[60,66–74]
		(18)					
		(22)					
		(23)					
	Hybrid model	(15)	Introducing microscopic parameters	The influence of two hydrate occurrence forms on permeability is considered	Too many empirical parameters for application	Reduce empirical parameters and consider how PF and GC interact to make effect on normalized permeability	[37]
		(24)	Combining PF and GC				
	Cylindrical accumulation	(30)	Extending to 3D space	Compared with the two-dimensional capillary model, it is more accurate	Homogeneous configuration with equal diameter	The unequal inner diameter of the capillary is not considered and empirical parameters are included.	[34]
		(32)					
	Spherical accumulation	(34)	Regarding particles as spheres	The spherical appearance of sediment particles is simulated	The unequal diameter of particles and inhomogeneity of distribution are not considered	It can be used as a basic model of clay mineral system	[34]
		(35)					
		(36)	Modification in fluid area of pores at PF mode.				
	Random accumulation	(37)	Representing random as arrangement as heterogeneity	The heterogeneity of formation is simulated by particle random distribution	The unequal diameter of sediment particles in the actual formation is not taken into account	The model has potential for further research in the future	[34]
		(38)					
	Gas water	(25)	In line with the actual flow characteristics, and no parameters	The gas–liquid two phase flow is considered, which accords with the objective flow law	It is still a two-dimensional structure, and there are many solving parameters. The model is not conducive to direct application in the field.	The model should be generalized from two dimensions to three dimensions	[52]
		(26)					
		(27)					
		(28)					
	TOUGH2 simulator	(39)	Widely applicable and without considering the occurrence form of hydrate	It is suitable for numerical simulation and has wide extension	Containing empirical parameters	Based on numerical results, it is hard to apply in the field	[35,76]
			The effect of capillary on gas–liquid flow is considered				
	Empirical model	(40)		Combining capillary force with two phase flow	Difficult to apply due to empirical parameters	Simplifying form and reducing empirical parameters to improve applicability	[78]

In the earliest study of sandstone reservoirs, it was found that the logarithm of absolute permeability has a linear relationship with porosity, which is

$$\ln K_0 = \ln a + b\phi \quad (41)$$

where K_0 and ϕ represent absolute permeability and porosity, respectively. a and b are empirical parameters. Although this formula is simple and can be obtained directly from logging data, it has some limitations in that Equation (49) can only reflect the properties of certain cores and cannot be applied to complex reservoirs.

In order to better describe pore properties in sediments, the Kozeny–Carman equation [56–59] can be converted to another form, which starts from the simplest homogeneous media.

$$K_0 = \frac{a\phi^3}{(1-\phi)^2\sigma^2} \quad (42)$$

where σ , ϕ , and a represent specific surface, porosity, and empirical parameters, respectively. Since σ cannot be obtained directly from logging data, the application of the KC formula is limited.

With the study, it was found that the sorting degree, consolidation degree, and porosity range of different rock samples greatly influenced permeability. Based on several groups of sandstone samples in the oilfield, Timur established a power function relation containing the permeability and reciprocal of saturation of irreducible water [79], which is expressed as

$$K_0 = \frac{a\phi^b}{S_{wr}^2} \quad (43)$$

where ϕ and S_{wr} represent porosity and irreducible water saturation, respectively. a and b are determined by statistics. According to Timur's statistical results, it is shown that the value range of b is between 3 and 5 to get better satisfaction.

At present, the microscopic properties of rock samples are difficult to observe directly, and the changes in permeability cannot be directly and continuously measured by logging data. Therefore, many scholars have established relation models between capillary pressure curve and permeability to indirectly reflect the flow capacity in sediments, which started from the throat size in the pores. The permeability is determined by the size of the interconnected pores, and the most direct way to measure the permeability of the cores is to inject mercury into the dry samples and obtain the capillary pressure curve, thus, finding the permeability.

$$P_c = \frac{2\gamma \cos \theta}{r} \quad (44)$$

where P_c (MPa), θ (°), and γ (dyn/cm) represent capillary pressure, wetting angle, and interfacial tension, respectively. In an ideal capillary pressure curve, mercury is first injected into the dry samples at a certain pressure. When the first breakpoint (injection pressure) occurs, mercury occupies a small portion of the pore. Then, the pressure builds up and most of the pore spaces are taken up by mercury. Eventually, a sharp increase in pressure is needed to force more mercury into the smallest pores.

Purcel derived a model for the relationship between permeability, porosity, mercury saturation, and pressure based on the capillary model and Darcy's seepage law [80].

$$K_0 = 0.66F\phi \int_{\rho=0}^{\rho=100} \frac{d\rho}{(P_c)^2} \quad (45)$$

where ϕ , F , ρ , and P_c represent porosity, formation factor, and the percentage of the entire pore occupied by fluid and capillary pressure, respectively.

Through statistical analysis of a large number of carbonate rocks and clastic rocks, Winland found that r_{35} (throat radius corresponding to 35% mercury saturation) has a

good correlation with permeability and porosity, so as to establish the corresponding semi-empirical model [81], as follows:

$$\lg r_{35} = 0.732 + 0.588 \lg K_0 - 0.864 \lg \varphi \quad (46)$$

where r_{35} , φ , and K_0 represent pore-throat radius corresponding to a mercury saturation of 35%, porosity, and permeability, respectively.

Swanson [82] provided a method for determining air and brine permeability from a single point on the capillary pressure curve. His method is to select the ratio of maximum mercury saturation to pressure from the capillary pressure curve, and this value can indicate all interconnecting spaces are saturated with mercury. In other words, this capillary pressure reflects the pore size with effective interconnection in the total pore system.

According to the linear regression relation, the simple form of Swanson's model is

$$K_0 = a \left[\frac{S_{Hg}}{P_C} \right]_{\max}^b \quad (47)$$

where a and b are constants, depending on the rock type (carbonate and sandstone) and fluid type (air or salt water). S_{Hg} is the mercury saturation equivalent to the total volume, which is directly proportional to porosity. Equation (44) shows that the capillary pressure is related to the pore-throat radius, so the Swanson model also indicates that the value of K_0 depends on the square of the pore size.

Pittman [83] combined Winland and Swanson's model to establish a statistical relation between the throat radius, corresponding to 10–75% mercury saturation, porosity, and permeability based on 202 sandstone samples.

$$\lg r_{apex} = -0.117 + 0.475 \lg K_0 - 0.099 \lg \varphi \quad (48)$$

where K_0 , φ , and r_{apex} represent permeability, porosity, and pore-throat radius corresponding to the apex, respectively.

The above permeability models are mainly predicted for carbonate rocks and sandstones, but HBSs are mineral systems containing clay. In general, the existence of clay minerals mainly affects the size, shape, and position of sediment particles, which later affects the permeability. For example, clay affects the specific surface in the Kozeny–Carman equation and the saturation of irreducible water in the Timur model. Therefore, clay minerals should be considered in permeability models for clayey-silt sediments without hydrates. According to the core data of consolidated marine sediments, Bryant used statistical methods to obtain the exponential relation between permeability and porosity [84], as follows:

$$K_0 = e^{B(\varphi)+\Omega} \quad (49)$$

where e , φ , Ω , B , and K_0 represent exponential or 2.718, porosity (not percent) computed from the void ratio ($\varphi = e/(e + 1)$), intercept, linear regression coefficient, and coefficient of permeability (hydraulic conductivity), respectively. The relation between porosity and permeability of different sediment types is shown in Table 3.

Table 3. Equations for permeability–porosity relationships [77].

Sediment Group	Equation	Sediment Type
1	$K_0 = e^{\varphi(15.75)-27.37}$	80% clay
2	$K_0 = e^{\varphi(14.18)-26.50}$	60–80% clay
3	$K_0 = e^{\varphi(15.59)-26.65}$	Silty clays and clayey silts
4	$K_0 = e^{\varphi(17.51)-26.93}$	Sandy clays and silts
All data	$K_0 = e^{\varphi(14.30)-26.30}$	

Note: The above Equations from (1) to (49) have been adjusted differently from the original formulas for unifying symbols.

4. Extension of Seepage Theories in NGHs Combined with Frontier Technology

With the upgrade in technology, a series of microscopic methods can describe the flow capacity of fluid in porous media more precisely, so some new methods that transform the existence and distribution of hydrates in complex porous media into images have been put forward. These methods for detecting flow capacity are based on enough gas or water source. The content and distribution of the hydrates in the internal pores of the HBS can be obtained by detecting the change and movement in the content of the liquid water.

It is difficult to apply the flow characteristics of HBS to the field. The production process on site is a macroscopic field-scale project, and the local microscopic data are not suited to support the change in the overall structure. Therefore, the research idea from micro to macro is a network staggered structure, as shown in Figure 8, below: (1) select a target point to be exploited in the actual occurrence area and attain samples in situ by drilling exploratory wells; (2) send samples to test by micro equipment in the laboratory and get a series of physical parameters (porosity, saturation, thickness, and distribution characteristics); (3) model the parameters to numerically simulate gas–liquid two-phase flow pore in the HBS; and (4) establish proper permeability characteristics of the equation according to the flow characteristics. The equation is inverted to the actual reservoir by similarity effect and is checked.

