Noncontact monitoring of thin hydrate layers with microwave cavity resonator

Bin Wang | Xiaoxiao Li | Lanchang Xing | Muzhi Gao | Meng Wang | Huimin Wang | Guoqing Wang | Xinmin Ge | Zhoutuo Wei

1 College of Control Science and Engineering, China University of Petroleum (East China), Qingdao, China
2 China Petroleum Engineering & Construction Corporation, Beijing, China
3 School of Geosciences, China University of Petroleum (East China), Qingdao, Shandong, China

Abstract
In oil/gas production and transportation systems, the formation of gas hydrates needs to be properly managed as they can potentially lead to plugging. Monitoring the thin hydrate layers during the initial formation stage is thus significantly critical for preventing such a risk. Noncontact monitoring of the thin hydrate layer with an open-ended microwave cavity resonator is presented in this study. The measuring mechanism of the proposed method was studied with numerical simulation, and the measurement ranges with two typical modes TM010/TM021s were experimentally investigated. The resonance frequency of the TM010 mode is applicable for measuring the thickness of hydrates within 20 mm, while the TM021 mode is only suitable for 8 mm. Then, formation/dissociation experiments of thin hydrate layers were conducted by using tetrahydrofuran to form the hydrate. Both simulation and experimental results showed that the resonant frequency can provide a sensitive response to the dielectric properties and layer thickness. Then the relationship between the resonant frequency and the fractions of solution/hydrate in the mixed layers was determined, and it was further optimized according to the simulation and experimental results. In addition, hydrate layer melting experiments were conducted with different layer thicknesses, and the volumetric fraction of the hydrate can be calculated with fixed layer thickness, thus the phase change during the hydrate melting process was precisely monitored with a time step of 1 min.

KEYWORDS
cavity resonator, gas hydrate, noncontact monitoring, thickness measurement

1 INTRODUCTION

A gas hydrate is a kind of crystalline substance in which guest molecules are caught in cages formed by bounded water molecules, which can steadily exist at low temperature and high-pressure conditions. During transportation in gas/oil pipelines, such as in deadlegs or deep water testing, the pressures and temperatures are ideal for hydrate formation, which forms critical flow risks in oil and gas pipelines. The generation of a
hydrate plug is believed to begin with thin hydrate layers on the pipeline wall, and these thin layers collapse into bulk hydrate lumps, which deteriorate into a plug. Kinds of jobs have been focused on hydrate detection inside the pipeline, and different detection means have been attempted, such as ultrasound, visual flow loop, electrical resistance, conjunct method of optic fiber and impedance spectra, neutron-induced analytical techniques, and so forth. Those research has revealed the potential of each method in hydrate detection. On the contrary, from here it can be inferred that each method also obtained its defect. For instance, the ultrasonic wave reflects the discontinuity on the pipeline wall. As a result, there will be strong and multiple reflection signals because of the interface between the transducer and the wall, and this part of ultrasonic signals may overlap with the target and interference signal. Although some noncontact measuring techniques like one using the ultrasonic focused transducer have emerged to obtain clear signals, their application scope was critically restricted, for example, they are only suitable for gas-rich pipelines. Electrical resistance is more sensitive to hydrate formation and dissociation than temperature and pressure, and it is an effective tool for quantitative detection of natural gas hydrates. The electrical resistance method is based on the change in conductivity caused by the change in ion content in the solution, while the hydrate is difficult to ionize. Therefore, in some cases electrical resistance cannot detect hydrate, when the solution is oil-based or nonconductive. Sensor-based on the conjunct method of optic fiber and impedance spectra is easily manufactured, inexpensive, and fully functional. However, this method must be in contact with the pipeline contents, and it may lead to corrosion, leakage, and other potential dangers. Although the neutron-induced analytical techniques are relatively simple and fast, the equipment of the neutron-induced analytical techniques is expensive and has potential radiation hazards, and it is not suitable for long-term dynamic monitoring in large areas. So developing a new detection method is helpful and necessary.

