

A permittivity-conductivity joint model for hydrate saturation quantification in clayey sediments based on measurements of time domain reflectometry

Lanchang Xing^{1,2,*}, Liang Gao¹, Zisheng Ma¹, Liyun Lao², Wei Wei³, Weifeng Han³, Bin Wang¹, Muzhi Gao¹,
Donghui Xing^{4,5}, Xinmin Ge⁶

¹ College of Control Science and Engineering, China University of Petroleum (East China), Qingdao, 266580, China

² School of Water, Energy and Environment, Cranfield University, Cranfield, MK43 0AL, UK

³ Department of Alternative Energy, PetroChina Research Institute of Petroleum Exploration & Development, Langfang, 065007, China

⁴ Guangzhou Marine Geological Survey, China Geological Survey, Guangzhou, 511458, China

⁵ National Engineering Research Center for Gas Hydrate Exploration and Development, Guangzhou, 511458, China

⁶ School of Geosciences, China University of Petroleum (East China), Qingdao, 266580, China

* Correspondence: xinglc@upc.edu.cn, lanchang.xing@cranfield.ac.uk

Abstract

Hydrate saturation (S_h) is one of the key parameters for resource assessment of hydrate reservoirs and production optimization of natural gas. There are still significant challenges in determining the S_h in clayey formations. Both dielectric and resistivity logging tools have been used for identifying and evaluating hydrate-bearing formations; however, there is little work on a joint analysis and modelling of the permittivity and resistivity for quantifying the S_h . To bridge the knowledge gap, we have proposed a novel permittivity-conductivity (P-C) joint approach based on TDR (time domain reflectometry)-derived parameters (i.e., apparent permittivity K_a and bulk conductivity σ_{dc}) in this work. The proposed P-C joint approach can provide a theoretical basis for the joint interpretation of dielectric and resistivity geophysical measurements on hydrate-bearing formations in the

field. First, the basic theory for deriving the K_a and σ_{dc} from the TDR responses of hydrate-bearing sediments was formulated based on the dielectric polarization and electrical conduction mechanisms. Second, an experimental campaign was carried out including the development of experimental system, calibration of TDR probe and design of experimental scheme. Third, the influences of hydrate saturation, clay mineralogy and clay content on the TDR responses of unconsolidated sediments were examined. Then the K_a and σ_{dc} were related to S_h respectively, and finally a novel P-C joint model for the quantification of S_h in clayey sediments was established and verified. It has been demonstrated that: (1) the K_a of the clayey samples with hydrates decreases almost linearly with an increasing clay content up to 20 %, while the σ_{dc} of the smectite-bearing samples decreases nonlinearly in contrast to the linear trend for illite; (2) the power-law mixing formula incorporating an empirical exponent is a preferable permittivity model for hydrate-bearing clayey sediments due to its merits of empirical and theoretical nature, while the Simandoux equation is effective to account for the clay effects on the conductivity of hydrate-bearing sediments with smectite and illite; (3) the P-C joint model can be established by utilizing the porosity of hydrate-bearing sediments as a bridge parameter between K_a and σ_{dc} . The variation behavior of K_a and σ_{dc} with different types and contents of clay minerals can be explained by the difference of the amount of bound water and swelling effects between the illite-bearing and smectite-bearing samples. The proposed P-C joint model outperforms the standalone permittivity-based and conductivity-based models especially for the clayey cases. The root-mean-squared errors of the P-C joint models are 7.339, 2.930 and 2.065 % for the clean-sand samples, clayey samples with illite and smectite, respectively.

Keywords: Gas hydrate, time domain reflectometry, hydrate saturation, dielectric permittivity, conductivity, joint approach

1 Introduction

Gas hydrate is a crystalline material consisting of gas and water. The water molecules form cages through hydrogen bonds as the host, while the gas molecules are trapped in the cages as the guests (Sloan, 2003; Hawkins and Davidson, 1966). Gas hydrates may appear in various scenarios as desirable or undesirable substances (Das et al., 2023; Wang et al., 2023; Rasool et al., 2022; Shi et al., 2022; Sadeq et al., 2017; Atik et al., 2010; Cao et al., 2023; Pandey et al., 2022; Cao et al., 2022; Zhang et al., 2022; Gambelli et al., 2019). As a new type of alternate energy resources, gas hydrates have attracted widespread interests due to its high energy density and huge reserves in nature (Tian et al., 2023; Chibura et al., 2022; Yin and Linga, 2019a; Chong et al., 2016; Koh et al., 2012; Moridis et al., 2009; Collett, 2002). It is well accepted that most of the natural hydrates are found in fine-grained unconsolidated marine sediments with clays (Park et al., 2022; Jang and Santamarina, 2016; Sriram et al., 2014; Liu et al., 2012; Boswell, 2009). Before any production operations for extracting natural gas from hydrate reservoirs, it is the first question to answer where and how much the hydrates are. Moreover, it is also desirable to know how the amounts of the original and re-formed hydrates vary in sediments during the dynamic exploitation process of hydrates. Therefore, it is imperative to evaluate the relative fractions of hydrates in sediments in situ and in real time to ensure an economic, efficient and safe production of natural gas. The term, hydrate saturation (S_h), represents the volumetric fraction of the hydrate relative to pore space. It is one of the prerequisite parameters for assessing the amount of gas resources and designing/optimizing the exploitation programs of hydrate reservoirs.

The appearance of gas hydrates resembles to snow and the physical properties (e.g., electrical, elastic, thermal) are similar to those of ice (Lee et al., 2010; Waite et al., 2009). The electrical properties of unconsolidated sediments containing hydrates have attracted extensive attentions due to their merits for evaluating the hydrate saturation. Geophysical techniques such as controlled-source electromagnetic survey (Liu et al., 2023; Attias et al., 2018, 2020), electrical resistivity well logging (Cook and Waite, 2018; Riedel et al., 2013; Wang et al., 2011a, 2011b; Shankar and Riedel, 2011; Hyndman et al., 1999) and dielectric well logging (Sun et al., 2011; Sun and Goldberg, 2005) have been utilized to identify and evaluate hydrate-bearing formations. Marine controlled-source electromagnetic survey is regarded as a complementary means to seismic approaches, because an independent measurement (i.e., electrical resistivity) sensitive to the inclusions in the pore space (e.g., water

and hydrate) can be acquired (Xing et al., 2020; Attias et al., 2018, 2020). The resistivity logging becomes an indispensable means for evaluating the porosity and saturation of hydration-bearing sediments. As a relatively new and costly means, the dielectric logging has not been used as extensively as the resistivity logging for gas hydrates. However, the higher vertical resolution of dielectric logs (e.g., < 5 cm) is attractive to the identification of thin hydrate layers that could not be resolved by other logging means (Sun and Goldberg, 2005; Sun et al., 2011). Efforts have been made to develop interpretation models for the electrical/electromagnetic measurements of hydrate-bearing sediments (Xing et al., 2023a, 2023b; Zhang et al., 2020; Jin et al., 2020; Dong et al., 2019; Hu et al., 2019; Lee, 2011; Lee and Collett, 2006, 2011; Miyairi et al., 1999). However, due to the complexity of hydrate-bearing formations such as dynamic variations of the pore-water salinity and micro-scale distribution in decomposition and re-formation processes of hydrates, and a variety of clay mineralogy and contents, it is still an open question to relate the electrical parameters to S_h reliably. It is an interesting idea to quantify the identical reservoir parameter (e.g., S_h) based on different types of physical mechanisms with an expectation of reducing the multiplicity and ambiguity of final solutions. Two physical mechanisms, i.e., electrical conduction and dielectric polarization, will be the focus of this work. The electrical parameters, i.e., resistivity/conductivity and permittivity, will be employed conjointly to quantify the S_h with a potential application to the interpretation of resistivity and dielectric well logs.

Time-domain reflectometry (TDR) has been adopted for estimating the water content and electrical conductivity of soils in laboratory and field applications. It is an attractive advantage that both the dielectric permittivity and electrical conductivity can be derived from TDR responses (Robinson et al., 2003; Dalton et al., 1984). The two electrical parameters can be assembled into a lumped parameter, i.e., complex electrical conductivity or complex dielectric permittivity (Tarasov and Titov, 2013; Revil, 2013). The two lumped parameters are equivalent in essence, but they are usually employed in lower and higher frequency (e.g., $\sim$ GHz in TDR) ranges, respectively. Considering the complex dielectric permittivity can be obtained from TDR measurements, we believe that the TDR becomes an efficient means to quantify the electrical properties of hydrate-bearing sediments comprehensively. Recently, the TDR has been adopted to measure the dielectric permittivity of hydrate-bearing samples for deriving the S_h . Wright et al. (2002) employed a three-rod TDR probe to measure the water content in hydrate-bearing silica silt samples. They proposed an empirical model to correlate the water content to

dielectric permittivity, and then estimated the S_h from the remaining pore water. Kliner and Grozic (2006) used a four-rod TDR probe to measure the dielectric permittivity of specimens consisting of Ottawa sand, water and hydrate. A distinct relationship between the S_h and the bulk dielectric permittivity of sand specimens. Hu et al. (2010) and Bu et al. (2019) applied coaxial and two-rod TDR probes to test the dielectric permittivity of hydrate-bearing samples, respectively. Then the water content and S_h were derived based on the empirical correlation proposed by Wright et al. (2002). Great progresses have been made in estimating the S_h from the dielectric permittivity in the aforementioned works. However, the TDR responses have not yet been fully utilized because the TDR-derived conductivity was discarded in the data interpretation. In other words, only the real part of the complex dielectric permittivity has been used, which results in an incomplete description of the electrical properties of the samples containing hydrates. In addition, the relationship between the TDR-derived permittivity and S_h were modelled as pure empirical correlations only. That poses a big challenge to apply the correlations to conditions beyond those for developing them. To summarize, there are significant knowledge gaps in characterizing the electrical properties of hydrate-bearing sediments with the conductivity and permittivity conjointly and petrophysical modelling for quantifying the S_h with more underlying physics incorporated.

To bridge the above knowledge gaps, in this work, we propose to employ both the dielectric permittivity and conductivity for characterizing the unconsolidated clayey sediments with hydrates. The basic idea is to make the best use of the electrical parameters representing both the dielectric polarization and electrical conduction mechanisms. The aim of this work is to establish a permittivity-conductivity (P-C) joint approach for quantifying the S_h in clayey sediments, which can be used not only in laboratory tests but also for joint interpretation of dielectric and resistivity logging data in the field. First, the basic theory for deriving the permittivity and conductivity from TDR responses was formulated as a foundation for experiment implementation and data analysis. Second, an experimental campaign was carried out including the development of experimental system, calibration of TDR probe and design of experimental scheme. Third, the influences of S_h , clay mineralogy and clay content on the TDR responses of clayey sediments were examined experimentally. Then the TDR-derived permittivity and conductivity were related to S_h respectively, and finally a novel P-C joint model for the quantification of S_h in clayey sediments was established and verified. The

outcome of this study can provide a theoretical foundation for the joint interpretation of dielectric and resistivity geophysical measurements on gas hydrate reservoirs.

2 Theory

2.1 Complex dielectric permittivity of porous media

After the application of an external electrical field on a medium, the movement behavior of free and bound charge carriers can be characterized by the parameters, i.e., electrical conductivity and dielectric permittivity of the medium, respectively. From the perspective of electromagnetic energy, the storage and loss of the energy can be characterized by the two electrical parameters, which can be assembled into a lumped parameter, i.e., complex dielectric permittivity. The complex dielectric permittivity of a medium under a time-harmonic electric field can be derived from the Maxwell equations (Eq. (1)) (Tarasov and Titov, 2013; Revil, 2013). The real part and imaginary part are associated with the storage and loss of the electromagnetic energy, respectively. To distinguish the energy losses due to dielectric relaxation (represented by $\varepsilon''_{\text{relax}}$) and electrical conduction (represented by σ_{dc}), the imaginary part is further split into two terms as indicated in Eq. (2).

$$\nabla \times \mathbf{H} = \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t} = j\omega \left(\varepsilon - \frac{j\sigma_{\text{dc}}}{\omega} \right) \mathbf{E} = j\omega \varepsilon_0 \varepsilon_r^* \mathbf{E} \quad (1)$$

$$\varepsilon_r^* = \varepsilon_r' - j \left(\varepsilon_{\text{relax}}'' + \frac{\sigma_{\text{dc}}}{2\pi f \varepsilon_0} \right) \quad (2)$$

where $\mathbf{J}$ (in A/m²) is the density of conduction current; $\mathbf{H}$ (in A/m) is the intensity of magnetic field; $\mathbf{D} = \varepsilon \mathbf{E}$ is the dielectric displacement (in C/m²); $\varepsilon = \varepsilon_0 (\varepsilon_r' - j\varepsilon_{\text{relax}}'')$ is the complex-valued permittivity (in F/m) that characterizes the dielectric relaxation behavior; and the symbols ε_0 and ε_r^* are the vacuum permittivity ($\varepsilon_0 = 8.854 \times 10^{-12}$ F/m) and relative complex permittivity (dimensionless), respectively. The intensity of the applied electrical field ($\mathbf{E} = \mathbf{E}_0 e^{j\omega t}$) has an angular frequency of ω (in rad/s, $\omega = 2\pi f$, j is the unit imaginary number).

Typical porous media such as soils, stones and sediments are usually composed of solid matrix (e.g., sand particles), liquid phase (e.g., water or oil), and gaseous phase (e.g., air or natural gas). This work focuses on the hydrate-bearing unconsolidated sediments. A certain amount of clay minerals is often included in the solid matrix and the liquid water phase is composed of free water and bound water components. The complex

dielectric permittivity (as shown in Eq. (2)) of a composite porous material are strongly dependent on the properties of each constituent, the relative fraction and micro-distribution in the material, and the frequency of the electric field applied. The characteristics of various dielectric polarization processes affect both the energy storage and loss and thus both the real and imaginary parts of complex dielectric permittivity.

Various dielectric polarization processes undergo when a multi-component porous medium is submitted to an alternative electric field. Typical types of the polarization mechanisms are frequency related, which include electrochemical polarization in the low-frequency band ($< \text{kHz}$), interfacial polarization (Maxwell-Wagner effect) in the intermediate-frequency band ($\sim \text{MHz}$), and molecular polarization of water in the high-frequency band ($\sim \text{GHz}$) (Revil, 2013; Leroy et al., 2008). The latter two polarization mechanisms control the TDR responses because the electromagnetic pulse used usually covers a range of frequencies from MHz to GHz (Robinson et al., 2003; Heimovaara, 1994). As mentioned above there are two types of water in hydrate-bearing clayey sediments, i.e., free water and bound water. The dielectric polarization behavior of the free water and bound water are different, which results in different dielectric permittivities of them (Robinson and Friedman, 2003). Therefore, care must be taken when analyzing the variations of TDR-derived permittivity under conditions of different clay types and contents, and modelling the relationship between the permittivity and S_h .

2.2 Measurement of apparent dielectric permittivity with TDR

The TDR probe can be considered as an ideal model of transmission line in the theoretical analysis and modelling of its electromagnetic characteristics. The velocity of an electromagnetic pulse propagating along the TDR probe can be measured. Based on the measured velocity the apparent dielectric permittivity of the material (i.e., samples of hydrate-bearing sediments in this work) around the TDR probe can be derived.