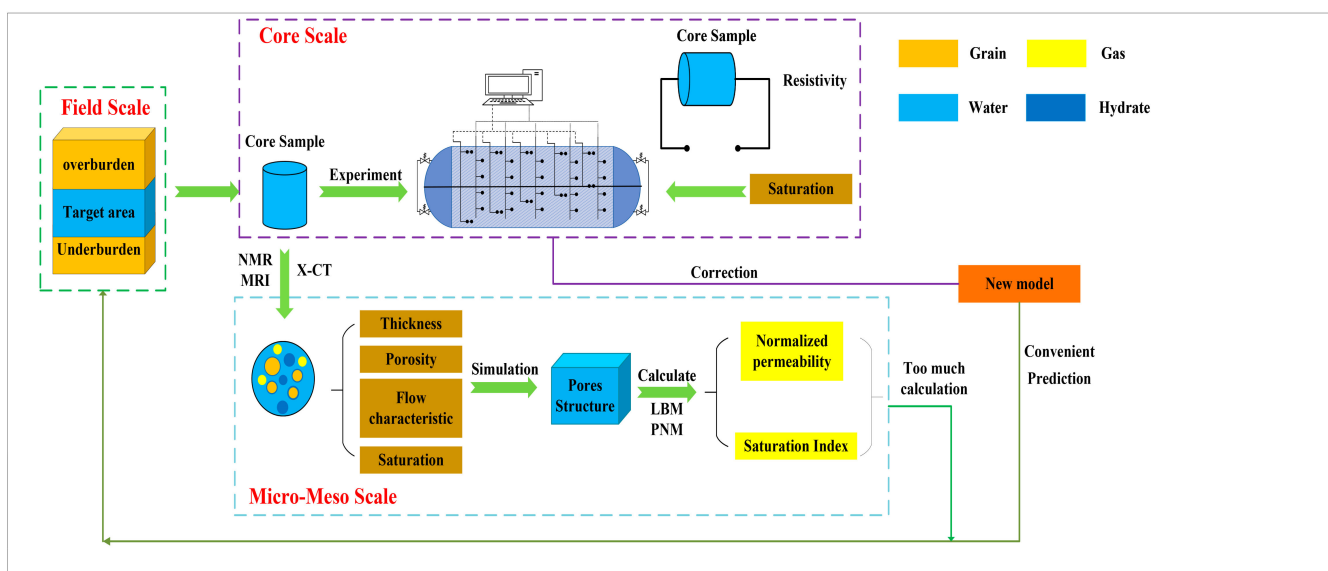


Figure 8. Field-scale permeability simulation based on combined micro-macro research.

Currently, there are two main methods for permeability research of HBS: one is to send the natural core obtained on site to the laboratory equipment for permeability measurement experiment and find the functional relationship between saturation and permeability through the experimental data. In this process, the determination of saturation is a difficult problem to solve. Traditional methods combine pressure data with the Peng–Robinson equation to calculate the saturation, which is often inaccurate. The saturation results can only reflect the whole value and cannot describe the saturation distribution of different areas. Therefore, resistivity measurement is introduced into the evaluation experiment of saturation measurement. Another method to study permeability is using high-precision microscopic instruments to obtain the corresponding saturation distribution, porosity, thickness, and flow characteristics. The distribution characteristics of HBS are reconstructed from these microscopic data to simulate the pore-throat structure. Furthermore, the permeability is calculated by PNM and LBM. Compared with the experimental method, computer simulation requires much calculation and is unsuitable for field-scale application. Therefore, the most direct and effective method is to build a permeability prediction model,

including hydrate saturation, and use experiments and microscopic instruments to correct and improve it to be applied in field exploitation.

4.1. Seepage Theories in NGHs Using CT Technique

The microscopic CT technique is a visual quantitative analysis method that can easily obtain 3D layers of porous media [85], which has been successively applied to relevant studies of gas hydrates since 1970. The CT technique is based on mapping the spatial-distributed absorption of the X-ray beam as it passes through the samples [86]. This technique can be used to image the distribution and arrangement of different components of HBS, to determine the microscopic pore structure of HBS and evaluate the flow capacity of the fluid.

The CT technique mainly obtains X-ray projection sequences with different attenuation coefficients through the difference in X-ray absorption degree of different components within the sample. This technique converts directly obtained two-dimensional grey density images into image binarization in a reasonable threshold area, and finally, superpositions the physical space to form three-dimensional numerical HBS cores. The specific research process of HBS microscopic detection and analysis by using the CT technique includes the following steps: (1) grey image acquisition, (2) image preprocessing, (3) core component extraction, (4) pore parameter analysis, and so on, as shown in Figure 9.

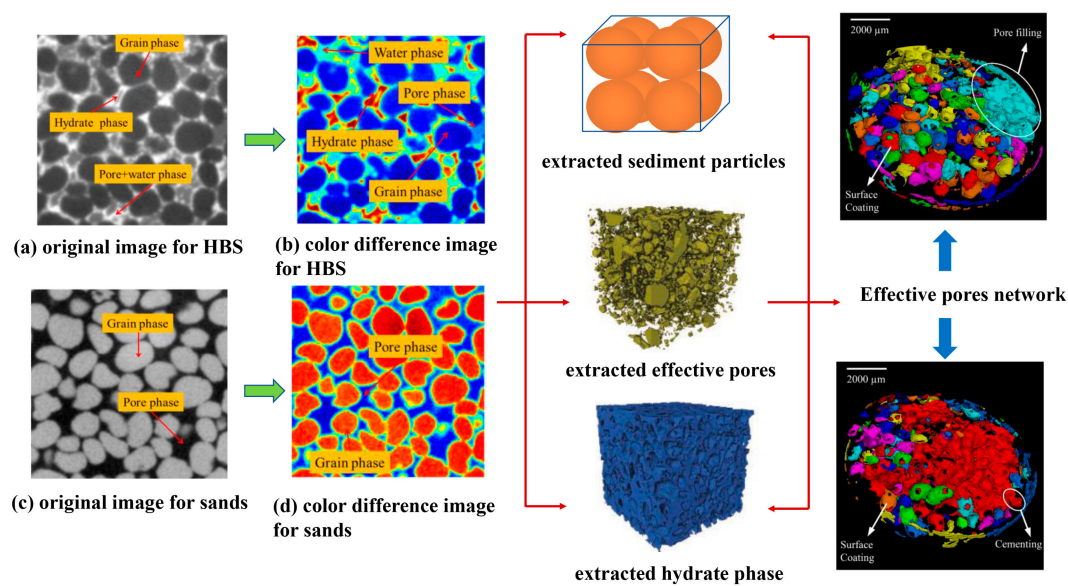


Figure 9. Analytical workflow of the pore-structure characteristics of the hydrate-bearing sediments using digital core method based on CT scanning (pores and phase from Zhang [87], (a–d) from Zhao [88], pore network from Jarrar [89]).

4.1.1. Grey Image Acquisition

According to the Lambert–Bee equation:

$$I_1 = I_0 e^{-\Gamma d} \quad (50)$$

where I_1 and I_0 represent the intensity of the X-ray transmitted through hydrate samples and initial radiation intensity at incident, respectively. I_0 can be controlled by an X-ray source and I_1 is gained by CT Scanner. d is the thickness of the hydrate sample. Γ is the linear absorption coefficient [90], which can be calculated by Equation (51):

$$\Delta = C \times (\Gamma - \Gamma_W) / \Gamma_W \quad (51)$$

where C is constant and Δ is CT number reported by CT image data. Γ_W is the linear absorption coefficient of pure water and is a comparison parameter. The value of Δ reflects

the change in CT images of different grey levels rather than an absolute value, so the higher the value is, the higher the sample density.

4.1.2. Image Preprocessing

Different phases of HBS in CT images are represented by different grey intensities. The similar difference in grey intensity is hard to distinguish by human vision. In addition, the hydrate phase and water phases are difficult to extract from the pores in multiphase materials with hydrates, which cause misunderstanding and overestimate the hydrate phase. Therefore, a color difference phase separation method is developed to deal with the problem. This method can highlight the hydrate phase and some tiny component phases with weak and similar gray intensity. The original grey intensity images are later converted to the color difference images. Moreover, the hydrate and grain phases in these colored images based on their color bars are also easily distinguished.

4.1.3. Core Component Extraction

HBS can be divided into sediment particles, pores, and hydrate phase. Sediment particles are the skeleton used to host HBS. The characteristics of the pores reflect the distribution, migration, dissolution, and storage of hydrates in HBS, and the hydrate phase represents the immobile area inside the HBS. More importantly, the pores extracted are effectively connected to each other because only the effective pores can observe the change in the hydrate phase.

4.1.4. Pore Parameter Analysis

Based on the pore parameters of HBS, many scholars have put forward new theories combined with experiments/simulations. The studies on seepage studies of HBS employing CT techniques are summarized in Table 4.

Liu [91] used the CT technique and simulation to establish an empirical formula for characteristic maximum pore diameter and saturation. Using this formula, a new normalized permeability model based on fractal theory was proposed.

$$k_t = \frac{(a + b - 1) \times \left(\frac{L_0}{\lambda_{\max,0}} \right)^{D_{\tau,0}} \times (\lambda_{\max,t})^{3+D_{\tau,0}D_{t\tau}}}{a + bD_{t\tau} - D_{tf}} \quad (52)$$

where $a = 3/D_{f,0}$, $b = D_{\tau,0}/D_{f,0}$, $\lambda_{\max,0}$, and $\lambda_{\max,t}$ represent maximal pore diameter in sediments without hydrates and normalized maximal pore diameter, respectively.

Kou [92] considered the effect of hydrate occurrence on pore inter-connectivity in HBS; the relationship between interconnectivity degree (m) and hydrate saturation (S_H) can be expressed as

$$m = 1 - S_H \quad (53)$$

The modified equations of normalized permeability are given as follows:

$$k_{t-GC} = (1 - S_H)^{n+3}, n = 1.5 \quad (54)$$

$$k_{t-PF} = \frac{(1 - S_H)^{n+4}}{(1 + S_H^{0.5})^2}, n = 0.7 \times S_H + 0.3 \quad (55)$$

In order to compare the simulated permeability from the real sample structure and the calculated permeability based on permeability reduction models, the KC equations are also employed to calculate the normalized permeability.