Permittivity measurement as a fast and accurate tool makes it a potentially real-time monitoring technique for layer thickness and component ratio evaluation in closed systems. Open-ended coaxial probes mounted nonintrusively can measure permittivity in a small aperture close to the wall, but the terminal of probes must penetrate the pipe wall and contact the measured media. Microwave resonators obtain more sensitive sensing because of their high Q-factor and resonator type sensors have been used in interface detection. The high sensitivity and resolution of the resonate cavity sensors have been revealed in the component’s evaluation of the mixture, such as water holdup measurement in gas–liquid two-phase flow, concentration of liquid solutions, characterization of alcohol/honey water mixture. The common means of those research is inserting the sample under test into the cavity space as perturbation, and further applying the perturbation theory which can predict the resonant frequency change, enables to detect the change of the component concentration or phase state.

Various chemical methods have been developed for hydrate prevention. The effectiveness of inhibitors should be carefully ascertained and adjustments accordingly applied, which call for a method of monitoring the hydrate layer thickness and the hydrate–liquid ratio, and preferably nonintrusive. Such technology would be helpful to obtain a better understanding of the hydrate agglomeration and dissociation process on the pipe wall, but evaluation and a monitoring method for the thin hydrate layer on pipeline walls have not been well studied.

An open-end microwave cavity resonator was used to measure the thickness of thin hydrate layers, and the potential of using microwave resonator-type sensors to evaluate the hydrate/liquid ratio was also verified in this study. Models of single-phase layers with known thickness and permittivity were built, and several experiments were developed to measure these layers with a sensor. Also, numerical simulation helped to determine the relationship between the resonating frequency and layer components. The results were used to verify the noncontact sensing capacity of the open-end cavity resonator. By using tetrahydrofuran (THF) to form the hydrate, the second series of experiments on the hydrate with different thicknesses were developed. THF has good miscibility with water and can generate a hydrate under atmosphere pressure, and moreover, the dielectric properties of the THF hydrate are quite similar to those of methane hydrate. Hence, all the conclusions obtained with THF hydrate can provide sufficient reference value to the future application of this sensing method on methane hydrate. Then the detecting features of the resonator sensor on hydrate layer thickness were studied at different resonating modes. An additional experimental series was done to imitate the hydrate dissociation process on the pipe wall, and the resonating frequencies of the sensor and temperature of the mixture samples were real-time recorded during the whole experiments. Finally, combined with the simulation results, the hydrate/liquid ratio of the dissociating layers was synchronously inverted according to the sensing data of the experiments. The capability of the noncontact sensing method, which is based on the microwave resonator cavity to detect and evaluate the hydrate layers under realistic conditions was further verified.
2 | METHODOLOGY AND EXPERIMENT CONFIGURATION

2.1 | Complex permittivity

The dielectric properties of the loss material are always characterized by complex permittivity, which measures the dielectric constant and loss factor. The complex permittivity is normally dispersive in the frequency domain and related to other physical properties, and it can be defined as:

\[ \varepsilon^* = \varepsilon' - j\varepsilon'' \]  

where \( \varepsilon^* \) is the relative complex permittivity, and the real part \( \varepsilon' \) and imaginary part \( \varepsilon'' \) refer to the dielectric constant and loss factor, respectively. Considering the resonating frequencies of the proposed resonator, the dispersion of the measured materials is due to molecular polarization. The interactions between different components, for example, the Maxwell–Wagner effect, which dominates below 100 MHz were not taken into account in this study, although they may potentially exist during the dissociation process of the hydrate layer. For components of fluid/solid layers in the pipeline is relatively simple, on the principle of not introducing new variables and to simplify the inversion, polarizations below 100 MHz are overlooked here.