To understand the theoretical relationship between the electromagnetic pulse velocity and apparent dielectric permittivity in the TDR system, the scenario where a plane wave propagates along a transmission line is analyzed as below. It is considered that a sinusoidal electromagnetic wave with the angular frequency of ω propagates along the transmission line. The transmission line that simulates the TDR probe can be modelled to be an equivalent circuit as shown in Robinson et al. (2003). A propagation constant (γ) of the simulated 'TDR

probe' can be defined based on the elements in the equivalent circuit as indicated in Eq. (3). Then the phase velocity of the plane wave (v_p) can be determined from the propagation constant as shown in Eq. (4) (Kraus, 1984).

$$\gamma = \sqrt{(R + j\omega L)(G + j\omega C)} = \alpha + j\beta \quad (3)$$

where L denotes the line inductance in series with the resistance R resulting from the skin effect along the TDR probe; G is the line conductance in parallel with the capacitance per unit length of the transmission line (C) that depends on the medium in the sensitive space of the TDR probe; and α and β are the attenuation and phase constants, respectively.

$$v_p = \frac{\omega}{\beta} \quad (4)$$

For the TDR probe including the medium in the sensitive space without any energy losses, i.e., both R and G in Eq. (4) are zero, the propagation velocity of the electromagnetic wave can be obtained from Eq. (5).

$$v_p = \frac{\omega}{\omega\sqrt{LC}} = \frac{1}{\sqrt{\mu_0\mu_r\epsilon_0\epsilon_r'}} = \frac{c}{\sqrt{\mu_r\epsilon_r'}} \quad (5)$$

where $c = 3 \times 10^8$ m/s is the propagation velocity of an electromagnetic wave in vacuum; $\mu_0 = 4\pi \times 10^{-7}$ H/m is the magnetic permeability of vacuum; and μ_r is the relative magnetic permeability, which is considered as unity for most geologic materials (Sharma, 1997). In the cases where the energy losses are taken into account, the propagation velocity of the electromagnetic wave is then expressed as Eq. (6) (Robinson et al., 2003).

$$v_p = \frac{c}{\sqrt{\frac{\mu_r\epsilon_r'}{2} \left\{ 1 + \sqrt{1 + \left[\left(\epsilon_{\text{relax}}'' + \frac{\sigma_{\text{dc}}}{\omega\epsilon_0} \right) / \epsilon_r'} \right]^2} \right\}}} = \frac{c}{\sqrt{K_a}} \quad (6)$$

where K_a is the relative apparent permittivity of the material around the transmission line (i.e., TDR probe). It can be seen that the K_a can be taken as an approximation to the real part (ϵ_r') of the relative complex permittivity only when the terms associating with energy losses (i.e., $\epsilon_{\text{relax}}''$ and $\sigma_{\text{dc}}/(\omega\epsilon_0)$) are small enough compared to ϵ_r' .

In the TDR measurement system, the electromagnetic pulse propagates along the probe and is reflected back at the end. Then the propagation velocity of the pulse can be determined based on the measurement of the travel

time as expressed in Eq. (7).

$$v = \frac{2l}{\Delta t} \quad (7)$$

$$\Delta t = \frac{2l\sqrt{K_a}}{c} \quad (8)$$

where l is the length (in m) of the probe; and Δt is the travel time (in s) of the round trip along the TDR probe. With a reference to Eq. (6) it can be seen that the K_a can be derived from the measured travel time. In addition, an apparent distance or length (denoted as L_a , in m) can be defined as indicated in Eq. (9), which is usually used in the presentation and analysis of the measured TDR waveforms.

$$K_a = \left(\frac{c\Delta t}{2l} \right)^2 = \left(\frac{L_a}{l} \right)^2 \quad (9)$$

The L_a identified from the measured TDR waveforms illustrates the distance between the starting point and ending point of the TDR probe in the waveforms. The length of the TDR probe (l) can be determined through laboratory calibrations of TDR probe as detailed in **Section 3.2**.

2.3 Measurement of bulk conductivity with TDR

When the electromagnetic pulse propagates along the waveguide (i.e., the cable and probe) in the TDR system, a fraction of the wave energy is reflected back if there is an impedance discontinuity along the travel path. Theoretically, the measured TDR waveforms result from the input voltage in terms of an electromagnetic pulse superimposed by the responsive voltage generated by the TDR probe. The waveforms can be presented in terms of a voltage or reflection coefficient against time or apparent distance equivalently. The reflection coefficient (denoted as $\rho(t)$ as a time function) is the ratio of the amplitude of the responsive voltage (denoted as $r(t)$) to that of the input voltage (denoted as v_0) (Heimovaara, 1994).

$$\rho(t) = \frac{r(t)}{v_0} = \frac{v(t) - v_0}{v_0} \quad (10)$$

where $v(t)$ is the recorded total voltage including the input voltage for excitation and the responsive voltage from the TDR probe.

The bulk electrical conductivity (denoted as σ_{dc}) of the material in the sensitive space of TDR probe can be derived from the measured TDR waveforms of reflection coefficients. When the multiple reflections in the TDR system stabilizes after a long time (i.e., at the ‘infinite time’), the DC (direct current) responses of the system can be obtained from the TDR waveforms. The section of the TDR probe with the tested material (e.g., hydrate-bearing sediments in this work) can be considered as a lumped termination of a transmission line. As a result, the electrical resistance (R_s) of the tested sample in the probe section can be derived from the reflected voltage as formulated in Eq. (11) (Castiglione and Shouse, 2003; Nadler et al., 1991).

$$R_s = Z_c \frac{V_i(\infty) + V_r(\infty)}{V_i(\infty) - V_r(\infty)} \quad (11)$$

where Z_c is the characteristic impedance of the cable (typical 50 Ω), from which the electromagnetic pulse is transmitted to the TDR probe; and $V_i(\infty)$ and $V_r(\infty)$ are the incident voltage and reflected voltage at the cable-probe interface at the infinite time. The σ_{dc} of the tested materials can be derived from Eq. (12).

$$\sigma_{dc} = \frac{K_p}{R_s} = \frac{K_p}{Z_c} \frac{1 - \rho_{\infty}}{1 + \rho_{\infty}} \quad (12)$$

where $\rho_{\infty} = V_r(\infty)/V_i(\infty)$ is reflection coefficient at the infinite time; and K_p is the geometric factor of the TDR probe (i.e., probe constant, in 1/m). For a TDR probe with the geometry of a coaxial line, the probe constant can be derived from the characteristic parameters of the probe as expressed in Eq. (13).

$$K_p = \frac{\epsilon_0 c Z_0}{l} \quad (13)$$

where Z_0 is the geometric impedance, i.e., the characteristic impedance with air as the tested material.

To eliminate the resistance contributions from the cable and fittings to the TDR-derived sample resistance and obtain the real resistance of the sample, Castiglione and Shouse (2003) proposed to employ the TDR waveform with the reflection coefficient (ρ_{sample}) scaled by those for a shorted circuit (ρ_{short}) and an open circuit (ρ_{open}) in air. The scaled reflection coefficient (denoted as ρ_{scaled}) can be computed from Eq. (14). The σ_{dc} of the tested materials is then calculated based on Eq. (15) by replacing the ρ_{∞} in Eq. (12) with ρ_{scaled} .

$$\rho_{scaled} = 2 \frac{\rho_{sample} - \rho_{open}}{\rho_{open} - \rho_{short}} + 1 \quad (14)$$

$$\sigma_{dc} = \frac{K_p}{Z_c} \frac{1 - \rho_{scaled}}{1 + \rho_{scaled}} \quad (15)$$

It can be seen that the bulk electrical conductivity (σ_{dc}) of the tested material can be derived from the known geometric factor (K_p) of the probe, characteristic impedance of the cable (Z_c) and measured TDR waveforms of reflection coefficients in the tests. The K_p can be determined through laboratory calibrations of TDR probe as detailed in **Section 3.2**.

3 Experimental campaign

3.1 Development of TDR-based experimental system

TDR-based experimental system was developed to simulate the processes of hydrate formation/decomposition in unconsolidated sediments and test the TDR responses of the hydrate-bearing sediments. The schematic diagram and photos of the experimental system are illustrated in **Fig. 1** and **2**, respectively. The experimental system can be divided into two function units, i.e., the sample-preparation unit and parameter-test unit. The former was designed to achieve the hydrate formation processes and obtain hydrate-bearing samples. The latter was employed to collect the test data of TDR waveforms (e.g., reflection coefficient against apparent distance as shown in **Section 4.2**) and temperature evolutions of the samples during the hydrate formation processes (e.g., temperature time trace as shown in **Section 4.1**).

The sample-preparation unit consists of a reaction vessel and an air bath incubator. The reaction vessel was made with Polypropylene (PP), which is an ideal material for electrical insulation and corrosion prevention. It took a cylindrical shape with the length of 20 cm and the cross-section diameter of 4.6 cm. The geometry and dimensions were designed to accommodate the geometrical parameters of the TDR probe such as the length and spacing of the three rods (**Fig. 2**). A lid was manufactured to cover the sample on the top of the reaction vessel for minimizing the volatilization of the pore solution (e.g., THF and water) in the samples during the testing processes. The temperature of the samples in the reaction vessel was controlled with a deviation less than 0.25 °C from a preset value (e.g., -2 °C) to the air-bath incubator. It is important to maintain a steady temperature of samples for electromagnetic measurements (e.g., in TDR tests) due to the high sensitivity of electrical

parameters to temperature variations.

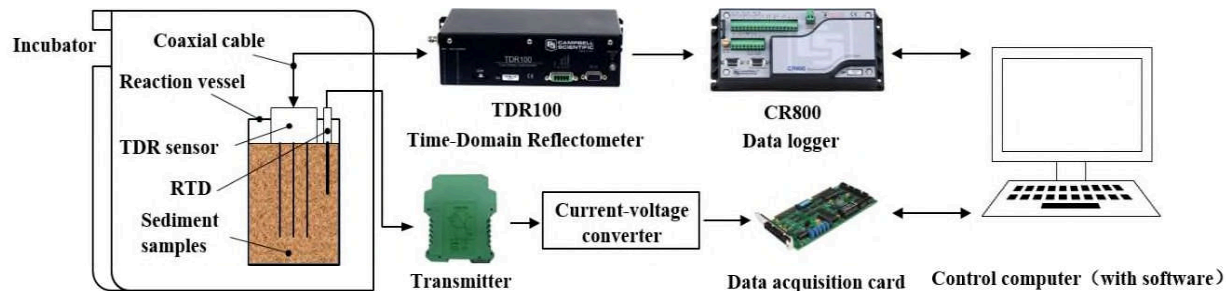


Fig. 1 Schematic of TDR-based experimental system

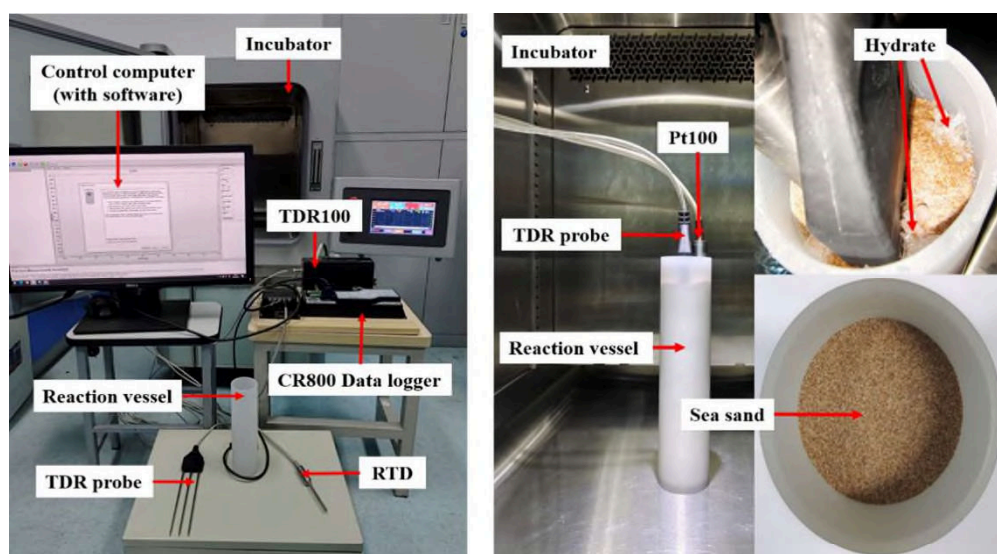


Fig. 2 Photos of the components of TDR-based experimental system

The parameter-test unit is comprised of a TDR testing system, a temperature-measurement part, and a computer with multiple sets of software for instrument control and data manipulation. The TDR testing system includes the TDR100 time-domain reflectometer, CR800 data logger, three-rod CS630 TDR probe, and PC-TDR/PC200W software. Both the output impedance of the time-domain reflectometer (TDR100) and the characteristic impedance of the coaxial cable for connecting the TDR100 and probe were $50\ \Omega$ (i.e., $Z_c = 50\ \Omega$ as used for deriving the bulk conductivity in **Section 2.3**). The nominal lengths of the rods of the TDR probe were 150 mm, and the spacing between the central rod and the two external rods was 30 mm. The TDR100 time-domain reflectometer is used to generate an electromagnetic pulse with the duration time and amplitude of $14\ \mu\text{s}$ and 250 mV, respectively. The pulse propagates down along the coaxial cable and the TDR probe (with

the tested sample) and then reflects back to the TDR100 time-domain reflectometer and CR800 data logger. The TDR responses in terms of the voltage or reflection-coefficient waveforms against apparent distance can be recorded by the CR800 data logger. The recorded data are then sent to the computer for displaying and detailed analysis with the aid of the software sets PC-TDR/PC200W. The measurement part for temperature includes a resistive temperature detector (i.e., RTD and Pt100 in **Fig. 2**), a resistance to current transmitter, a current to voltage converter, and a data acquisition (DAQ) card. The DAQ card is responsible for the collection of the voltage signals representing the measured temperature of samples. The total uncertainty of the temperature-measurement part is less than 0.15 °C. The uncertainty of temperature measurements is acceptable to the analysis of the hydrate formation process as shown in **Section 4.1** and to the temperature corrections of parameters used in the models as shown in **Section 4.3 and 4.4**.

3.2 Calibration of TDR probe

It has been presented in **Section 2.2** and **2.3** that the apparent permittivity and bulk conductivity can be derived from the TDR responses theoretically. There are two key parameters, i.e., the real length of the rods (l) and the probe constant (K_p), to be calibrated before any actual tests and formal data analysis. The real length of the rods, i.e., the distance over which the electromagnetic pulse travels, is not exactly equal to the physical length. An inaccurate value assigned to the l of TDR probe in Eq. (9) will result in a direct error in the derived apparent permittivity. A typical case is that the three rods are not parallel absolutely, which leads to a discrepancy between the real and physical lengths. In addition, the K_p can be computed theoretically for a coaxial line probe as indicated in Eq. (13). However, the TDR probe made of several rods is only an approximation to the coaxial line in geometry (Spaans and Baker, 1993). Consequently, the K_p for a rod-based TDR probe has to be determined accurately through experimental calibrations.

To determine the real length of the TDR probe, standard materials such as the deionized water at different temperatures and air were used in the calibration operations. The reference values of the relative permittivities of the tested water were computed with a well-accepted empirical correlation (i.e., Eq. (16)) reported by Stogryn (1971).

$$K_{\text{ref}}(T) = 87.740 - 0.4008T + 9.398 \times 10^{-4}T^2 - 1.410 \times 10^{-6}T^3 \quad (16)$$

where K_{ref} is the reference permittivity of the deionized water at different temperatures (T in $^{\circ}\text{C}$). Based on the known permittivities of air and deionized water and Eq. (9), an average of the real lengths was finally determined as 150.60 mm for the TDR probe used in this work. The calibrated l was employed to analyze the whole set of TDR waveforms and the permittivities of the deionized water under test were derived. As shown in **Fig. 3** the relative error of the TDR-derived permittivity ranges from 0.06 to 0.32 % with the mean value (i.e., mean of the absolute values of errors) of 0.19 %.