Kou [93] built new permeability reduction models to indicate real sample structure based on KC equation. For better prediction, hydrate saturation is modified by average saturation. The normalized permeability of GC, PF, and averaged hydrate saturation are as follows:

$$k_{t-GC} = (1 - \overline{S_H})^n \quad (56)$$

$$k_{t-PF} = (1 - \overline{S}_H)^{n+2} / (1 + \overline{S}_H^{0.5})^2, n = 0.7 \times \overline{S}_H + 0.3 \quad (57)$$

$$\overline{S}_H = \sum_{i=1}^m S_H / m \quad (58)$$

Table 4. The application of CT technique to hydrate seepage studies.

Year	Method	Direction	Results	Reference
2013	CT + Experiment	Calculated the absolute permeability of each phase and detected the movement of the displacement front.	With the increase of saturation, the growth mode from GC to PF.	[94]
2014	CT + PNM	Simulated gas invasion, hydrate decomposition, gas expansion.	Confirmed the fitting parameters in permeability models.	[45]
2016	CT + PNM	Simulated the influence mechanism of particles size and porosity on permeability.	Porosity increases with the increase of particles size.	[95]
2019	CT + Experiment	Seepage experiments on the clayey-silt sediments in the Shenhua area of the South China Sea.	Power-law relation between effective permeability and porosity.	[96]
2019	CT + Simulation	Simulated different existence modes of fractal parameter of pores in sediments and the influence law of pores radius.	Equation (52)	[91]
2020	CT + Experiment	Pore-scale distribution and reformation characteristics of gas hydrate in HBS, during dissociation.	Mass and heat transfer can lead to GC to PF.	[97]
2021	CT + Experiment	Detected pore structure characteristics of NGHs in HBS.	Equations (53)–(55)	[92]
2021	CT + Experiment	The differences in distribution and morphology properties of NGHs under two gas occurrence patterns have been analyzed	During formation, gas diffusion is the crucial factor that influences the growth habit and morphology.	[98]
2021	CT + Experiment	To define the hydrate phase heterogeneity degree of HBS	Equations (56)–(58)	[93]
2022	CT + Experiment	To understand the memory effect of HBS.	Memory effect can not only shorten the induction time of hydrate nucleation but also reduce the formation rate.	[99]
2022	CT + Experiment	To understand the interactions between NGHs decomposition and heat/mass transfer.	The mass transfer of gas shows significant effects on hydrate morphology evolution.	[100]

4.2. Seepage Theories in NGHs by NMR and MRI

It is known that Nuclear Magnetic Resonance (NMR) and Magnetic Resonance Imaging (MRI) are two useful techniques to obtain information about the molecular level and microscopic dynamics.

In NMR, the transverse relaxation time T_2 is an effective parameter for observing the porous media. In the study of HBS, the transverse magnetization attenuation index is M . The relation with time changes follows the law.

This section may be divided into subheadings. It should provide a concise and precise description of the experimental results, their interpretation, as well as the experimental conclusions that can be drawn:

$$M_t = M_0 e^{(-t/T_2)} \quad (59)$$

where M_t and M_0 represent the transverse magnetization vector intensity at any time and the maximum transverse magnetization vector. The velocity of the transverse relaxation process is consistent with the uniformity of the magnetic field in which the nucleus is located, and the internal structure of porous media is more uniform as T_2 gets longer.

As for MRI, the change in liquid water content in HBS pores can be quantitatively detected, and the content of hydrates can be evaluated by the change in MI (mean intensity) data [101]. Zhao [102] found the methane hydrate saturation during the dissociation was obtained from the MRI intensity data. Their results showed that the hydrate saturation initially decreased rapidly, and then slowed down, which was in line with predictions based on pressure solely. The relationship between hydrate saturation with MRI intensity data is as follows:

$$S_{Ht} = \frac{G_0 - G_t}{G_t} \times 100\% \quad (60)$$

On this basis, Chen [103] revised the relationship between saturation and MI data based on experiments. The equation can be given as

$$S_{Ht} = 1.25 \frac{(G_0 - G_t) S_{W0}}{G_t} \times 100\% \quad (61)$$

where S_{W0} , G_0 , and G_t represent the state that the HBS pores are completely saturated with water in the initial stage, the value of MI at the initial time, and MI at any time, respectively.

NMR and MRI are two important methods to study the distribution of water and hydrates in HBS. The formation and decomposition of hydrates can be observed by these two methods, as shown in Figure 10. The summary of the seepage characteristics of HBS employing NMR/MRI techniques is presented in Table 5.

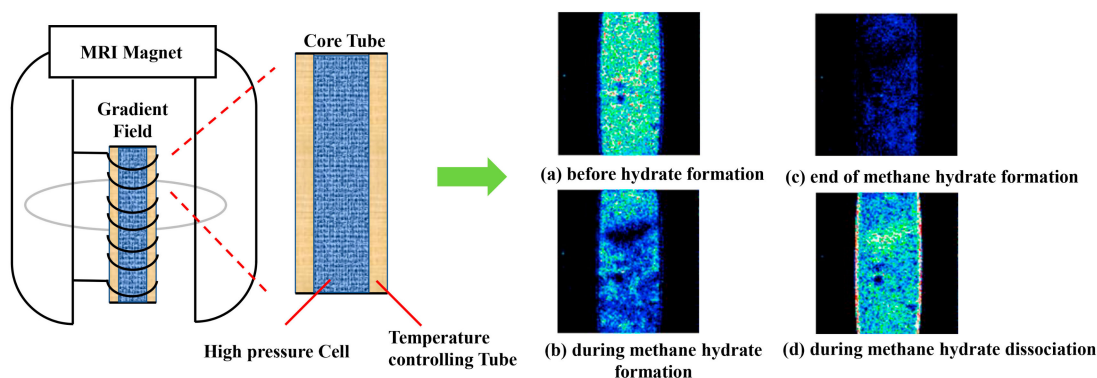


Figure 10. MRI Images during methane hydrate formation and dissociation ((a–d) adapted from Yang [42]).

4.3. Predicting Permeability of HBS by Electrical Resistivity

The Archie formula mainly applies to pure sandstone systems, and there are clays in the actual existence environment of HBS. In order to get closer to the actual seabed environment, the resistivity model needs to be revised in different directions. The resistivity method is applied in HBS, which is mainly developed from two aspects: (1) the distribution and content of the fluid in the HBS are reflected by the value of the resistivity, so as to calculate the saturation and tortuosity of hydrates; (2) resistivity index can be calculated by the ratio of resistivity for a part of the water and complete water, thereby combining the irreducible water content to simultaneously calculate the relative permeability in the water phase of HBS.

Table 5. The seepage characteristics of NMR/MRI technique on hydrate studies.

Year	Method	Subject	Highlights	Reference
2003	NMR + Experiments	Natural samples in Monterey Bay	Measuring relaxation time to reveal hydrates tended to replace water in the largest pore spaces.	[32]
2005	NMR + MRI + Experiments	THF hydrates in the Laboratory	Measuring and monitoring the lattice relaxation times of THF hydrate formation/dissociation and patterns.	[104]
2012	MRI + Experiments	THF hydrates in Laboratory	To investigate the growth law and microstructure of hydrates in porous media, the growth process of THF hydrates under different concentrations.	[105]
2014	NMR + Experiments	Natural samples in shenhu	Pore-filling hydrates significantly affect the permeability of HBS.	[106]
2015	MRI + Experiments	Methane hydrates in Laboratory	Calculation by Equation (60)	[102]
2021	MRI + Experiments	Methane hydrates in Laboratory	Calculation by Equation (61)	[103]

Lee [107] added a muddy modification method to the Archie formula.

$$S_H = 1 - \left(\frac{aR_W(1 - R_H Q_{clay})}{R_H \varphi^m} \right)^{1/n} \quad (62)$$

where R_W , R_H , Q_{clay} , and φ represent resistivity of the connate water, formation resistivity with gas hydrate, effective clay conductivity, and porosity, respectively. a and m are Archie constants. n is an empirically derived parameter close to 2 and varies between 1.715 (unconsolidated sediment) and 2.1661 (sandstone).

Li [108] conducted a three-dimensional study using electrical and acoustic measurement methods and found that the discontinuity of hydrate distribution was caused by concentration, temperature, and fluid viscosity. The relationship between saturation with resistivity can be written as

$$R_H = a \times \varphi \times (1 - S_H)^{-m} R_W \quad (63)$$

where R_W , R_H , and φ represent resistivity of the pore water at a special temperature, formation resistivity with gas hydrate, and porosity, respectively. a and m are empirical parameters set at 1 and 1.5, respectively [63].

Li [109] eliminated the influence of free gas by injecting saline with saturated methane. The results of Archie formula regression under different saturations showed that both the cementation index m and saturation index n deviated significantly from the expected values.

Therefore, the modifications and characteristics of Archie's formula are summarized in Table 6.

4.4. Simulation of Hydrate Seepage under Pore Network

Traditional theoretical models are based on the basis of fixed HBS skeleton, so they are suitable for calculating and evaluating the seepage with the change in hydrate saturation under certain existing conditions. Therefore, it is difficult to characterize the influence of HBS microstructure on the flow capacity. At present, some new simulation methods have been proposed to solve the problem of the difficulty in describing the microstructure inside HBS, among which the widely accepted methods are the Pore Network Model (PNM) and Lattice Boltzmann Method (LBM).