Using THF to form the hydrate offers many advantages for laboratory studies, for example, stability under atmosphere pressure, and complete miscibility in water that makes the layer homogeneous even if it is only several millimeters thick. Because the THF hydrate has analogical electrical and acoustic properties similar to methane hydrate, THF has been used to form the hydrate to study the hydrate's physical properties in many published studies.\textsuperscript{11,22,23} THF with purity >99.9% was mixed with deionized water at a mass ratio of 1:4.25 as a solution to guarantee that no liquid remains after hydrate forming is complete. The complex permittivity of all liquids (methanol, ethanol, THF solution, and water) and THF hydrate used in this study can be numerically described by the Cole–Cole model\textsuperscript{24,25}:

\[ \varepsilon^*(\omega) = \varepsilon' - j\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + \left(\frac{j\omega\tau}{\omega\tau}\right)^{1-\alpha}} - j\frac{\sigma}{\omega\varepsilon_0} \]  

where \( \varepsilon^*(\omega) \) is the dispersive complex permittivity; \( \varepsilon_s \) and \( \varepsilon_\infty \) are the dielectric constant at DC and infinitely high frequency, respectively; \( \omega \) is the angular frequency, \( \alpha \) is an index parameter less than 1; \( \tau \) is the relaxation time in s, and \( \sigma \) is the conductivity. For the prepared THF solution, the \( \sigma \) was less than 0.0001 S/m, which was verified by using a conductivity meter (model: DDS-11A from INESA). The amplitude and dispersive properties of the permittivity spectrum always depend on the temperature, which is true for both liquids and THF hydrate. Temperature dependence was applied based on our previous studies.\textsuperscript{23} The permittivity spectra of some representative media are presented in Figure 1.

The relative dielectric constant of air is 1, and the dispersion in permittivity of the hydrate is below 100 MHz. Dispersion of the present liquids' permittivity is mainly concentrated in the frequency range of GHz, and there are significant differences between the dielectric properties of various liquids.

2.2 | Configuration of the experiments

As shown in Figure 2, the main structure of the microwave cavity resonator prototype includes a cylindrical shell (inner height \( h = 30 \) mm, inner diameter \( a = 48 \) mm) with the top face open, and it is fed from the bottom with a semirigid coaxial cable. The outer conductor of the coaxial line is welded to the resonator cavity, which is filled with epoxy resin \( (\varepsilon = 2.1 \) with a negligibly small loss factor). At the feeding point, the inner conductor (diameter \( d_2 = 0.53 \) mm) and the polytetrafluoroethylene (PTFE) layer (diameter \( d_1 = 2.2 \) mm) of the semirigid coaxial line are inserted into the epoxy at a depth of \( l = 6 \) mm. The measured hydrate layer was prepared in a vessel made with PTFE, and the open-end of the cavity resonator was pressed to the flat bottom of the vessel wall (thickness was 3 mm).
The experimental scenario shown in Figure 2A was designed to simulate the pipe wall with hydrate or liquid layers or with a mixture, and this scenario comes about when multiphase flow and the specific condition are suitable for hydrate formation such as high pressure during pipeline transportation of natural gas. The resonator-type sensor was fixed on the PTFE wall, which corresponds to the actual pipe lining, and the permittivity of which is close to the filling material inside the cavity. There are mainly three motivations to set the open-end of the sensor prototype and the vessel wall as a flat plane but not as an arc surface. First, the curvature radius of the actual pipeline is always much larger than the size of the sensor, radius of the sensor's open-end hardly make differences and can be even ignored. Second, to ensure the universality of the research, a most common flat surface was selected. Third, according to practical situations, because of the fluid flow, the hydrate thin layer is initially formed along the annular pipe wall. The vessel with a flat bottom can generate the layer samples with uniform thickness more easily, whether the layer is liquid or solid, and thus it can better simulate the real situation.

As a consequence, the EM energy coupled as a diffused field reaches the target layer with a relatively small loss and leakage, and thus the precision and the sensitivity of the proposed noncontact measuring method can be guaranteed.