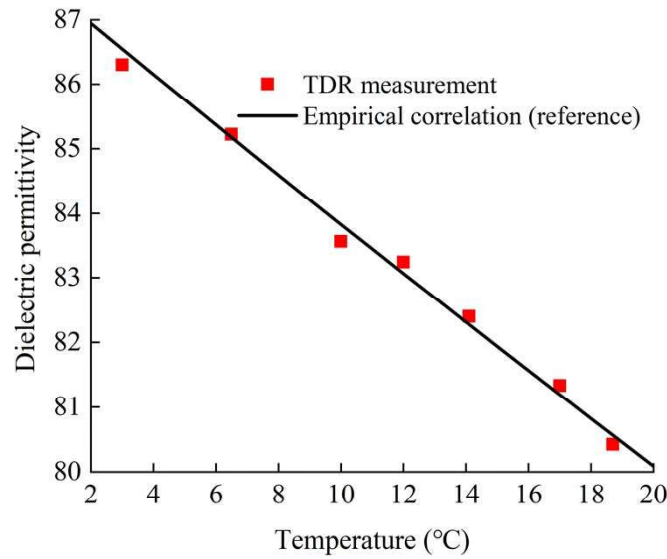


Fig. 3 Comparison between the TDR-derived and reference permittivities of deionized water at different temperatures

To determine the TDR probe constant, three sets of TDR tests were conducted with the probe in an open-circuit state (i.e., placed in air), in a shorted-circuit state (i.e., wrapped with tinfoil) and then inserted into NaCl solutions of different conductivities. The TDR waveforms in terms of reflection coefficient for an open circuit (ρ_{open}) and a shorted circuit (ρ_{short}) were obtained first. Then the stabilized reflection coefficient (i.e., ρ_{∞} or ρ_{sample} in Eq. (14)) was obtained from the tests on the NaCl solutions. Finally, the K_p of the TDR probe were determined based on Eq. (15) with known Z_c (i.e. 50 Ω as introduced in **Section 3.1**) and σ_{dc} (i.e., conductivity of the NaCl solutions). The reference values of the conductivities were computed from an empirical correlation (i.e., Eq. (17)) reported by (Sen and Goode, 1992) and confirmed by a conductivity meter (Model AZ8362).

$$\sigma_{\text{ref}}(T, C_f) = \left(5.6 + 0.27T - 1.5 \times 10^{-4} T^2\right) C_f - \left(\frac{2.36 + 0.099T}{1.0 + 0.214C_f}\right) (C_f)^{1.5} \quad (17)$$

where σ_{ref} (in S/m) is the conductivity of the NaCl solutions; C_f (in mol/L) is the salinity of the NaCl solutions. The K_p of the TDR probe was determined to be 3.36 m^{-1} in this work. The K_p was used for analyzing the whole set of TDR waveforms and the conductivities of the NaCl solutions were derived. The TDR-derived and reference conductivities are compared in **Fig. 4**. The relative error of the TDR-derived conductivity ranges from 1.08 to 5.98 %, and the mean relative error (i.e., mean of the absolute values of errors) is 2.73 %.

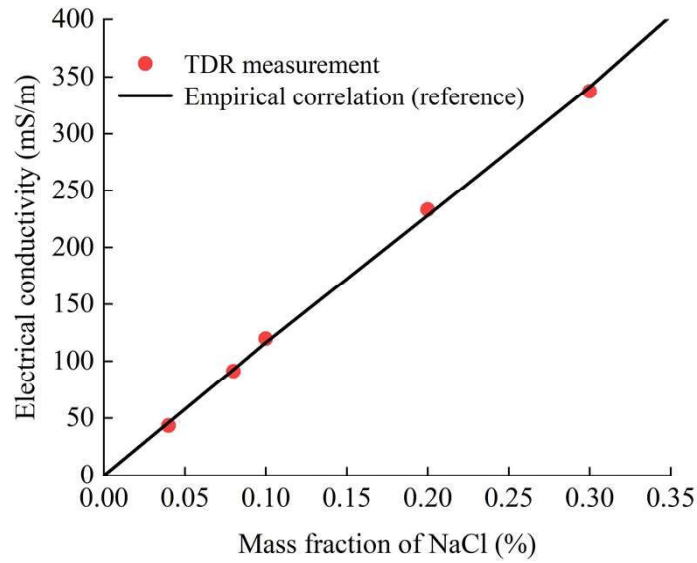


Fig. 4 Comparison between the TDR-derived and reference conductivities of NaCl solutions

3.3 Design of experimental scheme

The experimental scheme was designed for the collection of test data of TDR responses and temperatures of various hydrate-bearing samples. The apparent permittivity and bulk conductivity of samples were then derived from the recorded TDR waveforms according to the theoretical procedures as presented in **Section 2.2 and 2.3**.

There were three steps for carrying out the experiments, i.e., design of experimental conditions, preparation of samples, and testing for physical parameters. In the first step, the quantities of the required materials were calculated and prepared. In the second step, the materials were mixed together and added into the reaction vessel following a certain procedure. The reaction vessel holding the mixture was then transferred into the incubator, where the samples for simulating hydrate-bearing sediments were prepared under the control of an appropriate

temperature. In the third step, the data of the TDR waveforms and temperatures were recorded with the evolution of the hydrate formation processes. More details of the first two steps are introduced as below and the results of the third step are demonstrated with an example case as presented in **Section 4.1**.

A series of experimental conditions were designed including different hydrate saturations, clay types and clay contents to examine the effects of those factors. The materials used for the sample preparation included tetrahydrofuran (THF), deionized water, sodium chloride (NaCl), sea sand and clay minerals. Test samples with a range of hydrate saturations (i.e., $S_h = 0, 0.5$ to 1.0) were prepared. The pros and cons of using the THF hydrate as a proxy to natural gas hydrate have been discussed in detail in our previous works (Xing et al., 2022, 2023b), thus will not be repeated here for brevity. Most of the accumulated gas hydrates worldwide are hosted in fine-grained sediments. As reported by Wang et al. (2011a) and Liu et al. (2017), fine grains generally account for more than 80% of the cores recovered from sediments of South China Sea and the clay fraction can reach as high as 20%. The sea sand with the particle diameter ranging from 180 to 250 μm was selected to simulate the fine-grained sediments (Shepard, 1954) in this work. Two clay minerals were used, i.e., smectite and illite, due to their frequent occurrence in marine hydrate sediments (Ren et al., 2022; Liu and Li, 2021; Ma et al., 2020). Compared with the illite, the smectite has a larger specific surface area (SSA) and higher cation exchange capacity (CEC) and exhibits more significant swelling effects. The particle diameters of the smectite and illite used in this work were around 2.6 μm . The volumetric fraction of clay minerals (i.e., clay content V_c) in the samples up to 20 % were arranged according to the results of core analysis (Wei et al., 2019; Liu et al., 2012, 2015, 2017; Wang et al., 2011a).

Based on the design of experimental conditions stated above, the samples were then prepared and submitted for the TDR tests. First, the clay minerals (i.e., the smectite or illite) and sea sand were mixed together to simulate the dry clayey sediment. Then the mixture was loaded into the reaction vessel portion by portion. The pore fluid was prepared by mixing the THF and NaCl solution and then injected into each portion of the mixture in the vessel. The required quantities of THF and NaCl solution were calculated based on the theoretical chemical formula of THF hydrate (i.e., $\text{C}_4\text{H}_8\text{O} \cdot 17\text{H}_2\text{O}$). For example, 17 mol H_2O and 1 mol THF were needed to obtain 1 mol THF hydrate. To achieve the target values of S_h in the samples, it was assumed that the added THF was

converted into THF hydrate completely (Baldwin et al., 2003). It needs to be noted that uncertainties in the resultant S_h in samples stemmed from several sources, such as the deviation of hydration number from that in the theoretical chemical formula and uncompleted conversion from THF to THF hydrate. The conversion rate is affected by some factors such as the cooling mode or temperature history and initial THF/water ratio (Strauch et al., 2018; Yin et al., 2019b; Liu et al., 2019). In this work, repeat operations for the preparation and test of each sample with the same target S_h were performed to mitigate possible uncertainties. It is imperative to maintain the same salinity of the residual pore water in samples at the end of the hydrate formation process, because the pore-water conductivity affect both the electrical conduction and dielectric polarization characteristics. This was achieved by compensating for the ‘salt-removing effect’ in the process of hydrate formation. Different mass fractions of NaCl were used to prepare the NaCl solution for samples with different target S_h . The required amount of NaCl was calculated based on the amount of the residual water and targeted salinity (i.e., 0.5 % by mass in this work). More details of the sample preparation procedures can be found in our previous works (Xing et al., 2022, 2023b). Second, the TDR probe and RTD were inserted into the pore-fluid saturated sediment, and then the reaction vessel was covered with the lid to minimize the volatilization of THF. The reaction vessel was transferred into the incubator, and the data recording of TDR waveforms and temperature was started. The reaction vessel was left in the incubator at room temperature for hours until no significant differences of the TDR waveforms were observed. Third, the cooling mode of the incubator was started with a preset temperature $-2\text{ }^{\circ}\text{C}$, and the hydrate formation process was initiated. This process ended when the sample temperature recovered from a significant rise indicating the formation of hydrates and remained steady for a long time (e.g., 6 hours). Then the room temperature (e.g., $20\text{ }^{\circ}\text{C}$) was set to the incubator and the hydrate decomposition process was started. The above procedures were implemented at least twice to obtain a group of repeated test data for further analysis.

4 Results and analysis

4.1 Variation of TDR-derived electrical parameters in hydrate formation process

Both TDR waveforms and temperature were recorded in the hydrate formation process. The electrical parameters (i.e., K_a and σ_{dc}) of the tested samples were derived through an analysis of the TDR waveforms according to the theoretical approach presented in **Section 2**. The TDR-derived K_a and σ_{dc} vary in the hydrate

formation process due to the changes in temperature and amount of pore water and hydrate. **Fig. 5** illustrates the time traces of the measured temperature for a hydrate-bearing clean-sand sample with $S_h = 0.9$ and the TDR-derived K_a and σ_{dc} in the tested process of hydrate formation.

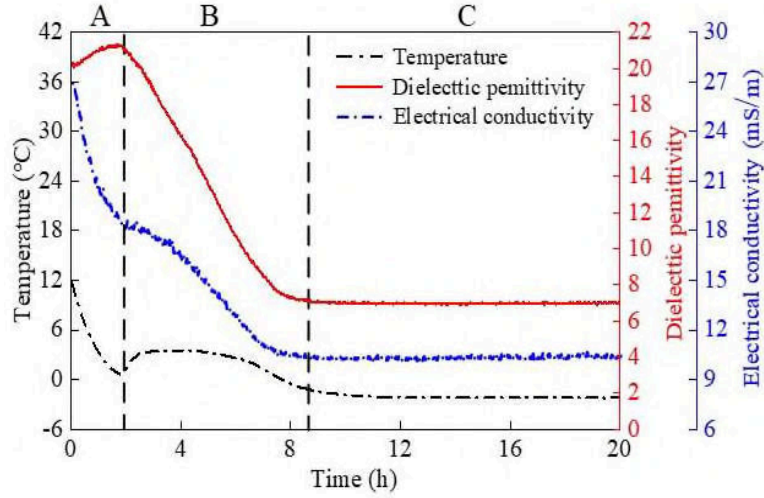


Fig. 5 Sub-processes characterized by variations of temperature and TDR-derived electrical parameters with time in hydrate formation process

To better understand the behavior of TDR responses in terms of the derived K_a and σ_{dc} during the evolution of the hydrate formation process, a set of sub-processes (labeled as A, B and C in **Fig. 5**) is identified according to the temperature variations. The three sub-processes are characterized by a temperature decrease without hydrate (A), hydrate formation accompanied with a temperature rise (B), and steady temperature with hydrate formed (C), respectively. Generally, the typical sub-processes identified above based on the temperature variation can also be recognized in the time traces of the TDR-derived derived K_a and σ_{dc} . It needs to be noted that, due to the unavoidable mismatch of the locations of TDR probe and temperature sensor in the sample (as illustrated in Fig. 2), the turning points separating the sub-processes on the time traces of K_a , σ_{dc} and temperature may not agree with each other perfectly.

In the sub-process of A as shown in **Fig. 5**, the TDR-derived K_a and σ_{dc} of the THF-solution-saturated clean-sand sample increases and decreases, respectively, and the temperature continues to decrease. The pore-water properties dominate the TDR-derived K_a and σ_{dc} of the sample because no hydrate has been formed yet. With a decreasing temperature of the sample, the polarization strength of water molecules increases and the mobility of ions in the pore water decreases. In the sub-process of B in **Fig. 5**, both the TDR-derived K_a and σ_{dc} decrease

continuously due to the consumption of pore water and the increased amount of THF hydrate. The resultant hydrate has a much lower permittivity (~ 5) and conductivity ($\sim 10^{-5}$ S/m) than those of the pore water (~ 80 and ~ 0.50 S/m). A significant portion of the current paths can be blocked by the solid-state hydrate, leading to a decrease of the TDR-derived σ_{dc} further. It is worth to be noted that there is a change in the decreasing rate of the TDR-derived σ_{dc} with time. The corresponding time-period is also characterized by a sharp rise of the temperature that is induced by the exothermic effect of hydrate formation. Both the exothermic effect and salt-removing effect accompanying the formation of THF hydrates disturbs the variations of TDR-derived K_a and σ_{dc} . In the sub-process of C in **Fig. 5**, the temperature, K_a and σ_{dc} remain steady for a long period, which shows that the hydrate formation has completed. The hydrate-bearing sample at the end of this sub-process is ready for further TDR tests.

4.2 Effects of saturation and clay on TDR responses

The influences of hydrate saturation, clay type and clay content on the TDR-derived K_a and σ_{dc} of the samples were examined experimentally. The TDR waveforms in terms of reflection coefficient, the TDR-derived K_a and σ_{dc} are presented for different test conditions in **Figs. (6) – (9)**.

Fig. 6 (a) demonstrates the variations of the reflection coefficients against the apparent distance (i.e., L_a in Eq. (9)) for clean-sand samples of different hydrate saturations. The starting and ending positions on the waveforms need to be identified for deriving the K_a . The starting position shows that the electromagnetic pulse arrives at the starting point of the TDR probe, while the ending position corresponds to the end of the probe. It can be seen clearly that the apparent distance between the starting and ending points decreases monotonically with the increase of S_h . The stabilized reflection coefficient at the higher end of the apparent distance (i.e., ρ_{sample} in Eq. (14)) increases monotonically with an increasing S_h , showing a decreasing attenuation level of electromagnetic energy. According to Eqs. (9) and (14) presented in **Section 2**, it is reasonable that both the TDR-derived K_a and σ_{dc} of hydrate-bearing sandy samples reduce monotonically with the elevation of S_h . This trend can be reproduced by the plots as presented in **Fig. 6 (b)**. It has been reported that the relative permittivity of hydrates (e.g., THF hydrate, methane hydrate) are around 5 under the application of an electromagnetic field above 100 MHz and the conductivity is about 50 μ S/m (Xing et al., 2021; Haukalid et al., 2017; Waite et al., 2009; Lee et

al., 2007). Both the permittivity and conductivity of the hydrate in samples are much lower than those of the pore water with the NaCl fraction of 0.5 %. Therefore, the K_a and σ_{dc} of hydrate-bearing samples are controlled by the amount and properties of the pore water. A higher S_h results in a less amount of water, leading to a lower K_a and σ_{dc} of the hydrate-bearing sample.