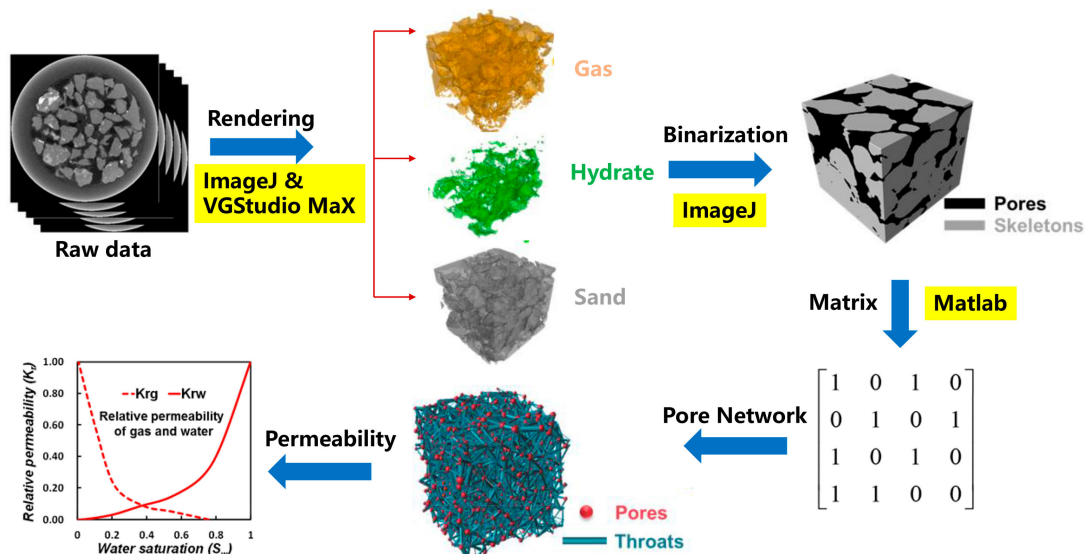
Table 6. The advances in electrical resistivity on hydrate saturation/permeability.

Year	Modification Points	Highlights	Reference
2006	Added the muddy modification	Equation (62)	[107]
2012	Considering the effect of brine saturations.	Exists linear relationship between (R_t/R_w) and $1-S_H$ on log–log coordinates.	[109]
2018	Considering the effect of effective porosity and temperature on the fluid.	Equation (63)	[108]
<2019	Considering the effect of saturation index.	The logarithmic relationship between saturation index and saturation is established.	[110]
2020	Considering the effect of gas, water, hydrate, and sediment on the overall resistance of HBS.	$\frac{L_a}{L} = \frac{1}{ak_{rw}}$	[111]

4.4.1. Pore Network Model

Fatt [112] established PNM to simulate the microstructure as the Pore Network system, which is shown in Figure 11. In this system, the hydrate phase and sand particles are used as the skeleton to provide pore channels for gas and liquid, and then the skeleton is transformed into a 3D structure to build a network. The sphere represents the pores and the tubes simulate the throats. The relative permeability of gas and liquid is calculated by controlling the two-phase flow in the pore structure. Many scholars have established PNM to simulate the influence on permeability in porous media with hydrates. Mahabadi [45] considered the difference between pores and throats and realized the combination of models with the CT technique through the maximum-ball algorithm. In the modified model, hydrate saturation is assigned according to the orders in which it occupies the bigger pores. Yang [113] developed a three-dimensional pore network structure and concluded that the permeability would decrease exponentially with increased hydrate saturation. Li [106] also concluded that permeability decreases exponentially with an increase in saturation by studying the difference between pore filling and grain coating. Heterogeneity in HBS can reduce fluidity and porosity and increase tortuosity in sediments. Dai [39] established the relationship between normalized permeability and hydrate saturation by using the PNM method, in accordance with the Kozeny–Carman equation, as shown in Equation (64).

$$k_t = \frac{(1 - S_H)^3}{(1 + 2S_H)^2} \quad (64)$$

**Figure 11.** The brief procedure of PNM (every unit from Yang, et al. [113]).

The PNM method can better characterize the relation between pore structure and fluid flow, but it is limited in its application. The equivalent process of characterizing the pore space will result in a lack of microscopic pore information. Besides, the over-simplified pore network neither accurately describes the structural characteristics of the pores nor reflects the spatial heterogeneity of hydrate saturation during decomposition.

4.4.2. Lattice Boltzmann Method

LBM is a micro-simulation method that simulates macroscopic characteristics of fluid by statistics of migration and collision of discrete particles among grid points after time and space are completely discrete. The Navier–Stokes equation does not need to be solved when calculating seepage, it only needs to describe the basic laws of discrete particles [114–116]. Some scholars [40,117] used the LBM method to calculate the relation between relative permeability and hydrate saturation in pores of HBS from CT images and put forward Equation (65). Chen [118] observed the formation of xenon hydrates by using CT technology and analyzed the change of gas-phase permeability with hydrate saturation combined with the LBM method, as shown in Equation (66).

$$K_t = -1.8 \times S_H + 1 \quad (65)$$

$$K_t = (1 - S_H) \cdot \exp(-4.95 \times S_H) \quad (66)$$

Compared with the PNM method, the application of the LBM method in the study of HBS is still in the development stage. Many models are limited to single-phase or two-phase flow in homogeneous media, and the chemical reactions between components are ignored during the establishment of microscopic models. However, this method can be used to deal with complex fluid–solid boundaries and multiphase flow interfaces.

5. Challenges and Prospects

Many research results have been achieved in permeability measurements, theoretical models, and multi-phase seepage characteristics of NGHs in Chinese and overseas exploitation. According to the literature review summarized in this paper, Figure 12 is made to summarize the development trend of some seepage studies in recent decades. The results show that there are more studies on the sediments without hydrates, before 2000. Then, after 2000, the research highlights gradually focused on HBS. In the whole research background, the research methods of seepage theories have also changed greatly, as shown in Figure 13. Before 2000, the research methods were more inclined to combine theoretical derivation with experimental verification. After 2000, numerical simulation and microscopic detection gradually began to occupy the space due to the obvious advantages. This difference indicates that the researchers' thinking has gradually transitioned from macroscopic multiphase seepage to microscopic mechanism. However, experimental means still occupy the largest proportion, and it is believed that the future research system will be the integration of theory–experiment–simulation–micro test.

In addition, Table 7 describes the main research progress of seepage theories in sediments that contain hydrates and those that do not. Obviously, the overall research process of hydrates is based on the basic structure of porous media, and a series of prediction models have been established. With the studies ongoing, the models are improved for the microscopic appearance inside the pores and the formation mechanism and distribution characteristics of hydrates.

With the upgrading of technology and the extension of hot spots, the following areas still need to be studied and improved to achieve a breakthrough in the magnitude of production [119]. The key points of development in seepage theories that need to be considered are shown in Figure 14.

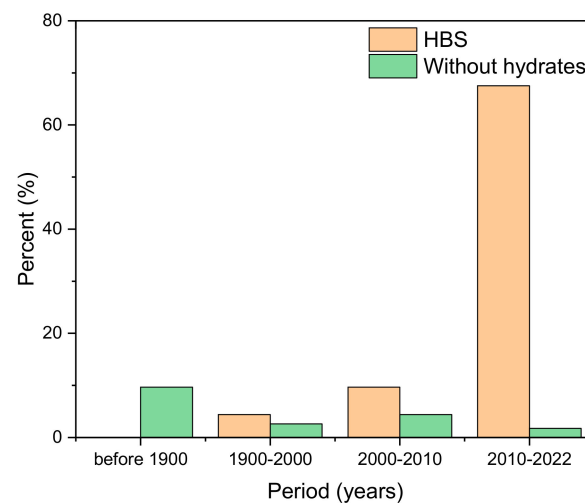


Figure 12. Research-trend of HBS and without hydrates on seepage in past few decades.

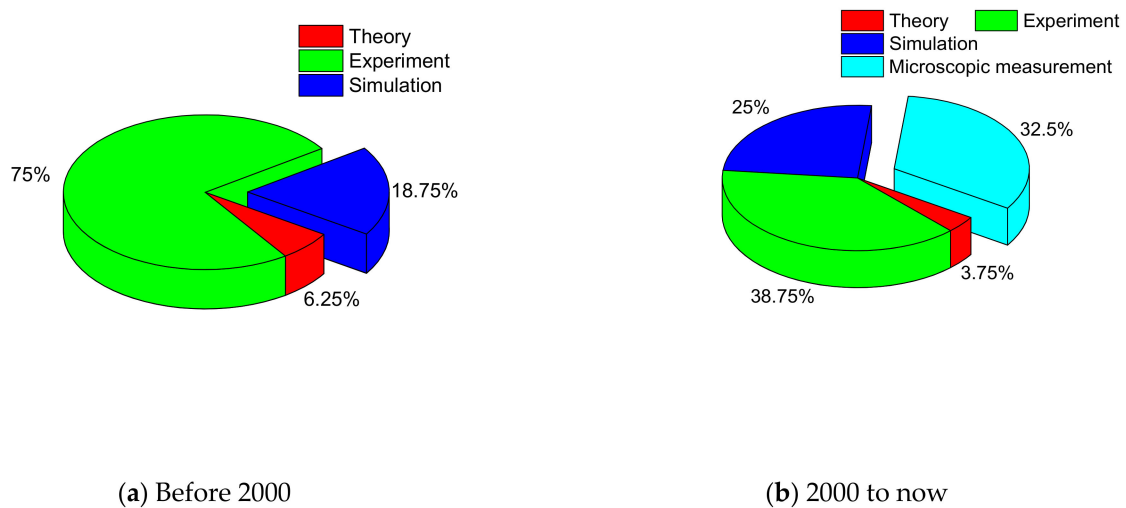


Figure 13. Advances in the research methods of NGHs in past few decades.

Table 7. Main progress and hotspots of seepage theories during past few decades.

Stage	Period	Hotspots
1	Before 1990	Build models and parameters measurements
2	1990–2000	Pore habits of porous media
3	2000–2010	Permeability models modification
4	2010–2020s	Microscopic mechanism

5.1. Influence of Reservoir Heterogeneity on Permeability

Currently, most seepage studies are focused on the coarse-grained HBS with a stable structure of sediments. Due to the single-particle composition and small size, reservoirs tend to form more homogeneous existence environments. Under such conditions, the absolute permeability of HBS measured is generally higher. However, there is heterogeneity in spatial distribution and phase saturation in the actual seafloor target area, which seriously affects production efficiency [120,121]. In particular, water production is affected by the absolute permeability, K_0 of the heterogeneous reservoir [122]. HBS is composed of unconsolidated clayey-silt with different particle sizes. The small particles in these porous media overlap and compress each other, resulting in narrow pore channels and a

pronounced capillary effect. At the same time, the narrow structure of pores makes the connectivity inside the reservoirs worse and affects the flow of gas and liquid in the pores. The existence of mud not only changes the size of the pore-throats, but makes the surface of the sediment particles coarse. Irregular shape will also affect the flow of the fluid medium in HBS. Furthermore, the muddy soft soil structure is characterized by a large specific surface and strong adsorption, so there are abundant charges in the soft soil. The uneven distribution of charges will make the force field between the components unbalanced. The most direct effect is that the cation adsorbed by clay particles will interact with water molecules to form water film, which will change the wettability of the particle surface and reduce the permeability of HBS.