The experimental instruments are sketched in Figure 3. The PTFE vessel was placed in a program-controlled thermotank, which offers a temperature condition with automatic control for hydrate formation/dissociation and standard liquid measurement. The cavity resonator was connected to the vector network analyzer (VNA; T5280A from Transcom Instruments, measuring frequency range covers the band from 300 kHz to 8 GHz) with a phase-stable coaxial cable, and the reference plane was calibrated at the SMA connector which linked the semirigid coaxial line and phase-stable coaxial cable. The reflection parameter S11 was recorded on the VNA in real-time. A Pt100 resistance
temperature probe inserted in the measured layers was used to measure the real-time temperature and record it on the temperature recorder.

### 2.3 Sensing principle

Resonator-type sensors always have considerable accuracy and sensitivity because of their high Q-factor. The perturbation method, which is based on resonator-type sensors, is widely used for dielectric property determination. In the perturbation approximations, the tested material occupies a small fraction of the cavity space, and theoretically, the electromagnetic field is negligibly changed by the sample's insertion.\(^{13,26}\) The assumptions are reliable if the sample is sufficiently small compared with the wavelength. However, when the material occupies a significant fraction of the cavities' volume or the permittivity/loss is relatively large, the assumptions are violated.\(^ {27}\) More importantly, in traditional permittivity measurement practices, the test samples are always placed inside the cavity, and that makes it very hard to satisfy the noncontacting/noninterventional measurement of hydrate layers on pipeline walls with such a sensor type.\(^ {18}\)

A practical solution to this problem is to place the samples outside the cavity, but still let the sample couple with the fringe field of the sensor. For the resonator used in this study with a single open bottom surface, there is a fringe/evanescent electromagnetic field at the open-end surface.\(^ {17}\) The dielectric properties of the material that are covered by the fringe field will couple with the electromagnetic power adjacent to the open-end, and make determining the resonating frequency and Q-factor different. Then the cavity is perturbed by such operations, and also, information about the dielectric properties of the sample can be inversed based on the analysis of differences between the resonant cavity performance before and after inserting the sample into the fringe field. Moreover, in this circumstance which is called “extra-cavity perturbation,” the perturbation caused by the tested samples is always smaller than the conventional resonator perturbation method. It has the potential to measure permittivity in very wide ranges and shows advantages in hydrate layer monitoring because there are many factors affecting the global dielectric properties, such as phase composition, layer thickness, and temperature.

If the microwave power is limited, the assumption can be made that the fringe field only exists in the area adjacent to the open-end surface and cannot penetrate the thin layer being tested even if its permittivity is small.\(^ {12}\) Therefore, it is rational to use this type of sensor to evaluate the thin hydrate layer and realize noncontact detection in some situations, if the cavity design and resonating modes are carefully optimized. As shown in Figure 4A, an experimental facility was set up to realize and verify the noncontact measurement properties of the thin hydrate layer with the extra-cavity perturbation method. The vessel wall between the hydrate layer and the cavity filler were both made of PTFE, which is often used as pipe lining materials and has a small dielectric constant and loss allowing more EM power of the fringe field to penetrate, making the fringe field energy focus in the detected layer. For the site installation scenario as shown in Figure 4B, because the hydrate is always initially formed at the pipe lining due to the annular gas–liquid two-phase flow, to discover and evaluate them, the resonator cavity is designed to be mounted at the metallic wall with the open bottom facing the pipe center. The open end of the resonator cavity can be slightly modified as an arc shape according to the real Teflon lining.

Owing to the gravity effect, generating the thin hydrate layer of uniform thickness on the annular wall...
in the laboratory is difficult, thus we used a vessel with a flat bottom to generate and support the tested layer. In conclusion, to ensure that the bottom is horizontal, the laboratory equipment with a flat bottom vessel can provide precise and controllable layer samples generation, and the PTFE vessel wall can fairly mimic in situ noncontact measuring situations. Referring to the other reasons listed in Section 2.2, it is reasonably easy to extend the result acquired by this study to real hydrate layer detection.