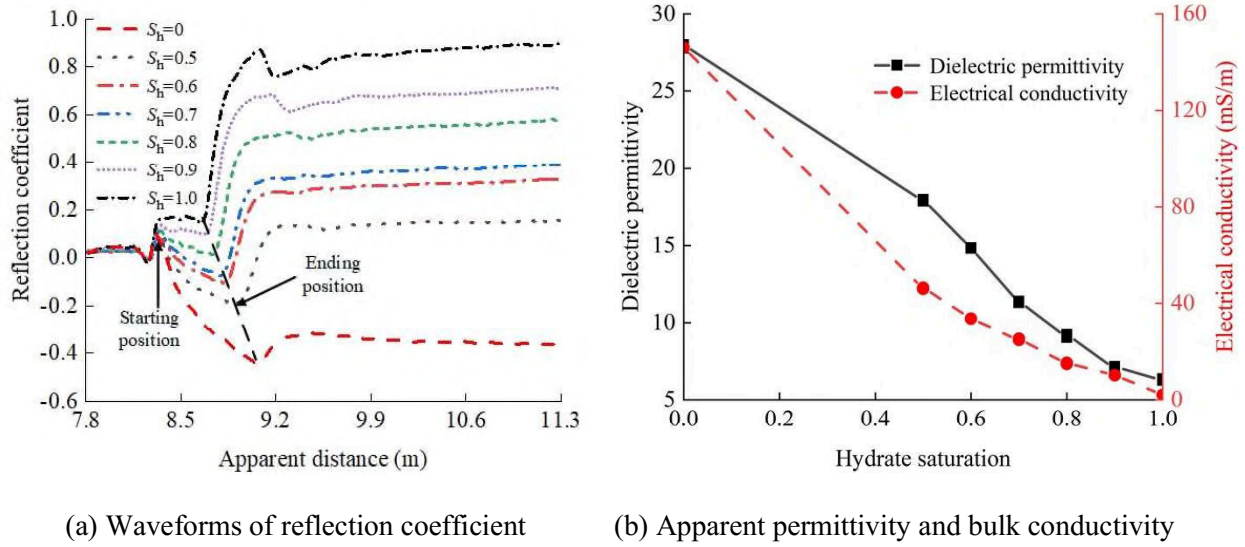


Fig. 6 TDR waveforms of reflection coefficient and TDR-derived electrical parameters for clean-sand samples of different hydrate saturations

To examine the effects of clay mineralogy on TDR responses, two clay minerals (i.e., smectite and illite) were adopted in the experimental tests. **Fig. 7** illustrates the TDR waveforms of reflection coefficient from the tests on samples with the clay content of 5 % and clean-sand samples (i.e., no clay). The test data acquired from the samples with the hydrate saturation of 0 (i.e., water saturated) and 1.0 (i.e., hydrate saturated) are illustrated in **Fig. 7 (a)** and **(b)**, respectively. Significant differences of the waveform characteristics among the water-saturated samples can be observed in **Fig. 7 (a)**. The apparent distance between the starting and ending points for the smectite-bearing sample is smaller than that of the illite-bearing sample, and the clean-sand sample has the greatest L_a . In addition, the highest ρ_{sample} (i.e., the stabilized reflection coefficient as introduced in Eq. (14)) can be found in the smectite-bearing sample and the lowest in the clean-sand sample. In contrast to the water-saturated cases, there is no much difference among the three samples filled with THF hydrate in the pore space as illustrated in **Fig. 7 (b)**. The reflection-coefficient waveforms overlap with each other and cannot be distinguished for identifying each of the three samples. This indicates that both the TDR-derived K_a and σ_{dc} are almost the same for the clean-sand sample and samples with different types of clay minerals. Indeed, there are

significant differences in the composition of the samples, i.e., the THF hydrate and sand particles for the clean-sand sample, and the hydrate, sand and clay particles for the clayey samples. However, the common feature of the three samples is that they do not have any water in the pore space under the hydrate-saturated condition. As a result, both the K_a and σ_{dc} of the tested samples are nearly identical due to the similar permittivities of the clay and sand particles.

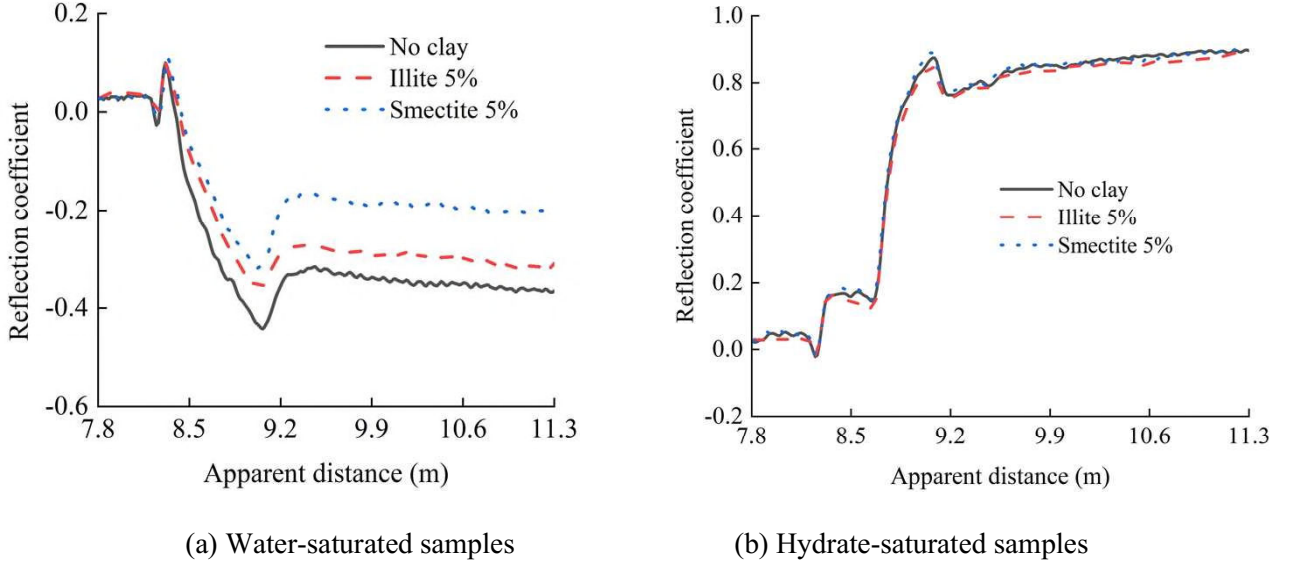


Fig. 7 TDR waveforms of reflection coefficient for water-saturated and hydrate-saturated clean-sand samples and samples with different clay minerals

Fig. 8 shows the TDR-derived K_a and σ_{dc} of clean-sand samples and smectite/illite-bearing samples with the S_h from 0.5 to 1.0. Generally, both the K_a and σ_{dc} decrease with an increasing S_h monotonically. This variation trend is reasonable because it is the volumetric fraction of the free-state pore water that controls the K_a and σ_{dc} of the samples. At the same S_h , the lowest K_a and σ_{dc} can be found with the smectite-bearing samples and the highest with the clean-sand sample. Additionally, the differences among the three types of samples reduce gradually with an increasing S_h . The difference of the σ_{dc} approaches to zero for samples with the S_h over 0.9 as indicated in **Fig. 8 (b)**. In those samples with a high S_h , the total water saturation is no more than 0.1 and all the residual water can be regarded as bound water.

The sand has a much lower SSA than clay minerals (e.g., illite and smectite used in this work). A significant amount of the pore water can be adsorbed to the particle surface of clay minerals. In this way, a portion of the pore water (i.e., free water) is transformed into bond water in the samples with smectite and illite. Due to the

limited mobility of the water molecules in bonded state, the dielectric permittivity of the bond water is significantly smaller than that of the free water. The smectite has a higher SSA than the illite, and thus a higher bond-water saturation is present in the smectite-bearing samples. In addition, a more significant volume-expansion effect (i.e., swelling effect) can be found in the smectite-bearing samples than that of the illite-bearing ones. The volume expansion of the smectite results in a stronger blockage effect to the flow paths of electric current than that of the illite. Consequently, the flow path shrinks further in terms of the effective cross-section area and becomes more tortuous in the smectite-bearing samples than that in the illite-bearing samples. To summarize, the presence of the smectite in hydrate-bearing samples results in even lower K_a and σ_{dc} due to the higher SSA, higher fraction of the bond water (i.e., lower fraction of the free water) and stronger swelling effects.

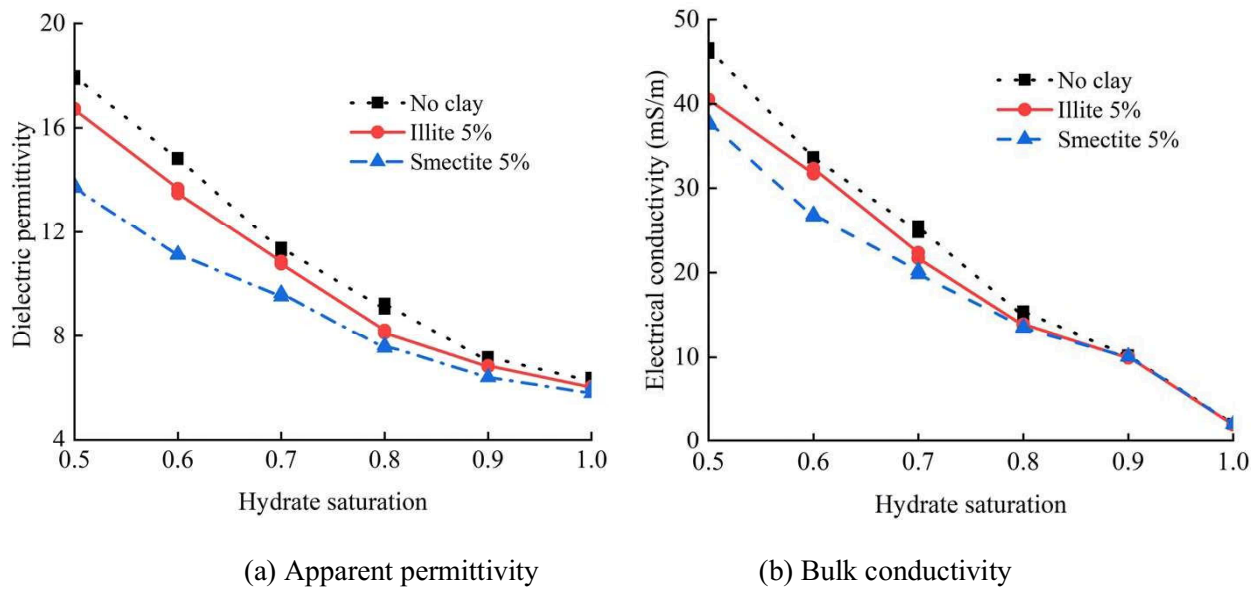
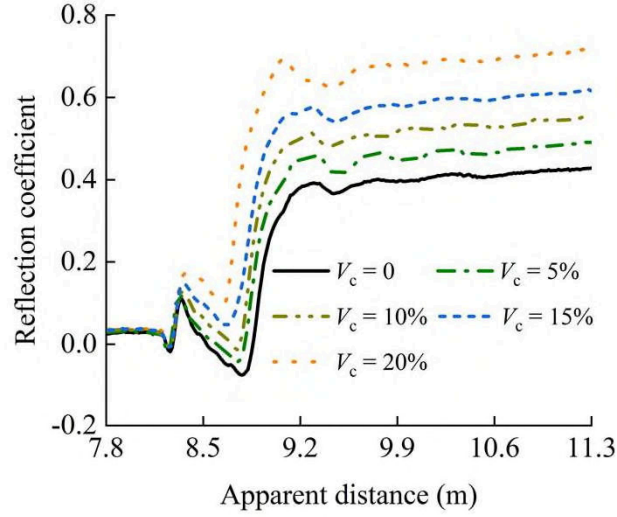
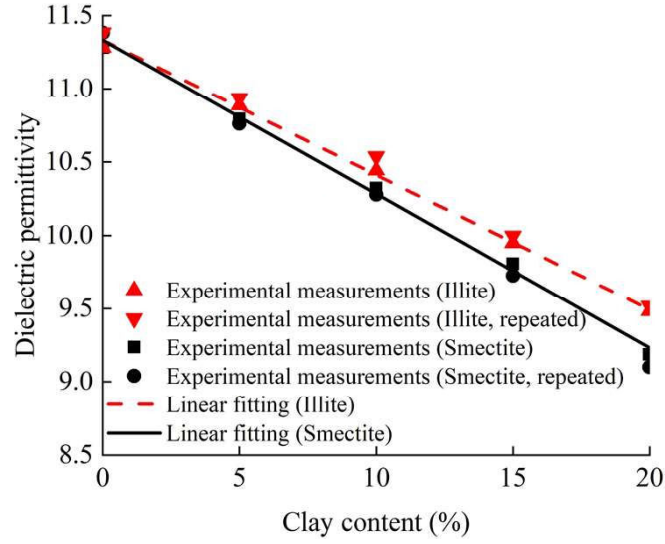


Fig. 8 TDR-derived apparent permittivity and bulk conductivity for clean-sand samples and samples with different clay minerals at various hydrate saturations

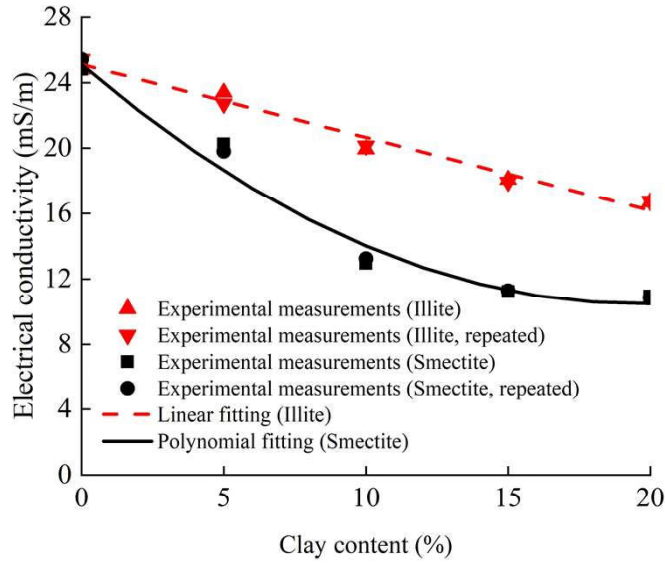
Fig. 9 presents the reflection-coefficient waveforms and TDR-derived K_a and σ_{dc} for the samples with the clay content (V_c) from 0 to 20 %. The test data from both the illite-bearing and smectite-bearing samples with a series of V_c at the same S_h (i.e., $S_h = 0.7$) are illustrated in **Fig. 9 (b)** and (c). It can be found in **Fig. 9 (a)** that the apparent distance between the starting and ending points decreases and the reflection coefficient (ρ_{sample}) increases monotonically with an increasing V_c . Accordingly, both the TDR-derived K_a and σ_{dc} of the hydrate-bearing samples decrease with an increasing V_c .



(a) Waveforms of reflection coefficient



(b) Apparent permittivity



(c) Bulk conductivity

Fig. 9 TDR waveforms of reflection coefficient (for illite cases) and TDR-derived electrical parameters for the samples of different clay contents at the same hydrate saturation ($S_h = 0.7$)

In the experiment of this work, it was assumed that the added clays were mainly distributed in a dispersive mode in the pore space of the samples. This is partially evidenced by the similarity of the porosity reduction to the volume fraction of clay. Generally, an increase of the V_c in hydrate-bearing samples result in a lower effective porosity of the sample and a higher fraction of bond water (i.e., a lower fraction of free water) in the total water phase. The reduction of the volumetric fraction of free water results in the decrease in the TDR-derived K_a and σ_{dc} of the samples. The bound-water saturation of the smectite-bearing samples remains to be higher than that of the illite-bearing samples due to the higher SSA of smectite. This explains why a more significant reduction of the K_a and σ_{dc} with an increasing V_c is present for the smectite-bearing samples as illustrated in **Fig. 9 (b)** and **(c)**. Additionally, the reduction trace of the σ_{dc} for the smectite-bearing cases evolves in a more complex way than that for the illite-bearing cases. This can be attributed to the difference of the water-swelling effects between the two clay minerals. More expansion in volume can be induced in the smectite-bearing samples due to the stronger swelling effects. Consequently, a more complex elevation characteristic of the electrical tortuosity appears leading to complex variation behavior of the σ_{dc} .