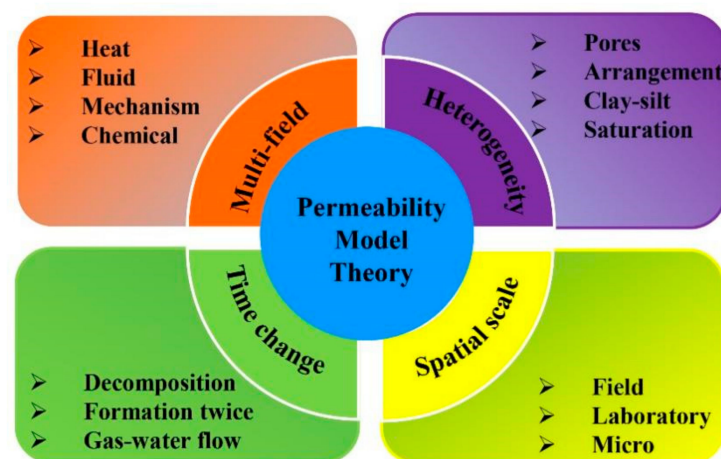


Figure 14. Key points of development in seepage theories in HBS.

5.2. Influence of Spatial Scale on Permeability

Existing research methods mainly use core and pore scale to carry out experiments and simulations. To comprehensively and systematically study the seepage mechanism of clayey-silt NGHs during the exploitation, it is necessary to explore the correlation mechanism between the occurrence characteristics of clayey-silt NGHs and the gas–water seepage characteristics by combining the field scale of HBS. In the actual environment, hydrates are stratified, mainly in the form of lenticular, nodular, block, and vein, and there are fractures in HBS. This distribution heterogeneity causes fluid migration within HBS to become discontinuous, resulting in reduced permeability.

5.3. Effect of Time Change on Permeability

The changeable permeability of HBS is not only affected by the heterogeneity of reservoirs, but will also constantly impact the gas–liquid distribution in the pores during the decomposition process of hydrates. Besides, distribution is linked with many factors, such as composition of sediments, pore structure, interface effect, and composition of pore water. Consequently, the decomposition process of hydrates is a complex heat–fluid–mechanical–chemical coupling model: decomposition needs to absorb heat. The seepage characteristics of HBS affect the flow of decomposed gas and liquid from the front of the HBS to the production well and also determine the pressure distribution and heat transfer in HBS. Moreover, pressure and temperature will directly affect the rate of the decomposition reaction. At the same time, the transformative structure caused by hydrate decomposition will affect the seepage and heat transfer characteristics of gas–water–sand in the sediments. These factors influence each other, restrict each other, and change dynamically.

5.4. Effect of Gas–Liquid Phase Change on Permeability

Because of the multi-phase flow of gas, water, and sand in the production process, the changeable seepage inside HBS is not enough to describe by using hydrate saturation as the

only variable. Therefore, the influence of the relative flow capacity of different phases in the microscopic pores of sediments should be viewed dialectically from the point of relative permeability. Generally speaking, the relative permeability of the gas phase and the water phase is negatively correlated. The relative permeability of the water phase increases with the increase in the water phase saturation, while the relative permeability of the gas phase decreases. Hence, it is necessary to indirectly increase the relative permeability in the gas phase by changing the relative permeability in the water phase to increase the final gas production. Under the existing experimental technology, it is difficult to obtain the relative permeability of each phase in the laboratory due to these two reasons: the experiment requires controlling the hydrate saturation and ensuring that the relative permeability of gas and water are measured at different saturation levels and, on the other hand, to accurately maintain the system temperature and pressure to meet the equilibrium of hydrate phase under high-pressure and low-temperature conditions.

6. Conclusions and Suggestions

The seepage theories of NGHs are still developing, and it is difficult to describe the complex conditions of the actual sediments and the seepage characteristics. This paper summarized and introduced several common permeability models in hydrate-bearing/hydrate-free sediments. CT, MRI/MRI, and resistivity play an important role in describing pore morphology and seepage characteristics of HBS. These new technologies can also be combined with experiments and simulations to provide fundamental information for building more accurate permeability prediction models of HBS.

Although significant developments have been made in obtaining the pore habits and seepage capacity of HBS, we suggest the following recommendations:

- (1) Comprehensive studies should be conducted on heterogeneous physical properties of sediments, such as particle arrangement, diameter, pore-throat size, and clay.
- (2) New technologies should be applied to improve the modelling of skeletal structure and hydrate occurrence patterns in HBS.
- (3) More research involving phase state change, heat and mass transfer, mechanical properties, and the combination of multiple fluids during the formation/decomposition of HBS should be carried out.

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Nomenclature

r	radius of capillary (m)
L	length of capillary (m)
ΔP	pressure difference (MPa)
μ	viscosity of fluid (mPa·s)
q	flow rate of single capillary on per unit cross-sectional area (m ³ /s)
Q	cumulative flow rate on per unit cross-sectional area (m ³ /s)
d	thickness of hydrate (m)
φ	porosity
K	permeability (D)
k	normalized permeability
S	phase saturation
τ	tortuosity
ν	shape factor
σ	specific surface (cm ² /cm ³)
F	formation factor, constant
R	resistivity ($\Omega \cdot m$)
α	fractal parameter
D	fractal dimension
X	number of capillaries
C_p	ratio of sediment particle radius to hydrate particle radius
π	3.14159265
a, b, β, η, Z	empirical parameter, variable
ψ	viscosity ratio of gas to liquid
A	total area
l	clay parameter, variable
λ	pore diameter
C	constant
L_a	actual flow length (m)
ε	pores ratio
e	2.718281828459
γ	interfacial tension (dyn/cm)
θ	angle, °
ρ	percentage of the entire pore occupied by fluid
B	linear regression coefficient
Ω	intercept
I	intensity
Δ	CT number
Γ	linear absorption coefficient
M	transverse magnetization vector intensity
t	at any time
T	Time (s)
G	value of MI
Superscript	
PF	pore filling
GC	grain coating
N, M	weight index
n	saturation index
Subscript	
0	initial condition without hydrate
H	hydrate phase
W	water phase
wr	irreducible water phase
g	gas phase
c	capillary
t	normalized parameter

f	pore-size
r	relative amount
min	Minimal state
max	maximum state
i	gas/liquid phase
1,2	parameter
Abbreviation	
NGH	Natural gas hydrates
HBS	Hydrate-Bearing sediments
NMR	nuclear magnetic resonance
MRI	magnetic resonance imaging
CT	computed tomography