In **Fig. 9 (b)**, it can be found that the TDR-derived K_a of both the smectite-bearing and illite-bearing samples decreases almost linearly with an increasing V_c up to 20 %. Therefore, linear correlations between the K_a and V_c were employed to fit the test data. The best-fit correlations for the illite-bearing and smectite-bearing samples are expressed in Eq. (18). As indicated in **Fig. 9 (c)**, the TDR-derived σ_{dc} of the smectite-bearing samples decreases nonlinearly with the increase of V_c , which is remarkably different from that of the illite-bearing samples. Consequently, linear and quadratic functions relating the σ_{dc} and V_c were employed to fit the test data from the illite-bearing and smectite-bearing samples, respectively. The best-fit correlations for the illite-bearing and smectite-bearing samples are formulated in Eq. (19). It need to be noted that the best-fit correlations (i.e., Eqs. (18) and (19)) are useful not only to demonstrate the variation behavior of the TDR-derived electrical parameters with the clay content, but also to estimate the clay content of samples from the TDR measurements.

$$\begin{cases} K_a = -0.092 V_c + 11.332 & (R^2 = 0.998, \text{Illite}) \\ K_a = -0.105 V_c + 11.332 & (R^2 = 0.997, \text{Smectite}) \end{cases} \quad (18)$$

$$\begin{cases} \sigma_{dc} = -0.447 V_c + 25.120 & (R^2 = 0.976, \text{ Illite}) \\ \sigma_{dc} = 0.038 V_c^2 - 1.491 V_c + 25.120 & (R^2 = 0.974, \text{ Smectite}) \end{cases} \quad (19)$$

4.3 Modelling of relationship between apparent permittivity and hydrate saturation

Modelling of the relationship between TDR-derived K_a and S_h plays a key role in estimating the S_h from TDR measurements. Many models have been proposed to determine the water content in soils from the TDR-derived K_a . In general, those models can be classified into three categories, i.e., the physics-based models, empirical models, and power-law mixing models. In this work, typical models were selected from each of the three categories for comparison and optimization purposes.

In the category of the physics-based models, the de Loor model (de Loor, 1968) has been widely used for theoretical analysis and comparison with newly established models. In the original model, the soil was treated as an isotropic mixture consisting of disc-shaped granules. There are two typical forms for the de Loor model used in soil science, i.e., one simplified version with three components and the other one treating the bound water as the fourth component (Dirksen and Dasberg, 1993; Jacobsen and Schjønning, 1995). In the category of the empirical models, the models proposed by Topp et al. (1980, 2000) and Topp and Davis (1985) have been well accepted for determining the water content in various soils. The classical refractive index (RI for short) model with the exponent of 0.5 can be considered as a specific example of the power-law mixing models. It needs to be mentioned that the Topp models were developed from the best fitting of their experimental data, and the RI model was established with the assumption of an ideal layered medium. Considering the ‘empirical’ nature and the ‘ideal’ nature of the Topp and RI models, a pure empirical model and a power-law mixing model with an empirical exponent were adopted and derived based on the experimental data in this work. A quadratic polynomial relation was used to fit the experimental data following the same way with the Topp model for comparison. In this work, to establish the power-law mixing models for the clean-sand and clayey samples containing hydrates, three-component and four-component formulas were employed, respectively. The bound water was treated as an independent component in the four-component versions of the de Loor model and power-law mixing models. The formulas (denoted as permittivity or permittivity-based models hereafter) employed in this work for modelling the relationship between the TDR-derived K_a and S_h are presented as Eqs. (20) – (26)

and **Table 1**.

The de Looer models used in this work are formulated as Eqs. (20) and (21) for the clean-sand and clayey samples containing hydrates, respectively. There are three components, i.e. the sand particle, pore water and hydrate, in the clean-sand samples. In the clayey samples, the bond water is the forth component in addition to the above three phases. The models for the clean-sand and clayey samples are called three-component and four-component de Looer models, respectively.

$$K_a = \frac{3\varepsilon_s + 2\varphi(\varepsilon_h - \varepsilon_s) - 2\varphi(1 - S_h)(\varepsilon_h - \varepsilon_w)}{3 + \varphi\left(\frac{\varepsilon_s}{\varepsilon_h} - 1\right) + \varepsilon_s\varphi(1 - S_h)\left(\frac{1}{\varepsilon_w} - \frac{1}{\varepsilon_h}\right)} \quad (20)$$

$$K_a = \frac{3\varepsilon_s + 2(\varphi_e - \theta_{bw})(1 - S_h)(\varepsilon_{fw} - \varepsilon_s) + 2\theta_{bw}(\varepsilon_{bw} - \varepsilon_s) + 2(\varphi_e - \theta_{bw})S_h(\varepsilon_h - \varepsilon_s)}{3 + (\varphi_e - \theta_{bw})(1 - S_h)\left(\frac{\varepsilon_s}{\varepsilon_{fw}} - 1\right) + \theta_{bw}\left(\frac{\varepsilon_s}{\varepsilon_{bw}} - 1\right) + (\varphi_e - \theta_{bw})S_h\left(\frac{\varepsilon_s}{\varepsilon_h} - 1\right)} \quad (21)$$

where K_a is the TDR-derived apparent (relative) permittivity of the hydrate-bearing sample; ε_s , ε_h and ε_w are the relative permittivities of the sand particle, hydrate and pore water in the clean-sand samples, respectively; ε_{fw} and ε_{bw} are the relative permittivities of the free water and bound water, respectively, in the clayey samples; φ and φ_e are the effective porosities of the clean-sand and clayey samples, respectively; and θ_{bw} is the volumetric fraction of bound water in the samples, respectively.

The model proposed in Topp et al. (1980) is formulated as a three-order polynomial equation as shown in Eq. (22). The experimental data collected in this work were fitted with polynomials following the same method with Topp et al. (1980). However, it was found that the best fitting performance was obtained with quadratic polynomials as shown in Eqs. (23) and (24).

$$K_a = -76.7[\varphi(1 - S_h)]^3 + 146.0[\varphi(1 - S_h)]^2 + 9.3\varphi(1 - S_h) + 3.03 \quad (22)$$

$$K_a = A_1[\varphi_e(1 - S_h)]^2 + B_1\varphi_e(1 - S_h) + C_1 \quad (23)$$

$$K_a = A_2[\varphi_e(1 - S_h)]^2 + B_2\varphi_e(1 - S_h) + C_2 \quad (24)$$

where (A_1, B_1, C_1) and (A_2, B_2, C_2) are the empirical parameters obtained from the best fitting of the test data collected in this work for the clean-sand and clayey samples with hydrates, respectively.

The power-law mixing models adopted in this work include the RI model and the best-fitting models for the clean-sand and clayey samples. The exponents (denoted as k_1 and k_2 for clean-sand and clayey samples respectively) of the power-law models as shown in Eqs. (25) and (26) were obtained from a best fitting of the experimental data in this work.

$$K_a^{k_1} = (1 - \varphi) \varepsilon_s^{k_1} + \varphi (1 - S_h) \varepsilon_w^{k_1} + \varphi S_h \varepsilon_h^{k_1} \quad (25)$$

$$K_a^{k_2} = (1 - \varphi_e) \varepsilon_s^{k_2} + (\varphi_e - \theta_{bw}) S_h \varepsilon_h^{k_2} + (\varphi_e - \theta_{bw}) (1 - S_h) \varepsilon_{fw}^{k_2} + \theta_{bw} \varepsilon_{bw}^{k_2} \quad (26)$$

It needs to be noted that the volumetric fraction (θ_{bw}) and permittivity of the bound water (ε_{bw}) in the hydrate-bearing clayey samples are required by both the de Looer models and power-law mixing models. The volumetric fraction of bound water in the clayey samples can be calculated by Eq. (27) with a reference to Leroy et al. (2006).

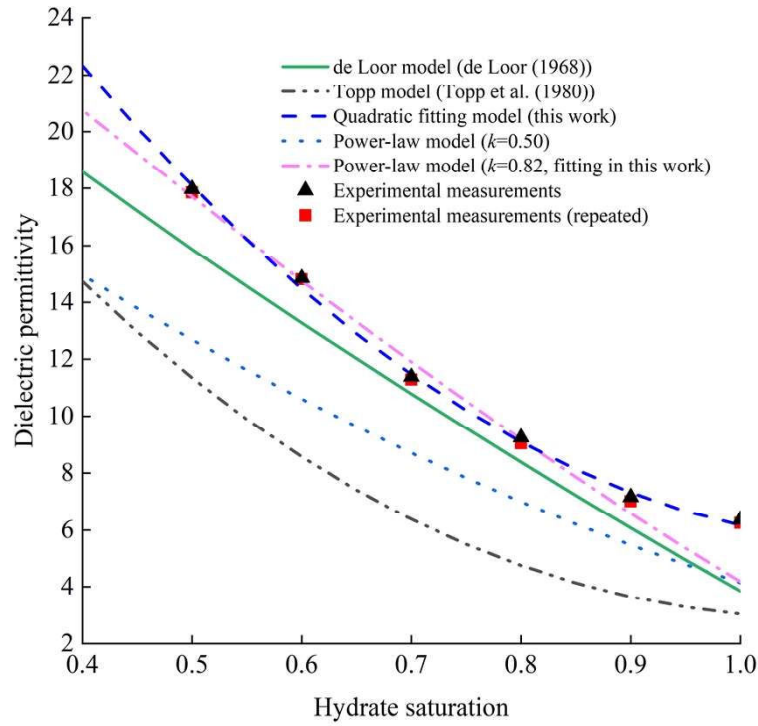
$$\theta_{bw} = \rho_g (1 - \varphi_e) S_{spc} V_c d_{bw} \quad (27)$$

where ρ_g is the grain density of the clay minerals (2650 kg/m³ in this work); S_{spc} is the SSA of the clay minerals (i.e., 346 m²/g for the smectite and 83 m²/g for the illite as reported by Macht et al. (2011)); and d_{bw} is the thickness of the bound-water layer. It is assumed that there are four layers and one layer of water molecules on the solid surface of smectite and illite particles, respectively. The thickness was determined as 10.65×10⁻¹⁰ m and 2.14×10⁻¹⁰ m for the smectite-bearing and illite-bearing samples, respectively, with the known size of water molecules and number of layers. The relative permittivity of the bound water (ε_{bw}) required in the four-component models can be derived based on the known thickness d_{bw} , which is 32.5 and 3.2, respectively, for the smectite and illite cases (Sun and Young, 2001).

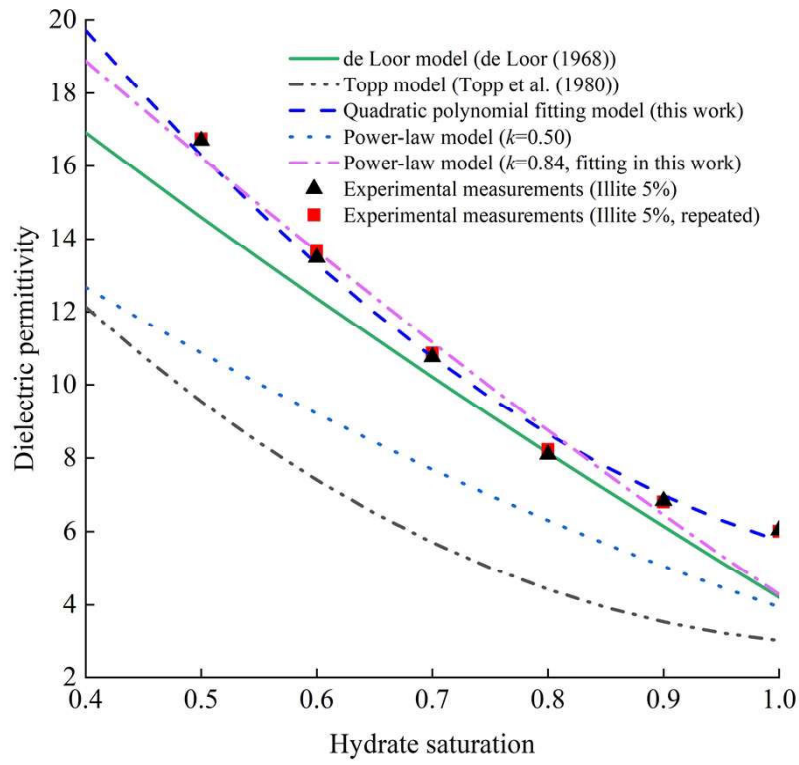
Table 1 Values of physical and empirical parameters in the permittivity models

Model	number of components	Physical parameters	Empirical Parameters	R^2
Theoretical models based on de Loor (1968)	3	$\varepsilon_s = 5.0, \varepsilon_h = 3.0, \varepsilon_w = 87.74,$ $\varphi = 0.40$	—	—
	4	$\varepsilon_{bw} = 3.2$ (illite), $\theta_{bw} = 0.15$ %, ε_{fw} $= 87.74, \varphi_e = 0.35$	—	—
	4	$\varepsilon_{bw} = 32.5$ (smectite), $\theta_{bw} =$ 3.17 %, $\varepsilon_{fw} = 87.74, \varphi_e = 0.35$	—	—
Polynomial models following Topp et al. (1980)	3	$\varphi = 0.40$	$(A_1, B_1, C_1) = (193.281,$ $20.935, 6.175)$	0.997
	4	$\varphi_e = 0.35, V_c = 5$ % (illite)	$(A_2, B_2, C_2) = (178.620,$ $29.064, 5.747)$	0.995
	4	$\varphi_e = 0.35, V_c = 5$ % (smectite)	$(A_2, B_2, C_2) = (118.718,$ $23.066, 5.685)$	0.994
Power-law mixing models	3	$\varepsilon_s = 5.0, \varepsilon_h = 3.0, \varepsilon_w = 87.74,$ $\varphi = 0.40$	$k_1 = 0.82$	0.965
	4	$\varepsilon_{bw} = 3.2$ (illite), $\theta_{bw} = 0.15$ %, ε_{fw} $= 87.74, \varphi_e = 0.35$	$k_2 = 0.84$	0.963
	4	$\varepsilon_{bw} = 32.5$ (smectite), $\theta_{bw} =$ 3.17 %, $\varepsilon_{fw} = 87.74, \varphi_e = 0.35$	$k_2 = 0.63$	0.970

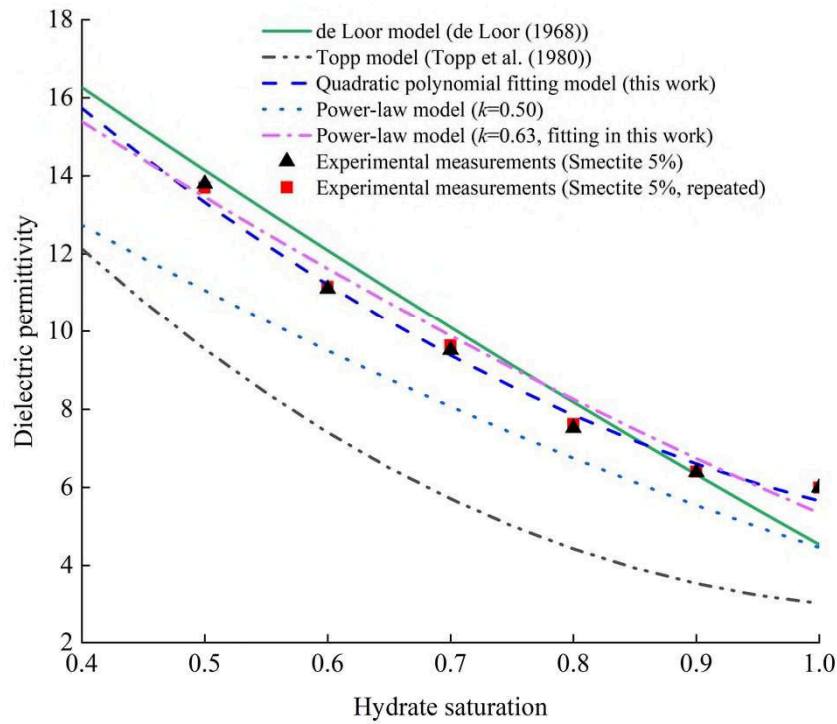
Fig. 10 compares the predictions of the above permittivity models and experimental measurements (i.e., TDR-derived K_a) for the clean-sand and clayey samples at different hydrate saturations. Generally, all the models predict the variation trend of the K_a with S_h . However, significant discrepancies can be observed between the experimental measurements and predictions from the models that did not take the data collected in this work into consideration. Those underperforming models include the ‘de Loor’ theoretical model, Topp model and RI model. It is not surprising that the Topp model and RI model perform the worst. This can be attributed to the pure ‘empirical’ nature and ‘ideal medium’ assumption, respectively. The ‘de Loor’ theoretical model performs better in the clayey cases especially for the smectite-bearing samples than the clean-sand samples. It is postulated that the pore space and clay particles of high-aspect ratio in the clayey samples is closer to the ‘disc-shaped granules’ assumption made in the model. It is reasonable and expected that the fitting models based on the test data of this work, i.e., the quadratic polynomial model and the power-law mixing model with a fitted exponent, perform better than the above three models. The power-law mixing model with a fitted exponent becomes a preferable permittivity model because it possesses both merits of empirical and theoretical models.