References

1. Reagan, M.T.; Moridis, G.J.; Johnson, J.N.; Pan, L.; Freeman, C.M.; Boyle, K.L.; Keen, N.D.; Husebo, J. Field-Scale Simulation of Production from Oceanic Gas Hydrate Deposits. *Transp. Porous Media* **2015**, *108*, 151–169. [\[CrossRef\]](#)
2. Sloan, E.D. Fundamental principles and applications of natural gas hydrates. *Nature* **2003**, *426*, 353–359. [\[CrossRef\]](#) [\[PubMed\]](#)
3. Veluswamy, H.P.; Kumar, R.; Linga, P. Hydrogen storage in clathrate hydrates: Current state of the art and future directions. *Appl. Energy* **2014**, *122*, 112–132. [\[CrossRef\]](#)
4. Changyu, S.; Wenzhi, L.; Xin, Y.; Fengguang, L.; Qing, Y.; Liang, M.; Jun, C.; Bei, L.; Guangjin, C. Progress in research of gas hydrate. *Chin. J. Chem. Eng.* **2011**, *19*, 151–162.
5. Reagan, M.T.; Moridis, G.J.; Collett, T.S.; Boswell, R.; Sloan, E.D. Toward Production From Gas Hydrates: Current Status, Assessment of Resources, and Simulation-Based Evaluation of Technology and Potential. *SPE Reserv. Eval. Eng.* **2009**, *12*, 745–771.
6. Chong, S.-H.; Santamarina, J.C. Soil compressibility models for a wide stress range. *J. Geotech. Geoenviron. Eng.* **2016**, *142*, 06016003. [\[CrossRef\]](#)
7. Collett, T.; Bahk, J.J.; Baker, R.; Boswell, R.; Divins, D.; Frye, M.; Goldberg, D.; Husebø, J.; Koh, C.; Malone, M. Methane Hydrates in Nature—Current Knowledge and Challenges. *J. Chem. Eng. Data* **2015**, *60*, 319–329. [\[CrossRef\]](#)
8. Makogon, Y.F. Natural gas hydrates—A promising source of energy. *J. Nat. Gas Sci. Eng.* **2010**, *2*, 49–59. [\[CrossRef\]](#)
9. Kim, J.; Moridis, G.J.; Rutqvist, J. Coupled flow and geomechanical analysis for gas production in the Prudhoe Bay Unit L-106 well Unit C gas hydrate deposit in Alaska. *J. Pet. Sci. Eng.* **2012**, *92*, 143–157. [\[CrossRef\]](#)
10. Zhang, Z.G.; Yu, W.; Gao, L.F.; Zhang, Y.; Liu, C.S. Marine Gas Hydrates: Future Energy or Environmental Killer? *Energy Procedia* **2012**, *16*, 933–938. [\[CrossRef\]](#)
11. Boswell, R.; Yoneda, J.; Waite, W.F. India National Gas Hydrate Program Expedition 02 summary of scientific results: Evaluation of natural gas-hydrate-bearing pressure cores. *Mar. Pet. Geol.* **2019**, *108*, 143–153. [\[CrossRef\]](#)
12. Yoo, D.G.; Kang, N.K.; Yi, B.Y.; Kim, G.Y.; Ryu, B.J.; Lee, K.; Lee, G.H.; Riedel, M. Occurrence and seismic characteristics of gas hydrate in the Ulleung Basin, East Sea. *Mar. Pet. Geol.* **2013**, *47*, 236–247. [\[CrossRef\]](#)
13. Yoneda, J.; Masui, A.; Konno, Y.; Jin, Y.; Egawa, K.; Kida, M.; Ito, T.; Nagao, J.; Tenma, N. Mechanical properties of hydrate-bearing turbidite reservoir in the first gas production test site of the Eastern Nankai Trough. *Mar. Pet. Geol.* **2015**, *66*, 471–486. [\[CrossRef\]](#)
14. Song, Y.; Yang, L.; Zhao, J.; Liu, W.; Yang, M.; Li, Y.; Liu, Y.; Li, Q. The status of natural gas hydrate research in China: A review. *Renew. Sustain. Energy Rev.* **2014**, *31*, 778–791. [\[CrossRef\]](#)
15. Li, J.F.; Ye, J.L.; Qin, X.W.; Qiu, H.J.; Wu, N.Y.; Lu, H.L.; Xie, W.W.; Lu, J.A.; Peng, F.; Xu, Z.Q. The first offshore natural gas hydrate production test in South China Sea. *China Geol.* **2018**, *1*, 5–16. [\[CrossRef\]](#)
16. Ye, J.; Qin, X.; Xie, W.; Lu, H.; Ma, B.; Qiu, H.; Liang, J.; Lu, J.A.; Kuang, Z.; Lu, C. Main progress of the second gas hydrate trial production in the South China Sea. *Geol. China* **2020**, *47*, 557–568.
17. Davy, H. On some of the combinations of oxymuriatic acid gas and oxygen and on the chemical relations of the properties. *Phil. Trans. Roy. Soc.* **1811**, *101*, 30–55.
18. Hammerschmidt, E. Formation of gas hydrates in natural gas transmission lines. *Ind. Eng. Chem.* **1934**, *26*, 851–855. [\[CrossRef\]](#)
19. Yi, W.; Li, X.S.; Gang, L.; Huang, N.S.; Feng, J.C. Experimental study on the hydrate dissociation in porous media by five-spot thermal huff and puff method. *Fuel* **2014**, *117*, 688–696.
20. Moridis, G.J.; Kowalsky, M.B.; Pruess, K. Depressurization-Induced Gas Production From Class-1 Hydrate Deposits. *SPE Reserv. Eval. Eng.* **2007**, *10*, 458–481. [\[CrossRef\]](#)
21. Eslamimanesh, A.; Mohammadi, A.H.; Richon, D.; Naidoo, P.; Ramjugernath, D. Application of gas hydrate formation in separation processes: A review of experimental studies. *J. Chem. Thermodyn.* **2012**, *46*, 62–71. [\[CrossRef\]](#)
22. Ohgaki, K.; Takano, K.; Sangawa, H.; Matsubara, T.; Nakano, S. Methane Exploitation by Carbon Dioxide from Gas Hydrates—Phase Equilibria for CO₂-CH₄ Mixed Hydrate System. *J. Chem. Eng. Jpn.* **1996**, *29*, 478–483. [\[CrossRef\]](#)
23. Xu, C.; Li, X.; Cai, J.; Chen, Z.; Chen, C. Advance on simulation exploitation of natural gas hydrate by replacement with CO₂. *CIESC J.* **2013**, *64*, 2309–2315.

24. Cui, Y.; Cheng, L.; Wu, M.; Yue, P.; Luo, W. Review of exploration and production technology of natural gas hydrate. *Adv. Geo-Energy Res.* **2018**, *2*, 53–62. [\[CrossRef\]](#)
25. Li, B.; Wei, W.N.; Wan, Q.C.; Peng, K.; Chen, L.L. Numerical Investigation into the Development Performance of Gas Hydrate by Depressurization Based on Heat Transfer and Entropy Generation Analyses. *Entropy* **2020**, *22*, 1212. [\[CrossRef\]](#)
26. Jingchun, F.; Xiaosen, L.; Yi, W.; Yu, Z.; Gang, L. Three-dimension Experimental Investigation of Hydrate Dissociation by the Combined Method with Dual Horizontal Wells. *Geoscience* **2016**, *30*, 929–936.
27. Jin, L.; Wang, G.; Wang, Z.; Jing, C.; Fan, X. A review on pore structure characterization in tight sandstones. *Earth Sci. Rev.* **2018**, *177*, 436–457.
28. Ren, X.; Zhao, Y.; Deng, Q.; Li, D.; Wang, D. A relation of hydraulic conductivity–Void ratio for soils based on Kozeny-carman equation. *Eng. Geol.* **2016**, *213*, 89–97. [\[CrossRef\]](#)
29. Ren, X.W.; Santamarina, J.C. The hydraulic conductivity of sediments: A pore size perspective. *Eng. Geol.* **2018**, *233*, 48–54. [\[CrossRef\]](#)
30. Priest, J.A.; Druce, M.; Roberts, J.; Schultheiss, P.; Nakatsuka, Y.; Suzuki, K. PCATS Triaxial: A new geotechnical apparatus for characterizing pressure cores from the Nankai Trough, Japan. *Mar. Pet. Geol.* **2015**, *66*, 460–470. [\[CrossRef\]](#)
31. Nimblett, J.; Ruppel, C. Permeability evolution during the formation of gas hydrates in marine sediments. *J. Geophys. Res. B Solid Earth* **2003**, *108*, 2420. [\[CrossRef\]](#)
32. Kleinberg, R.L.; Flaum, C.; Griffin, D.D.; Brewer, P.G.; Malby, G.E.; Peltzer, E.T.; Yesinowski, J.P. Deep sea NMR: Methane hydrate growth habit in porous media and its relationship to hydraulic permeability, deposit accumulation, and submarine slope stability. *J. Geophys. Res. B Solid Earth* **2003**, *108*, 2508. [\[CrossRef\]](#)
33. Masuda, Y.; Naganawa, S.; Ando, S.; Sato, K. *Numerical Calculation of Gas Production Performance from Reservoirs Containing Natural Gas Hydrates*; Society of Petroleum Engineers: Long Beach, CA, USA, 1997.
34. Katagiri, J.; Konno, Y.; Yoneda, J.; Tenma, N. Pore-scale modeling of flow in particle packs containing grain-coating and pore-filling hydrates: Verification of a Kozeny–Carman-based permeability reduction model. *J. Nat. Gas Sci. Eng.* **2017**, *45*, 537–551. [\[CrossRef\]](#)
35. Moridis, G.; Apps, J.; Pruess, K.; Myer, L. EOSHYDR: A TOUGH2 Module for CH₄-Hydrate Release and Flow in the Subsurface. In *Ernest Orlando*; Lawrence Berkeley National Laboratory: Berkeley, CA, USA, 1998.
36. Stone, H.L. Probability Model for Estimating Three-Phase Relative Permeability. *J. Pet. Technol.* **1970**, *22*, 214–218. [\[CrossRef\]](#)
37. Delli, M.L.; Grozic, J.L. Prediction performance of permeability models in gas-hydrate-bearing sands. *SPE J.* **2013**, *18*, 274–284. [\[CrossRef\]](#)
38. Delli, M.L.; Grozic, J. Experimental determination of permeability of porous media in the presence of gas hydrates. *J. Pet. Sci. Eng.* **2014**, *120*, 1–9. [\[CrossRef\]](#)
39. Dai, S.; Seol, Y. Water permeability in hydrate-bearing sediments: A pore-scale study. *Geophys. Res. Lett.* **2014**, *41*, 4176–4184. [\[CrossRef\]](#)
40. Kang, D.H.; Yun, T.S.; Kim, K.Y.; Jang, J. Effect of hydrate nucleation mechanisms and capillarity on permeability reduction in granular media. *Geophys. Res. Lett.* **2016**, *43*, 9018–9025. [\[CrossRef\]](#)
41. Lv, J.; Zhao, J.; Jiang, L.; Liu, Y.; Mu, H. A review of micro computed tomography studies on the gas hydrate pore habits and seepage properties in hydrate bearing sediments. *J. Nat. Gas Sci. Eng.* **2020**, *83*, 103555. [\[CrossRef\]](#)
42. Yang, M.; Chong, Z.R.; Zheng, J.; Song, Y.; Linga, P. Advances in nuclear magnetic resonance (NMR) techniques for the investigation of clathrate hydrates. *Renew. Sustain. Energy Rev.* **2016**, *74*, 1346–1360. [\[CrossRef\]](#)
43. Ren, X.; Guo, Z.; Ning, F.; Ma, S. Permeability of hydrate-bearing sediments. *Earth Sci. Rev.* **2020**, *220*, 103100. [\[CrossRef\]](#)
44. Jang, J.; Santamarina, J.C. Hydrate bearing clayey sediments: Formation and gas production concepts. *Mar. Pet. Geol.* **2016**, *77*, 235–246. [\[CrossRef\]](#)
45. Mahabadi, N.; Jang, J. Relative water and gas permeability for gas production from hydrate-bearing sediments. *Geochem. Geophys. Geosyst.* **2014**, *15*, 2346–2353. [\[CrossRef\]](#)
46. Mahabadi, N.; Dai, S.; Seol, Y.; Sup Yun, T.; Jang, J. The water retention curve and relative permeability for gas production from hydrate-bearing sediments: Pore-network model simulation. *Geochem. Geophys. Geosyst.* **2016**, *17*, 3099–3110. [\[CrossRef\]](#)
47. Dai, S.; Santamarina, J.C.; Waite, W.F.; Kneafsey, T.J. Hydrate morphology: Physical properties of sands with patchy hydrate saturation. *J. Geophys. Res. B Solid Earth* **2012**, *117*, B11205. [\[CrossRef\]](#)
48. Waite, W.F.; Santamarina, J.C.; Cortes, D.; Dugan, B.; Yun, T.S. Physical properties of hydrate-bearing sediments. *Rev. Geophys.* **2009**, *47*, 465–484. [\[CrossRef\]](#)
49. Collett, T.S.; Riedel, M.; Cochran, J.; Boswell, R.; Kumar, P.; Sathe, A.; Expedition, N. *Geologic Controls on the Occurrence of Gas Hydrates in the Indian Continental Margin: Results of the Indian National Gas Hydrate Program (NGHP) Expedition 01 Initial Reports*; AAPG Annual Convention: San Antonio, TX, USA, 2008.
50. Opening a New Era of “Combustible Ice” Exploration—an Overview of the Results of Natural Gas Hydrate Resource Exploration. Available online: https://www.cgs.gov.cn/xwl/cgkx/201603/t20160309_285790.html (accessed on 31 July 2014).
51. Murray, D.R.; Fukuhara, M.R.; Osawa, O.R.; Endo, T.R.; Namikawa, T.R. Saturation, Acoustic Properties, Growth Habit, and State of Stress of a Gas Hydrate Reservoir from Well Logs. *Petrophys* **2006**, *47*, 129–137.
52. Singh, H.; Myshakin, E.M.; Seol, Y. A nonempirical relative permeability model for hydrate-bearing sediments. *SPE J.* **2019**, *24*, 547–562. [\[CrossRef\]](#)