(a) Clean-sand samples



(b) Illite-bearing samples



(c) Smectite-bearing samples

Fig. 10 Comparison of model predictions and TDR-derived permittivity for clean-sand samples and clayey samples with illite and smectite ($V_c = 5\%$) at different hydrate saturations

4.4 Modelling of relationship between bulk conductivity and hydrate saturation

Similar to the permittivity models presented in **Section 4.3**, the relationship between the TDR-derived σ_{dc} and S_h was modelled based on the test data collected in this work. The Archie model (Archie, 1942) and Simandoux model (Simandoux, 1963) were employed for the clean-sand and clayey samples containing hydrates, respectively.

The ratio of the sample conductivity at water-saturated state (i.e., σ_0) to the conductivity with the hydrate present (i.e., TDR-derived σ_{dc}) can be defined as the conductivity index, which is denoted as I (dimensionless) according to the Archie's law. The product of the formation factor (F) and the saturation index I is then expressed as the ratio of the conductivity of the pore water (σ_w) to that of the TDR-derived σ_{dc} as shown in Eqs. (28) and (29).

$$\frac{\sigma_w}{\sigma_{dc}} = \varphi^{-m} (1 - S_h)^{-n} \quad (28)$$

$$\ln \left(\frac{\sigma_w}{\sigma_{dc}} \right) = -n \ln (1 - S_h) - m \ln(\varphi) \quad (29)$$

where m and n are the cementation and saturation exponents, respectively. **Fig. 11** illustrates a best-fitting operation to quantify the empirical parameters (i.e., m and n) in Eq. (29) based on the test data for the clean-sand samples. It can be derived from **Fig. 11** that m and n are 1.905 and 1.0 ($R^2 = 0.927$), respectively. As a result, the relationship between the TDR-derived σ_{dc} and S_h can be modelled as Eq. (30).

$$\sigma_{dc} = \varphi^{1.905} (1 - S_h) \sigma_w \quad (30)$$

In the Simandoux model, it is assumed that the conductivity of a clayey sample is attributed to two contributions. For the water-saturated samples, one contribution is made by the conductivity of the sand portion filled with pore water and the other is made by the clay minerals. The two contributions to the bulk conductivity function in parallel as formulated mathematically in Eq. (31).

$$\sigma_0 = Q_{sd} + Q_c \quad (31)$$

where σ_0 denotes the conductivity of a clayey sample; and Q_c and Q_{sd} are the conductivity contributions from the

clay portion and sand portion, respectively. It is assumed that the hydrate can only form in the sand portion with the amount of pore water reduced for the clayey samples. The TDR-derived σ_{dc} of the clayey samples containing hydrates is then formulated as Eqs. (32) – (34).

$$\sigma_{dc} = (1 - V_c) \varphi_e^{m^*} (1 - S_h)^{n^*} \sigma_w + V_c \sigma_c \quad (32)$$

$$\ln \Phi^* = n^* \ln \left(\frac{1}{1 - S_h} \right) - m^* \ln \varphi_e \quad (33)$$

$$\Phi^* = \frac{(1 - V_c) \sigma_w}{\sigma_{dc} - V_c \sigma_c} \quad (34)$$

where $\varphi_e = \varphi - V_c$ is the effective porosity of the clayey samples; σ_w and σ_c are the conductivities of the pore water and clay portion, respectively; and m^* and n^* are the cementation and saturation exponents, respectively. The pore-water conductivity (i.e., σ_w) is 0.499 S/m in the experiment of this work. The conductivity of the clay portion (i.e., σ_c) in the Simandoux model is affected by several factors, such as the various physico-chemical properties of the clay mineral and pore water (Kibria et al., 2017). The conductivity of the clay portion was determined as 0.041 S/m from Eq. (32) with the S_h of 1.0 based on the experimental data as shown in **Fig. 8(b)**.

Fig. 12 illustrates the linear best-fitting operation for the determining the unknown exponents, i.e., m^* and n^* , in Eq. (33). The values of m^* and n^* were determined as 1.798 and 1.012 ($R^2 = 0.966$) for the illite-bearing samples and 2.0 and 0.912 ($R^2 = 0.957$) for the smectite-bearing samples, respectively, based on the experimental data in this work. Finally, the relationship between the TDR-derived σ_{dc} and S_h is formulated as Eqs. (35) and (36) for the clayey samples containing illite and smectite, respectively.

$$\sigma_{dc} = \varphi_e^{1.798} (1 - S_h)^{1.012} (1 - V_{cl}) \sigma_w + V_{cl} \sigma_{cl} \quad (\text{Illite}) \quad (35)$$

$$\sigma_{dc} = \varphi_e^{2.0} (1 - S_h)^{0.912} (1 - V_{cs}) \sigma_w + V_{cs} \sigma_{cs} \quad (\text{Smectite}) \quad (36)$$

where V_{cl} and V_{cs} are the volumetric fraction of illite and smectite in the samples, respectively; and σ_{cl} and σ_{cs} are the conductivity of the illite and smectite portions, respectively.

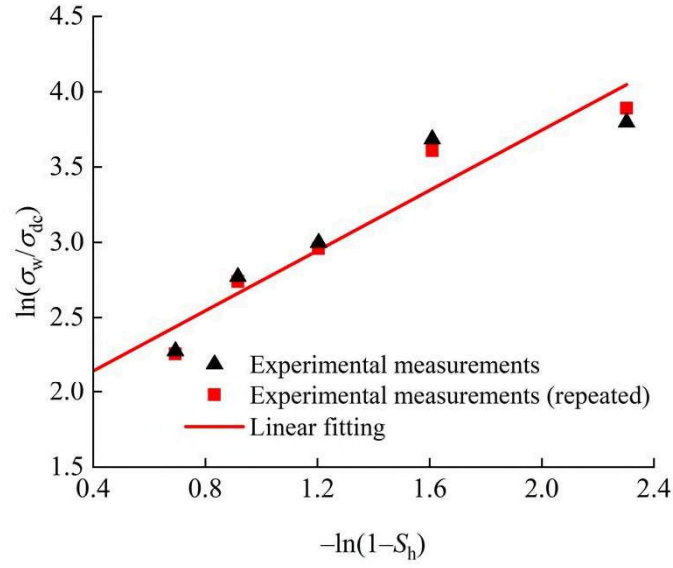


Fig. 11 Best-fitting of experimental data for determining the cementation and saturation exponents in the Archie model for clean-sand samples

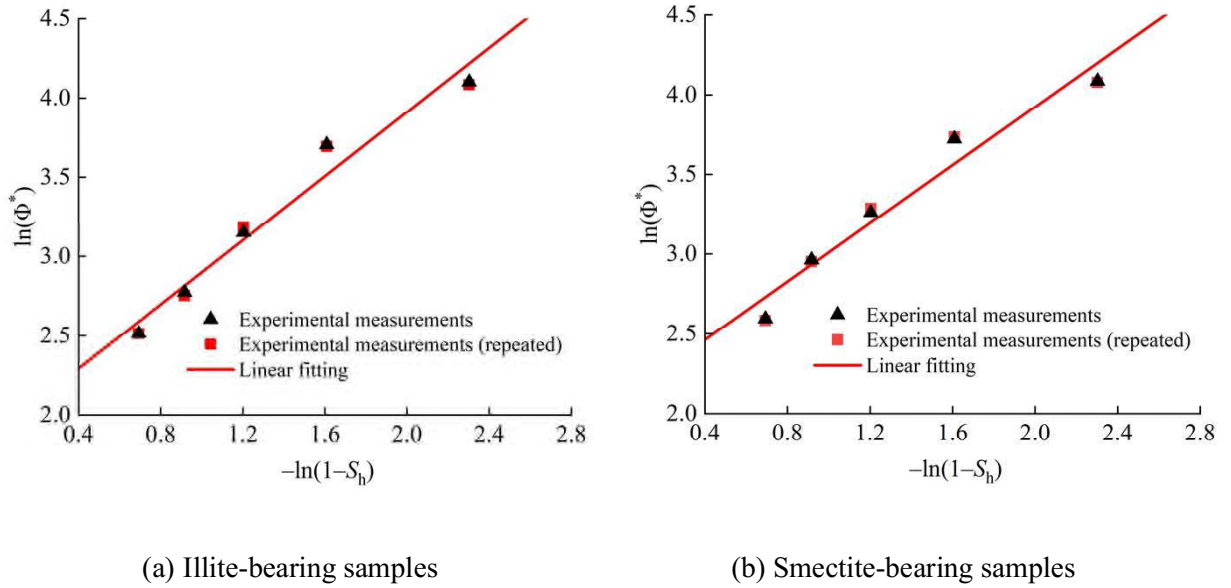


Fig. 12 Best-fitting of experimental data for determining the cementation and saturation exponents in the Simandoux model for illite-bearing and smectite-bearing samples

4.5 Permittivity-conductivity joint model for hydrate saturation quantification

As presented in **Section 4.3** and **4.4**, the relationship between the TDR-derived electrical parameters (i.e., K_a and σ_{dc}) and hydrate saturation was modelled based on theoretical, semi-empirical and empirical models. Generally, the performance of the theoretical models (e.g., de Loor model) and existing empirical models (e.g.,

Topp model) are inferior to the semi-empirical and empirical models developed based on the test data collected in this work. This is reasonable because the assumptions made in the theoretical models may not hold in the experimental conditions of this work and the existing empirical models were established from the data within a limited range of conditions. Therefore, to develop hydrate-saturation quantification models, it is more sensible to employ the semi-empirical models and empirical models that can acquire knowledge from the experimental data of this work. However, considering the pure ‘empirical’ nature of the empirical models (e.g., those established following the method of Topp model), the semi-empirical models such as the power-law mixing model, Archie model and Simandoux model, were chosen for establishing hydrate-saturation quantification models below.

A permittivity-conductivity (P-C) joint model for quantifying the S_h in clean-sand and clayey samples from TDR-derived K_a and σ_{dc} was proposed. The basic idea of this modelling approach is to make the best use of the electrical information embedded in TDR measurements. The TDR-derived K_a and σ_{dc} correspond to the energy storage and dissipation of the electromagnetic wave, respectively. The electromagnetic pulse travels along the TDR probe and hydrate-bearing samples. It is sensible and preferable to utilize both the K_a and σ_{dc} for conjointly characterizing the interactions between the electromagnetic wave and tested samples. It is expected to obtain more reliable hydrate-saturation quantification based on the P-C joint model due to the incorporation of the dielectric polarization and electrical conduction mechanisms.

As presented in **Section 4.3** and **4.4**, the TDR-derived K_a and σ_{dc} have been related to the S_h quantitatively, respectively. The formulas can serve as permittivity or conductivity prediction models with known hydrate saturations. Meanwhile they can also be taken as hydrate-saturation quantification models, i.e., the permittivity-based and conductivity-based models, respectively. To derive the P-C joint model, it is the first step to find a shared or bridge parameter to connect the two kinds of models. This parameter should be an intrinsic one that can characterize the sample and influence the electrical properties of the sample. As a result, the porosity of the sample was selected as the bridge parameter to derive the P-C joint model. For the clean-sand samples with hydrates, the porosity was obtained from the Archie model (i.e., Eq. (30)) and then substituted into the three-component power-law mixing model (i.e., Eq. (25)). Likewise, for the clayey hydrate-bearing samples, the

effective porosity was derived from the Simandoux model (i.e., Eq. (35) or (36)) and then substituted into the four-component power-law mixing model (i.e., Eq. (26)). Finally, the P-C joint models for quantifying the S_h in clean-sand and clayey samples were obtained as formulated by Eqs. (37) and (38), respectively. It needs to be noted that the two P-C joint models had to be formulated in an implicit form, which posed challenges to solution processes. A fix-point iteration method (FPIM) was utilized to solve the implicit equations of the P-C models for solutions to the S_h based on the TDR-derived K_a and σ_{dc} (Xing et al, 2014).

$$S_h = \frac{\varepsilon_w^{k_1} - \varepsilon_s^{k_1} - (K_a^{k_1} - \varepsilon_s^{k_1}) \left[\frac{(1 - S_h)^n \sigma_w}{\sigma_{dc}} \right]^{\frac{1}{m}}}{\varepsilon_w^{k_1} - \varepsilon_h^{k_1}} \quad (37)$$

$$S_h = 1 - \left\{ \frac{(\sigma_{dc} - V_c \sigma_c) [-\varepsilon_s^{k_2} + S_h \varepsilon_h^{k_2} + (1 - S_h) \varepsilon_{fw}^{k_2}]^{m^*}}{\sigma_w (1 - V_c) [K_a^{k_2} - \varepsilon_s^{k_2} + \theta_{bw} S_h \varepsilon_h^{k_2} + \theta_{bw} (1 - S_h) \varepsilon_{fw}^{k_2} - \theta_{bw} \varepsilon_{bw}^{k_2}]^{m^*}} \right\}^{\frac{1}{n^*}} \quad (38)$$

To assess the performance of the P-C joint models for quantifying the S_h , three error specifications, i.e., the absolute, relative and root-mean-squared errors, were adopted. The absolute and relative errors (denoted as E_A and E_R , respectively) were used to examine the model performance for each test point individually, while the root-mean-squared error (denoted as E_{RMS}) was employed to assess the overall performance of the models within the specific test range. The three error specifications were computed by using Eqs. (39) – (41), respectively.

$$E_A(i) = S_{hp}(i) - S_{hr}(i) \quad (39)$$

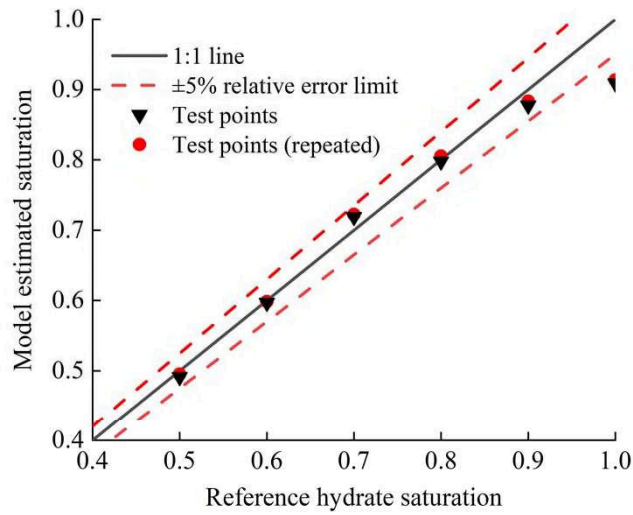
$$E_R(i) = \frac{E_A(i)}{S_{hr}(i)} \times 100 \% \quad (40)$$

$$E_{RMS} = \sqrt{\frac{1}{N} \sum_{i=1}^N \left(\frac{E_A(i)}{S_{hr}(i)} \right)^2} \times 100 \% \quad (41)$$

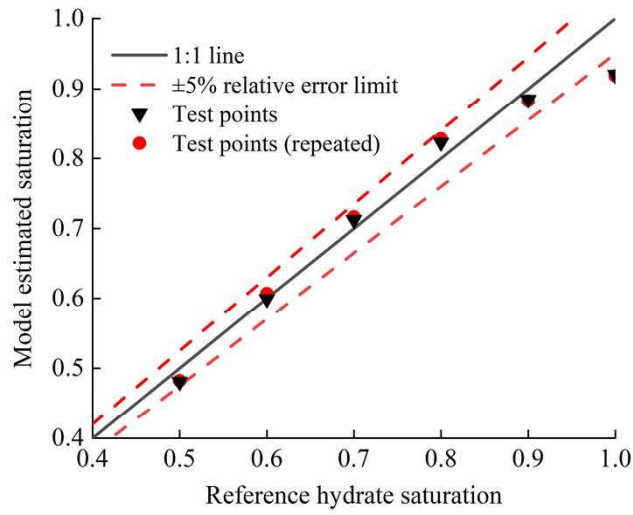
where $S_{hp}(i)$ and $S_{hr}(i)$ are the model-predicted and reference values of S_h for the test point labeled with i ; and N is the total count of the test points. The E_A and E_R of the S_h predicted by the permittivity-based, conductivity-based and P-C joint models are listed in **Tables 2–7**, respectively, for the tested hydrate-bearing samples. **Figs. 13–15** compare the model-predicted hydrate saturations and the corresponding reference. The relative error

bounds of $\pm 5\%$ are illustrated in the figures for clarity.

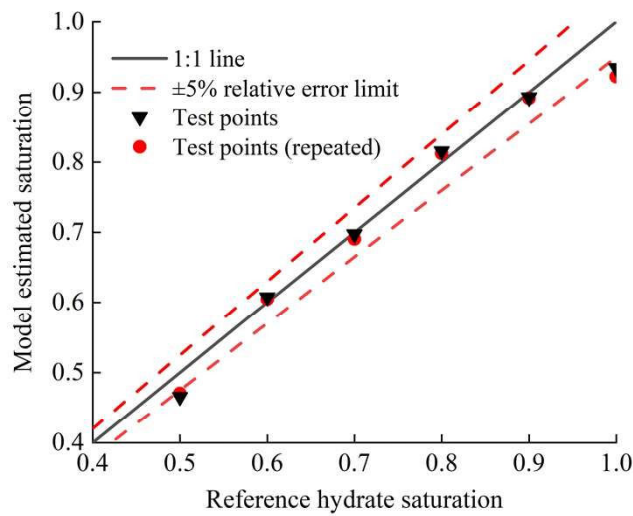
The power-law mixing models with data-fitted exponents as presented in Eqs. (25) and (26) were used as the permittivity-based models for predicting the S_h of clean-sand and clayey samples, respectively. As can be observed in **Fig. 13**, most of the test points with the S_h above 0.5 are located within the E_R bounds of $\pm 5\%$ for samples with and without clays. As shown in **Table 2** the absolute value of E_R ranges from 0.167 to 8.878 % for all the tested samples. It needs to be noted that there are remarkably higher errors for the test points with the S_h of 1.0 and 0.5. Referring to the derivation process of the permittivity-based models as indicated in **Fig. 10**, it can be found that there are significant deviations between the model-predicted permittivities and the measured (as reference) values for the test points with the S_h of 1.0. Thus, it is reasonable that significant errors appear there due to the low-performance fitting process for deriving the model parameters, i.e., the exponents of the power-law formulas. In the range of the S_h from 0.5 to 0.9, the highest E_R appears at the saturation of 0.5 for the clayey sample containing smectite, i.e., -6.416 % as shown in **Table 2**. This is acceptable considering the small denominator for calculating the E_R as indicated in Eq. (40) although the E_A is as low as -0.032 as shown in **Table 3**. The E_{RMS} of the S_h predicted by the permittivity-based models is 3.967, 4.018 and 4.041 % for the clean-sand samples, clayey samples with illite and smectite, respectively.



(a) Clean-sand samples



(b) Illite-bearing samples



(c) Smectite-bearing samples

Fig. 13 Comparison between the reference and model-estimated hydrate saturations for permittivity-based models

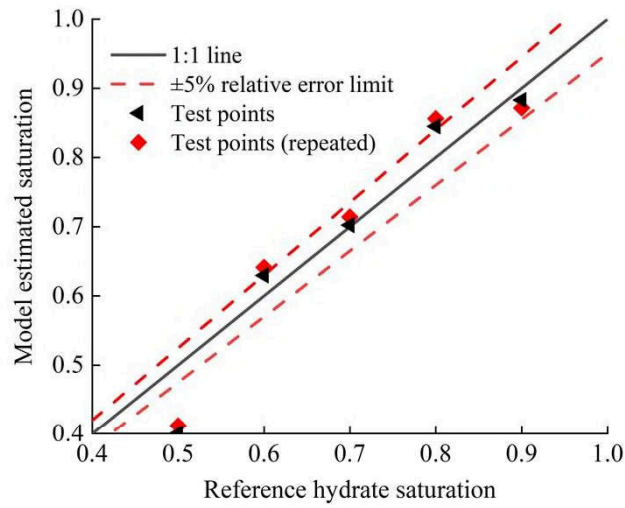
Table 2 Relative errors (E_R) of estimated hydrate saturations from permittivity-based models

Samples	Hydrate saturations					
	0.5	0.6	0.7	0.8	0.9	1.0
Clean-sand	-1.374	-0.402	2.947	0.167	-2.197	-8.878
Illite-bearing	-3.715	0.490	2.048	3.187	-1.791	-8.078
Smectite-bearing	-6.416	1.038	-0.874	1.746	-0.853	-7.154

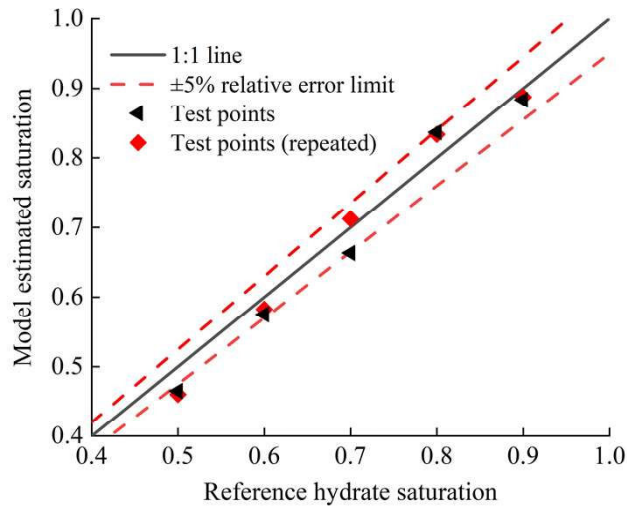
Table 3 Absolute errors (E_A) of estimated hydrate saturations from permittivity-based models

Samples	Hydrate saturations					
	0.5	0.6	0.7	0.8	0.9	1.0
Clean-sand	-0.007	-0.002	0.021	0.001	-0.020	-0.089
Illite-bearing	-0.019	0.003	0.014	0.025	-0.016	-0.081
Smectite-bearing	-0.032	0.006	-0.006	0.014	-0.008	-0.072

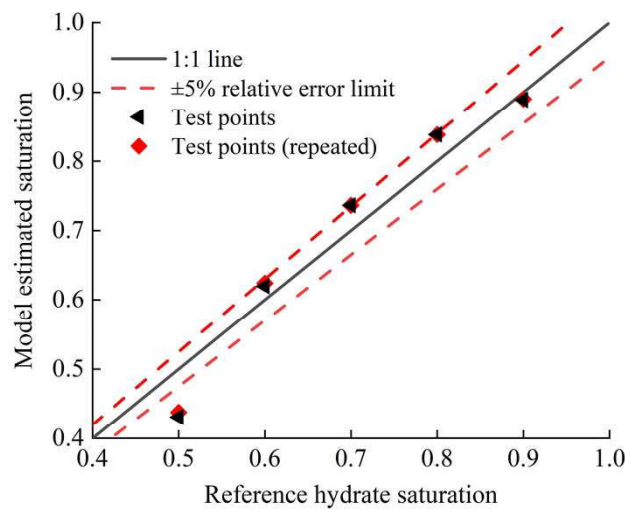
The Archie model and Simandoux models with data-fitted parameters as presented in Eqs. (30), (35) and (36) were used as the conductivity-based models for predicting the S_h of clean-sand samples and clayey samples, respectively. The analysis on the conductivity-based model is limited to the hydrate-saturation range from 0.5 to 0.9 because there is little conduction effect in the hydrate-saturated samples (i.e., $S_h = 1.0$) as indicated in **Figs. 7 and 8**. In the range of 0.6 to 0.9 for the S_h , almost all the test points are located within the E_R bounds of $\pm 5\%$ (**Fig. 14**) and the absolute value of E_R ranges from 1.143 to 6.316 % (**Table 4**). For the test points with the S_h of 0.5 there are significantly higher errors (E_R and E_A). As shown in **Tables 4 and 5**, the E_R and E_A range from -7.476 to -18.740 % and from -0.037 to -0.094, respectively, for the tested samples with the S_h of 0.5. The E_A is regarded as the dominating factor that leads to the higher E_R because it is significantly higher than that of the cases with the S_h from 0.6 to 0.9 as shown in **Table 5**. The E_{RMS} of the conductivity-based models is 9.315, 4.321 and 6.893 % for the clean-sand samples, clayey samples with illite and smectite, respectively.



(a) Clean-sand samples



(b) Illite-bearing samples



(c) Smectite-bearing samples

Fig. 14 Comparison between the reference and model-estimated hydrate saturations for conductivity-based models

Table 4 Relative errors (E_R) of estimated hydrate saturations from conductivity-based models

Samples	Hydrate saturations				
	0.5	0.6	0.7	0.8	0.9
Clean-sand	-18.740	5.914	1.166	6.316	-2.537
Illite-bearing	-7.476	-3.516	-1.742	4.417	-1.596
Smectite-bearing	-13.200	3.661	5.214	4.808	-1.143

Table 5 Absolute errors (E_A) of estimated hydrate saturations from conductivity-based models

Samples	Hydrate saturations				
	0.5	0.6	0.7	0.8	0.9
Clean-sand	-0.094	0.035	0.008	0.051	-0.023
Illite-bearing	-0.037	-0.021	-0.012	0.035	-0.014
Smectite-bearing	-0.066	0.022	0.037	0.038	-0.010

The permittivity-conductivity joint models as presented by Eqs. (37) and (38) were used for predicting the S_h of clean-sand and clayey samples, respectively. Similar to the permittivity-based and conductivity-based models, it can be found from **Fig. 15** that most of the test points are located within the E_R bounds of $\pm 5\%$ for samples with and without clays. As shown in **Table 6** the absolute value of E_R ranges from 0.950 to 6.876 % for all the tested samples except one clean-sand sample (i.e., $S_h = 0.5$). Compared with the clayey cases there are more outliers for the clean-sand samples. The highest E_R and E_A (i.e., 12.670 % and 0.063 respectively) appear in the clean-sand cases with the S_h of 0.5 as shown in **Tables 6** and **7**. The significant high errors are in accord with those in the conductivity-based model (i.e., -18.740 % and -0.094 at $S_h = 0.5$), but a significant reduction of the errors have been obtained in the newly developed P-C joint model. It is postulated that the worst estimation of S_h originates from the inaccuracy in the conductivity-based part of the P-C joint model. The E_{RMS} of the P-C joint models is 7.339, 2.930 and 2.065 % for the clean-sand samples, and clayey samples with illite and smectite, respectively. It is interesting to note that the lowest E_{RMS} have been obtained by the P-C joint model for the clayey cases among the three models (i.e., permittivity-based model, conductivity-based model and P-C joint

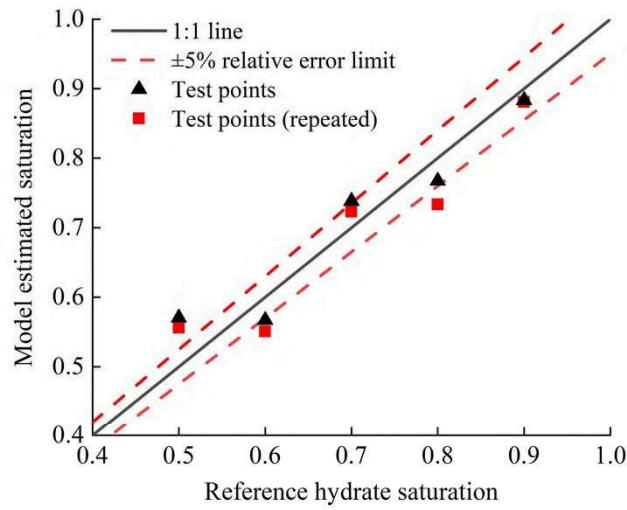
model). For the clean-sand samples, the E_{RMS} of the P-C joint model sits between those of the other two types of models. To summarize, by using the P-C joint model developed in this work, a higher accuracy in the prediction of S_{h} can be achieved. In essence, this can be attributed to the merit that the P-C joint model incorporates more physical mechanisms (i.e., both dielectric polarization and electrical conduction) and information (i.e., both permittivity and conductivity) of the hydrate-bearing samples.