53. Tohidi, B.; Anderson, R.; Clennell, M.B.; Burgass, R.W.; Biderkab, A.B. Visual observation of gas-hydrate formation and dissociation in synthetic porous media by means of glass micromodels. *Geology* **2001**, *29*, 867–870. [\[CrossRef\]](#)
54. Mahabadi, N.; Dai, S.; Seol, Y.; Jang, J. Impact of hydrate saturation on water permeability in hydrate-bearing sediments. *J. Pet. Sci. Eng.* **2019**, *174*, 696–703. [\[CrossRef\]](#)
55. Scheidegger, A.E. The Physics of Flow Through Porous Media. *Soil Sci.* **1958**, *86*, 355. [\[CrossRef\]](#)
56. Yasuhide, S.; Takeshi, K.; Kuniyuki, M.; Norio, T.; Tsutomu, Y.; George, Z. Laboratory-Scale Experiments of the Methane Hydrate Dissociation Process in a Porous Media and Numerical Study for the Estimation of Permeability in Methane Hydrate Reservoir. *J. Thermodyn.* **2010**, *2010*, 9879–9884.
57. Pape, H.; Clauser, C.; Iffland, J. Permeability prediction based on fractal pore-space geometry. *Geophysics* **1999**, *64*, 1447–1460. [\[CrossRef\]](#)
58. Pape, H.; Clauser, C.; Iffland, J. Variation of Permeability with Porosity in Sandstone Diagenesis Interpreted with a Fractal Pore Space Model. *Pure Appl. Geophys.* **2000**, *157*, 603–619. [\[CrossRef\]](#)
59. Daigle, H. Relative permeability to water or gas in the presence of hydrates in porous media from critical path analysis. *J. Pet. Sci. Eng.* **2016**, *146*, 526–535. [\[CrossRef\]](#)
60. Peng, X.; Yu, B. Developing a new form of permeability and Kozeny–Carman constant for homogeneous porous media by means of fractal geometry-ScienceDirect. *Adv. Water Resour.* **2008**, *31*, 74–81.
61. Bo-Ming, Y.; Jian-Hua, L. A geometry model for tortuosity of flow path in porous media. *Chin. Phys. Lett.* **2004**, *21*, 1569–1571. [\[CrossRef\]](#)
62. Boudreau, B.P. The diffusive tortuosity of fine-grained unlithified sediments. *Geochim. Cosmochim. Acta* **1996**, *60*, 3139–3142. [\[CrossRef\]](#)
63. Sen, P.N.; Scala, C.; Cohen, M.H. A self-similar model for sedimentary rocks with application to the dielectric constant of fused glass beads. *Geophysics* **1981**, *46*, 781–795. [\[CrossRef\]](#)
64. Iversen, N.; Bo, B.J. Diffusion coefficients of sulfate and methane in marine sediments: Influence of porosity. *Geochim. Cosmochim. Acta* **1993**, *57*, 571–578. [\[CrossRef\]](#)
65. Liu, L.; Zhang, Z.; Ning, F.; Li, C.; Cai, J.; Wang, D.; Liu, C.; Wu, N. A fractal model for the relative permeability prediction of hydrate-bearing sediments. *SCIENTIA SINICA Phys. Mech. Astron.* **2019**, *49*, 034614. [\[CrossRef\]](#)
66. Zhang, Z.; Li, C.; Ning, F.; Liu, L.; Cai, J.; Liu, C.; Wu, N.; Wang, D. Pore fractal characteristics of hydrate-bearing sands and implications to the saturated water permeability. *J. Geophys. Res. B Solid Earth* **2020**, *125*, e2019JB018721. [\[CrossRef\]](#)
67. Luo, N. Numerical analysis of Archie formulae and its meanings. *Acta Pet. Sin.* **2007**, *28*, 111–114.
68. Kozeny, J. Über kapillare leitung der wasser in boden. *R. Acad. Sci. Vienna Proc. Cl. I* **1927**, *136*, 271–306.
69. Carman, P.C. Fluid flow through granular beds. *Trans. Inst. Chem. Eng.* **1937**, *15*, 150–166. [\[CrossRef\]](#)
70. Carman, P.C. Permeability of saturated sands, soils and clays. *J. Agric. Sci.* **1939**, *29*, 262–273. [\[CrossRef\]](#)
71. Carman, P.C. *Flow of Gases through Porous Media*; Butterworths Scientific Publications: London, UK, 1956.
72. Zhang, J.; Luo, J.; Xia, Y.; Wenliang, H.U.; Zhang, G.D.; Yuchun, H.E.; Yang, K.B. Limitation analysis and modification of the Archie equation. *Chin. J. Geophys.* **2018**, *61*, 311–322.
73. Zhisong, Z. Theoretical roots of Archie formulas. *Prog. Geophys.* **2020**, *35*, 1514–1522.
74. Spangenberg, E. Modeling of the influence of gas hydrate content on the electrical properties of porous sediments. *J. Geophys. Res. B Solid Earth* **2001**, *106*, 6535–6548. [\[CrossRef\]](#)
75. Li, G.; Wu, D.M.; Li, X.S.; Lv, Q.N.; Li, C.; Zhang, Y. Experimental measurement and mathematical model of permeability with methane hydrate in quartz sands. *Appl. Energy* **2017**, *202*, 282–292. [\[CrossRef\]](#)
76. Genuchten, V.; Th, M. A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Sci. Soc. Am. J.* **1980**, *44*, 892–898. [\[CrossRef\]](#)
77. Parker, J.C.; Lenhard, R.J.; Koppusamy, T. A parametric model for constitutive properties governing multiphase flow in porous media. *Water Resour. Res.* **1987**, *23*, 618–624. [\[CrossRef\]](#)
78. Singh, H.; Mahabadi, N.; Myshakin, E.M.; Seol, Y. A Mechanistic Model for Relative Permeability of Gas and Water Flow in Hydrate-Bearing Porous Media With Capillarity. *Water Resour. Res.* **2019**, *55*, 3414–3432. [\[CrossRef\]](#)
79. Timur, A. An investigation of permeability, porosity, and residual water saturation relationships. *Log. Anal.* **1968**, *9*, 8–17.
80. Purcell, W.R. Capillary Pressures-Their Measurement Using Mercury and the Calculation of Permeability Therefrom. *J. Pet. Technol.* **1949**, *186*, 39–48. [\[CrossRef\]](#)
81. Kolodzie, S. Analysis of Pore Throat Size And Use of the Waxman-Smiths Equation To Determine Oil in Spindle Field, Colorado. In Proceedings of the SPE 55th Annual Technical Conference and Exhibition, Dallas, TX, USA, 21 September 1980.
82. Swanson, B. A Simple Correlation Between Permeabilities and Mercury Capillary Pressures. *J. Pet. Technol.* **1981**, *33*, 2498–2504. [\[CrossRef\]](#)
83. Pittman, E.D. Relationship of porosity and permeability to various parameters derived from mercury injection-capillary pressure curves for sandstone. *AAPG Bull.* **1992**, *76*, 191–198.
84. Bryant, W.R.; Hottman, W.; Trabant, P. Permeability of unconsolidated and consolidated marine sediments, Gulf of Mexico. *Mar. Georesour. Geotechnol.* **1975**, *1*, 1–14. [\[CrossRef\]](#)
85. Cnudde, V.; Boone, M.N. High-resolution X-ray computed tomography in geosciences: A review of the current technology and applications. *Earth Sci. Rev.* **2013**, *123*, 1–17. [\[CrossRef\]](#)

86. Li, S.; Liu, L.; Chai, P.; Li, X.; Wei, L. Imaging hydraulic fractures of shale cores using combined positron emission tomography and computed tomography (PET-CT) imaging technique. *J. Pet. Sci. Eng.* **2019**, *182*, 106283. [\[CrossRef\]](#)
87. Yongchao, Z.; Changling, L.; Nengyou, W. Advances in the pore-structure characteristics and microscopic seepage numerical simulation of the hydrate-bearing sediments. *Mar. Geol. Front.* **2020**, *36*, 23–33.
88. Zhao, Z.; Zhou, X.-P. Pore-scale effect on the hydrate variation and flow behaviors in microstructures using X-ray CT imaging. *J. Hydrol.* **2020**, *584*, 124678. [\[CrossRef\]](#)
89. Jarrar, Z.A.; Alshibli, K.A.; Al-Raoush, R.I.; Jung, J. 3D measurements of hydrate surface area during hydrate dissociation in porous media using dynamic 3D imaging. *Fuel* **2020**, *265*, 116978. [\[CrossRef\]](#)
90. Vesselli, E. X-rays and Extreme Ultraviolet Radiation: Principles and Applications. *Nucl. Instrum. Methods Phys. Res. A* **2019**, *940*, 497. [\[CrossRef\]](#)
91. Liu, L.; Zhang, Z.; Li, C.; Ning, F.; Cai, J. Hydrate growth in quartzitic sands and implication of pore fractal characteristics to hydraulic, mechanical, and electrical properties of hydrate-bearing sediments. *J. Nat. Gas Sci. Eng.* **2019**, *75*, 103–109. [\[CrossRef\]](#)
92. Kou, X.; Li, X.-S.; Wang, Y.; Wan, K.; Chen, Z.-Y. Pore-scale analysis of relations between seepage characteristics and gas hydrate growth habit in porous sediments. *Energy* **2021**, *218*, 119503. [\[CrossRef\]](#)
93. Kou, X.; Li, X.-S.; Wang, Y.; Liu, J.-W.; Chen, Z.-Y. Heterogeneity of hydrate-bearing sediments: Definition and effects on fluid flow properties. *Energy* **2021**, *229*, 120736. [\[CrossRef\]](#)
94. Konno, Y.; Jin, Y.; Uchiumi, T.; Nagao, J. Multiple-pressure-tapped core holder combined with X-ray computed tomography scanning for gas–water permeability measurements of methane-hydrate-bearing sediments. *Rev. Sci. Instrum.* **2013**, *84*, 064501. [\[CrossRef\]](#)
95. Wang, J.; Zhao, J.; Zhang, Y.; Wang, D.; Li, Y.; Song, Y. Analysis of the effect of particle size on permeability in hydrate-bearing porous media using pore network models combined with CT. *Fuel* **2016**, *163*, 34–40. [\[CrossRef\]](#)
96. Lu, C.; Xia, Y.; Sun, X.; Bian, H.; Qiu, H.; Lu, H.; Luo, W.; Cai, J. Permeability Evolution at Various Pressure Gradients in Natural Gas Hydrate Reservoir at the Shenhu Area in the South China Sea. *Energies* **2019**, *12*, 3688. [\[CrossRef\]](#)
97. Kou, X.; Li, X.-S.; Wang, Y.; Zhang, Y.; Chen, Z.-Y. Distribution and reformation characteristics of gas hydrate during hydrate dissociation by thermal stimulation and depressurization methods. *Appl. Energy* **2020**, *277*, 115575. [\[CrossRef\]](#)
98. Kou, X.; Li, X.-S.; Wang, Y.; Liu, J.-W.; Chen, Z.-Y. Effects of gas occurrence pattern on distribution and morphology characteristics of gas hydrates in porous media. *Energy* **2021**, *226*, 120401. [\[CrossRef\]](#)
99. Kou, X.; Feng, J.-C.; Li, X.-S.; Wang, Y.; Chen, Z.-Y. Memory effect of gas hydrate: Influencing factors of hydrate reformation and dissociation behaviors. *Appl. Energy* **2022**, *306*, 118015. [\[CrossRef\]](#)
100. Kou, X.; Feng, J.-C.; Li, X.-S.; Wang, Y.; Chen, Z.-Y. Visualization of interactions between depressurization-induced hydrate decomposition and heat/mass transfer. *Energy* **2022**, *239*, 122230. [\[CrossRef\]](#)
101. Chen, B.; Sun, H.; Zheng, J.; Yang, M. New insights on water-gas flow and hydrate decomposition behaviors in natural gas hydrates deposits with various saturations. *Appl. Energy* **2020**, *259*, 114185. [\[CrossRef\]](#)
102. Zhao, J.; Lv, Q.; Li, Y.; Yang, M.; Liu, W.; Yao, L.; Wang, S.; Zhang, Y.; Song, Y. In-situ visual observation for the formation and dissociation of methane hydrates in porous media by magnetic resonance imaging. *Magn. Reson. Imaging* **2015**, *33*, 485–490. [\[CrossRef\]](#)
103. Chen, B.; Sun, H.; Zhao, G.; Wang, B.; Yang, M. Experimental observation of methane hydrate dissociation via different depressurization modes under water phase flow. *Fuel* **2021**, *283*, 118908. [\[CrossRef\]](#)
104. Gao, S.; House, W.; Chapman, W.G. NMR/MRI Study of Clathrate Hydrate Mechanisms. *J. Phys. Chem. B* **2005**, *109*, 19090–19093. [\[CrossRef\]](#)
105. Xue, K.; Zhao, J.; Song, Y.; Liu, W.; Lam, W.; Zhu, Y.; Liu, Y.; Cheng, C.; Liu, D. Direct observation of THF hydrate formation in porous microstructure using magnetic resonance imaging. *Energies* **2012**, *5*, 898–910. [\[CrossRef\]](#)
106. Li, C.; Zhao, Q.; Xu, H.; Feng, K.; Liu, X. Relation between relative permeability and hydrate saturation in Shenhu area, South China Sea. *Appl. Geophys.* **2014**, *11*, 207–214. [\[CrossRef\]](#)
107. Lee, M.W.; Collett, T.S. A method of Shaly sand correction for estimating gas hydrate saturations using downhole electrical resistivity log data. *U.S. Geol. Surv. Sci. Investig. Rep.* **2006**, 5121.
108. Li, N.; Sun, Z.F.; Sun, C.Y.; Li, P.; Chen, G.J.; Ma, Q.L.; Liu, B. Simulating natural hydrate formation and accumulation in sediments from dissolved methane using a large three-dimensional simulator. *Fuel* **2018**, *216*, 612–620. [\[CrossRef\]](#)
109. Li, F.G.; Sun, C.Y.; Li, S.L.; Chen, G.J.; Zhang, K. Experimental Studies on the Evolvement of Electrical Resistivity during Methane Hydrate Formation in Sediments. *Energy Fuels* **2012**, *26*, 6210–6217. [\[CrossRef\]](#)
110. Dong, H.; Sun, J.; Zhu, J.; Liu, L.; Lin, Z.; Golsanami, N.; Cui, L.; Yan, W. Developing a new hydrate saturation calculation model for hydrate-bearing sediments. *Fuel* **2019**, *248*, 27–37. [\[CrossRef\]](#)
111. Jin, Y.; Li, S.; Yang, D. Experimental and theoretical quantification of the relationship between electrical resistivity and hydrate saturation in porous media. *Fuel* **2020**, *269*, 117378. [\[CrossRef\]](#)
112. Fatt, I. The network model of porous media. *Trans. AIME* **1956**, *207*, 144–181. [\[CrossRef\]](#)
113. Yang, L.; Ai, L.; Xue, K.; Ling, Z.; Li, Y. Analyzing the effects of inhomogeneity on the permeability of porous media containing methane hydrates through pore network models combined with CT observation. *Energy* **2018**, *163*, 27–37. [\[CrossRef\]](#)
114. Sun, J.; Zhang, Z.; Wang, D.; Liu, C.; Lu, H.; Song, K. Permeability change induced by dissociation of gas hydrate in sediments with different particle size distribution and initial brine saturation. *Mar. Pet. Geol.* **2021**, *123*, 104749. [\[CrossRef\]](#)

115. He, X.; Shan, X.; Doolen, G.D. Discrete Boltzmann equation model for nonideal gases. *Phys. Rev. E Stat. Phys. Plasmas Fluids Relat. Interdiscip. Top.* **1998**, *57*, R13–R16. [[CrossRef](#)]
116. Xi-Chong, Y.U.; Liu, Y.; Song, Y.C.; Qing-Ping, L.I.; Pang, W.X.; Bai, Y.H. Study of multiphase flow laws in sediment with gas hydrate based on LBM method. *J. China Univ. Pet.* **2011**, *35*, 99–103.
117. Keehm, Y.; Yoon, P. Pore-scale Modeling of Gas Hydrate Formation And Comparison to Lab Experiments. In Proceedings of the 2008 SEG Annual Meeting, Las Vegas, NV, USA, 9–14 November 2008.
118. Chen, X.; Verma, R.; Espinoza, D.N.; Prodanovic, M. Pore-Scale Determination of Gas Relative Permeability in Hydrate-Bearing Sediments Using X-ray Computed Micro-Tomography and Lattice Boltzmann Method. *Water Resour. Res.* **2018**, *54*, 600–608. [[CrossRef](#)]
119. Wu, N.; Li, Y.; Wan, Y.; Sun, J.; Huang, L.; Mao, P. Prospect of marine natural gas hydrate stimulation theory and technology system. *Nat. Gas Ind. B* **2021**, *8*, 173–187. [[CrossRef](#)]
120. Yin, Z.; George, M.; Rong, C.Z.; Tan, H.K.; Praveen, L. Numerical analysis of experimental studies of methane hydrate dissociation induced by depressurization in a sandy porous medium. *Appl. Energy* **2018**, *230*, 444–459. [[CrossRef](#)]
121. Yin, Z.; Moridis, G.; Tan, H.K.; Linga, P. Numerical analysis of experimental studies of methane hydrate formation in a sandy porous medium. *Appl. Energy* **2018**, *220*, 681–704. [[CrossRef](#)]
122. Yin, Z.; Moridis, G.; Linga, P. On the importance of phase saturation heterogeneity in the analysis of laboratory studies of hydrate dissociation. *Appl. Energy* **2019**, *255*, 113861. [[CrossRef](#)]