Table 6 Relative errors (E_{R}) of estimated hydrate saturations from P-C joint models

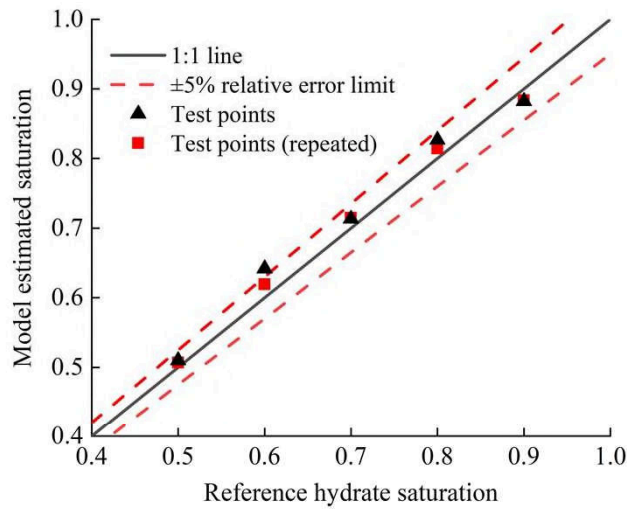
Samples	Hydrate saturations				
	0.5	0.6	0.7	0.8	0.9
Clean-sand	12.670	-6.867	4.357	-6.213	-2.011
Illite-bearing	1.700	5.083	2.000	2.556	-1.911
Smectite-bearing	1.270	1.372	-3.536	2.088	0.950

Table 7 Absolute errors (E_{A}) of estimated hydrate saturations from P-C joint models

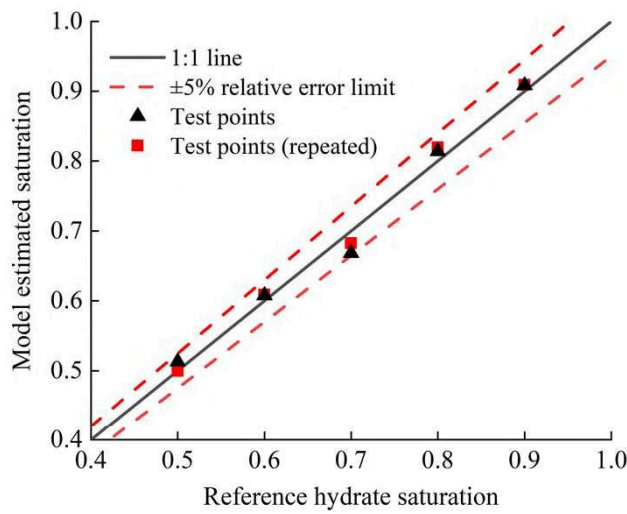
Samples	Hydrate saturations				
	0.5	0.6	0.7	0.8	0.9
Clean-sand	0.063	-0.041	0.031	-0.050	-0.018
Illite-bearing	0.009	0.031	0.014	0.020	-0.017
Smectite-bearing	0.006	0.008	-0.025	0.017	0.009



(a) Clean-sand samples



(b) Illite-bearing samples



(c) Smectite-bearing samples

Fig. 15 Comparison between the reference and model-estimated hydrate saturations for P-C joint models

5 Discussion

5.1 Application of K_a in modelling

As presented in **Section 4.3** the relationship between the TDR-derived K_a and S_h was modelled with different models such as the physics-based models, empirical models and power-law mixing models. Among those models, we have chosen the power-law mixing model with an empirical exponent for establishing the P-C joint model. Compared with the conductivity-based model, the permittivity-based model exhibits lower errors (e.g., E_{RMS} , E_R and E_A) in predicting the S_h as shown in **Section 4.5**. Additionally, the permittivity-based model even outperforms the P-C joint model for the clean-sand samples. Therefore, it is reasonable to claim that the larger uncertainty originating from the conductivity-based model has been reduced significantly by introducing the permittivity-based model into the P-C joint model. It can be concluded that there are several impressive advantages in the permittivity-based models. However, we still need to pay attention to some issues related to the modelling based on the permittivity in order to upgrade the P-C joint model further in future.

The issue to be discussed in this section stems from the difference between the TDR-derived K_a and the real part (ϵ'_r) of complex dielectric permittivity (ϵ^*_r). As introduced by Eqs. (2) and (6) in **Section 2**, theoretically the TDR-derived K_a includes the contributions from both the ϵ'_r and ϵ''_r , and the ϵ^*_r includes the contributions from ϵ''_{relax} and $\sigma_{dc}/(\omega\epsilon_0)$. In short, both the K_a and ϵ^*_r characterize the behavior of the excited electromagnetic pulse in the TDR system, i.e., the propagation speed and energy losses. However, it becomes a common practice to treat the K_a as ϵ'_r instead of ϵ^*_r when relating the TDR-derived K_a of a mixture to the permittivities of its constituents. Consequently, an intrinsic uncertainty has been introduced into the permittivity-based models and further into the P-C models. The uncertainty limits the potential for improving the accuracy and reliability of the model predictions.

The permittivity-based models presented in **Section 4.3** only adopted the ϵ'_r of each constitute but ignored the fact that the ϵ''_{relax} and $\sigma_{dc}/(\omega\epsilon_0)$ have been incorporated into the TDR-derived K_a according to Eq. (6) in **Section 2.2**. Taking the clayey samples containing hydrates for example, there are five constituents, i.e., sand grains, clay particles, free water, bound water and hydrate. The dielectric relaxation frequencies of bound water and hydrate are located in the frequency range of the TDR electromagnetic pulse (i.e., MHz – GHz). Besides, the

Maxwell-Wagner relaxation due to the differences in permittivities and conductivities of the contacted constituents becomes prominent in the frequency range of $\sim$ MHz. The above relaxation processes contribute to the term $\varepsilon''_{\text{relax}}$, which has been ignored in modelling the dielectric permittivity properties of mixtures (i.e., hydrate-bearing clayey sediments in this work). The particle surface conductivity increases with an increasing V_c , SSA and CEC of clay minerals. The surface conductivity contributes to the term $\sigma_{dc}/(\omega\varepsilon_0)$ although this issue can be alleviated with an increase in the electric-field frequency. Most of the natural hydrates in the world exists in marine sediments with a significant amount of clay minerals and high pore-water salinity. Therefore, it is also necessary to address the effects of the term $\sigma_{dc}/(\omega\varepsilon_0)$ besides the $\varepsilon''_{\text{relax}}$ in the development of the permittivity-based model.

Two possible approaches are recommended to deal with the above issues for the future work. First, an apparent ‘complex dielectric permittivity’ of the tested composite media (i.e., hydrate-bearing clayey samples in this work) is defined straightforwardly with the TDR-derived K_a and $\sigma_{dc}/(\omega\varepsilon_0)$ as the real and imaginary parts respectively. In addition, the complex dielectric permittivity instead of only the real-part permittivity of each constituent in the hydrate-bearing clayey samples are used for developing the permittivity-based models. Second, the term $\sigma_{dc}/(\omega\varepsilon_0)$ is removed from the TDR-derived K_a . This is realizable because the σ_{dc} can be derived from TDR responses. Then the resultant apparent dielectric permittivity of the hydrate-bearing clayey samples is correlated with the dielectric permittivities (i.e., only the real parts) of all the constituents. By implementing the above two approaches the imaginary part of complex permittivity (i.e., Eq. (2)) have been taken into consideration to some extent (only the term σ_{dc} but not for $\varepsilon''_{\text{relax}}$). It is expected that the updated permittivity-based models will perform better in characterizing the relationship between the TDR-derived K_a and S_h . The P-C joint model for quantifying the S_h will also benefit from the improvement of the permittivity-based models finally.

5.2 Determination of basic parameters for modelling

To examine the effects of clay mineralogy and content on the responses of TDR, a series of volumetric fractions of illite and smectite were added into clean sands for preparing the clayey samples with hydrates. Due to the difficulties and a lack of efficient methods to measure the porosity of hydrate-bearing clayey samples, in this

work, it was assumed that the added clay minerals occupied the pore space only. Consequently, the addition of the clay mineral simply resulted in a reduction of the original porosity of the corresponding clean-sand sample. For example, the porosity of a clayey sample was treated as 0.35 after 5 % clay mineral was added into the clean-sand sample with the original porosity of 0.40. Uncertainties can be introduced into the permittivity-based and conductivity-based models due to the simplified approach for determining the porosity of hydrate-bearing clayey samples. However, it is interesting to note that the porosity was cancelled out during the establishment of the P-C joint model as formulated by Eqs. (37) and (38) in **Section 4.5**. As a result, the inaccurate parameter, i.e., porosity, did not appear in the P-C joint model although it was used in the permittivity-based and conductivity-based models. Thereby, it is expected that the uncertainty of the P-C joint model induced by the uncertainty in the resultant porosity could be reduced to some extent. In the future work, it is recommended to develop an efficient and reliable means to measure the in-situ porosity of hydrate-bearing clayey sediments to achieve a more reliable P-C joint modelling approach.

There are difficulties in determining the properties of the bound water in clayey samples. As listed in **Table 1** in **Section 4.3**, the volumetric fraction and permittivity of the bound water for different clay minerals, i.e., illite and smectite in this work, are indispensable parameters in the permittivity-based and P-C joint models. The volumetric fraction of the bound water is closely related with the SSA of the tested samples, which is controlled by the mineralogy and content of clays. In addition, the permittivity of the bound water is influenced by several factors such as the thickness of bound-water layer on the surface of particles, salinity, pH, temperature and frequency of the electromagnetic field. In this work, the SSA was determined based on the measurements reported in literature. Similarly, the number of layers of water molecules on the surface of solid particles was assumed, i.e., four layers and one layer for the smectite and illite particles, respectively. Finally, the volumetric fraction of the bound water was determined based on the known SSA and number of the water-molecule layers. Additionally, the bound-water permittivity for a specific type of clay mineral was calculated based on a model with the known number of water-molecule layers. It needs to be noted that uncertainties in the parameters of the bound water can be introduced into the S_h quantification models (i.e., permittivity-based, conductivity-based and P-C joint models) directly. The sources of the uncertainties include the reference-based SSA, assumed number of water-molecule layers and permittivity-calculation model. It has been recognized that the SSA of

porous materials can be determined through different methods and instruments, but different results will be obtained. Consequently, it is an open question how to obtain an appropriate SSA for hydrate-bearing clayey samples. Bearing the above issues in mind, it becomes a desirable undertaking to optimize the approaches of determining the bound-water parameters for improving the accuracy of the P-C joint model in this work.

5.3 Limitations of experimental campaign

The hydrate saturation of samples was restricted to a specific range in the experimental tests of this work. In addition, the micro-scale distribution properties of the THF hydrate and clay minerals in samples were not detected and assessed in the experimental campaign. Consequently, the effects of the micro-distribution modes of hydrate and clays were not taken into account in the data analysis and modelling processes.

The preparation of hydrate-bearing sediment samples with a specified S_h is a key step for TDR testing in this work. As detailed in **Section 3.3**, the S_h is controlled and evaluated based on the initial amounts of THF and water. Ideally, the whole range of S_h from 0 to 1.0 should be implemented in the samples. However, some practical difficulties were encountered in the cases with lower S_h in the experiment. First, it is a challenge to achieve a full conversion from the THF to THF hydrate in the tested samples. As reported by Strauch et al. (2018) the conversion rate is affected by the initial ratio of the THF to water and decreases with a decreasing THF amount in water excess conditions. Consequently, the deviation between the target and actual values of S_h is more significant in samples with lower S_h (e.g. lower than 0.5). Second, the process of hydrate formation exhibits strong stochastic characteristics. For example, the THF hydrate failed to form in the temperature decreasing stage at the first time but formed successfully after a cycle of temperature decrease and increase. As can be seen in **Section 4.1**, the hydrate formation process was identified from the time traces of temperature where a temperature hump appeared due to the exothermic effect. It needs to be noted that the temperature hump can be identified only at a higher target S_h because the dissipation of the released heat becomes dominant at low S_h (e.g. lower than 0.4 based on experiences). Taking into account the above practical difficulties, in this work, only the samples with the S_h from 0.5 to 1.0 were prepared for TDR testing. The lack of lower S_h samples limits the data acquirement of TDR responses and the application conditions of the proposed S_h quantification models. As the future work, effective detection techniques need to be developed for directly monitoring the evolution process of hydrate formation at lower S_h .

(i.e., lower than 0.5) conditions.

Both gas hydrates and clay minerals exhibit a series of micro-scale distribution modes in marine sediments. There are differences in the processes of nucleation, growth and dissociation between gas hydrates and THF hydrate. However, it was observed through X-CT that the THF hydrate in clays is segregated and heterogeneous and the heterogeneous and fracture morphology of gas hydrates in clays can be simulated by THF hydrate well (Liu et al., 2019). This is different from sandy sediments where the THF hydrate forms as a pore constituent with less heterogeneity than that in clays. In this work, the skeletons of the tested samples includes clay minerals ($V_c < 20\%$) and fine sands with a diameter ranging from 180 to 250 μm . Presumably, the micro-scale distribution modes of THF hydrates become more complicated than those in pure sandy sediments and clays. Additionally, the clays may exhibit dispersed, laminated, structural and coating modes in hydrate-bearing sediments (Xing et al., 2023a; Hu et al., 2019). The distribution characteristics of the constituents in hydrate-bearing clayey sediments, i.e., sand grains, clay particles, hydrate, and free-state/bound-state water, affect the electromagnetic properties of the mixtures. Despite realizing the importance of the micro-distributions of THF hydrates and clay minerals, we have not included the analysis of their effects on the TDR responses in this work due to the lack of an effective means to detect them. Consequently, the application of the S_h quantification models proposed in this work may be restricted due to the ignorance of various distribution modes of hydrates and clay minerals.

6 Conclusions

A permittivity-conductivity (P-C) joint approach was proposed for characterizing the unconsolidated sediments with both hydrates and clay minerals, and quantifying the hydrate saturation (S_h) based on TDR measurements. An experimental campaign was carried out consisting of the development of experimental system, calibration of TDR probe and design of experimental scheme. The influences of S_h , clay mineralogy and clay content on the responses of TDR were examined and the relationship between the TDR-derived electrical parameters (i.e., apparent permittivity K_a and bulk conductivity σ_{dc}) and S_h was established. Finally, a novel P-C joint model was developed based on the permittivity-based and conductivity-based models.

(1) Both the TDR-derived K_a and σ_{dc} of hydrate-bearing samples reduce monotonically with the elevation of S_h

due to the controlling role played by the amount of pore water. The K_a of clayey samples with hydrates decreases almost linearly with an increasing clay content up to 20 %. The σ_{dc} of the smectite-bearing samples decreases nonlinearly, which is remarkably different from that of the illite-bearing samples. As the clay content increases, the volumetric fraction of the free-state pore water drops due to the reduction of the porosity and increase of the bound water. A higher amount of bound water due to the higher SSA and more complex elevation behavior of the electrical tortuosity due to the stronger water-swelling effect in the smectite-bearing samples explain the lower K_a and σ_{dc} and nonlinear behavior compared with the illite-bearing samples.

(2) The power-law mixing formula incorporating an empirical exponent is a preferable permittivity model based on TDR-derived K_a for hydrate-bearing sediments due to its merits of empirical and theoretical nature as opposed to the pure theoretical model (e.g., de Loor model) and pure empirical models (e.g., Topp model). The Simandoux equation is effective to account for the clay effects on the TDR-derived σ_{dc} of hydrate-bearing sediments with smectite and illite. The empirical exponents required in the permittivity-based and conductivity-based models need to be determined based on the test data that covers a specific range of clay types and contents.

(3) By using the porosity of hydrate-bearing sediments as a bridge parameter, a P-C joint model for quantifying the S_h can be established. The joint model outperforms the permittivity-based and conductivity-based models especially for the clayey cases. The better performance of the joint model can be attributed to its incorporation of both the dielectric polarization and electrical conduction mechanisms of clayey sediments with hydrates under the application of TDR electromagnetic field.

Limitations of this study have been identified which may trigger much research work in future. The TDR-derived K_a was used for developing the S_h quantification models based on the assumption that the two terms corresponding to the energy loss mechanism can be neglected. An appropriate method to separate the energy loss terms from K_a needs to be developed. In addition, a limited range of the S_h (i.e., 0.5 to 1.0) was used in the experimental tests and the effects of the micro-distribution modes of hydrate and clays were not taken into account in data analysis and modelling processes. The application of the proposed P-C joint models may be restricted. It is desirable to develop effective detection means for directly monitoring the evolution process of

hydrate formation (especially for lower S_h) and micro-distribution modes of hydrates and clay minerals.

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Xing, Lanchang; Gao, Liang; Ma, Zisheng; Lao, Liyun; Wei, Wei ...

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