For a typical cylindrical cavity enclosed by metal walls, there are two categories of modes: the transverse electric mode (TEmnp) and transverse magnetic mode (TMmnp). Coefficient m, n, and p correlate with the field distribution of the mode in r, φ, and z directions in the cylindrical coordinate system.12 Whether a resonating mode belongs to TE or TM type depends on if there are no components of electric or magnetic vectors along the cylinder axis direction. An analytical expression of the resonating frequency is:

$$f_r = \frac{1}{2\pi\sqrt{\mu\varepsilon}} \left( \frac{X_{mn}}{R} \right)^2 + \left( \frac{p\pi}{l} \right)^2, \quad (3)$$

when the mode is TM mode and $X_{mn}$ is the n-th root of the m-th order Bessel function. When the mode is TE mode, $X_{mn}$ is the derivative of the n-th root of the m-th order Bessel function. The $\varepsilon$ and $\mu$ are the permittivity and permeability of the filled medium, respectively. The resonating frequencies of a resonator with a standard shaped and enclosed cavity are easily calculated. The resonating frequencies and corresponding modes below 8 GHz of an enclosed cavity resonator with the same geometrical dimensions as the sensor used in this study are listed in Table 1.

The sensing principle of a cavity resonator with an open-end used in this study can be approached by perturbation theory. The measured media is externally placed at the specific face of the cylindrical resonator without a metallic wall, and a small amount of electromagnetic power is coupled as the diffuse field of the fringe field. The majority of the EM power is held inside the resonator. Under this condition, the impact of the measured media (in this study, it mainly comes from the layer thickness and corresponding dielectric properties) is small, and the relationship between the shift of the resonating frequency and the original resonating frequency can be determined by the extra-cavity perturbation theory:28

$$\frac{\Delta f}{f} = -\frac{\iiint_{V_c} (\Delta \varepsilon |E_0|^2 + \Delta \mu |H_0|^2) dV}{\iiint_{V_c} (\varepsilon |E_0|^2 + \mu |H_0|^2) dV}, \quad (4)$$

where $E_0$ and $H_0$ are electric field and magnetic field inside the cavity, respectively, and $\Delta \varepsilon$ and $\Delta \mu$ are the equivalent change of the filling permittivity and permeability, respectively. Furthermore, it can be found from (4) that a slight increase in equivalent permittivity of the filling material of the cavity decreases its resonating frequency. $V_c$ is the volume of the resonant cavity and $V_s$ is the volume of the sample.29 In this study, the permittivity of epoxy as the filling material in $V_c$ was very stable during the whole experiment. However, because of the existence of the fringe field at the open end, changes in the outer layer’s properties can cause variation of the equivalent permittivity, and then make the resonating frequency different. From theoretical data in Table 1, all the resonating frequencies of the proposed sensor are in a frequency range higher than 2 GHz, in which the dielectric constant of the hydrate is fundamentally constant, and with nearly no dielectric loss. In this case, at the measured frequencies (actually when the measured layer properties change, there would be a small drift around the resonating points of the enclosed cavity), there are fundamental differences between the complex permittivity of the THF solution and the THF hydrate. It is rational to use this method to monitor the hydrate layer and evaluate its properties, but first, some standard layer samples with known permittivity should be tested to verify the sensing capability of the method.

3 | RESULTS AND ANALYSIS

3.1 | Verification of the sensing capability

Before applying the proposed method to the thin hydrate layer measurements, some standard materials were used as test samples to check their feasibility. The finite-difference time-domain (FDTD) was used as the

| TABLE 1 | Resonating frequencies below 8 GHz of the proposed cavity resonator when the open-end face is enclosed. |
|---|---|---|---|---|---|---|---|---|
| Mode | TMmnp | TMmnp | TMmnp | TMmnp | TMmnp | TMmnp | TMmnp | TMmnp |
| Resonating frequency (GHz) | 2.71 | 3.93 | 4.33 | 5.80 | 6.23 | 6.85 | 5.17 | 3.52 | 4.46 |
numerical simulation method to obtain the reflection coefficient (S11) and the corresponding EM field distribution, which can help to analyze the sensing mechanism and capability. First, liquid layers of pure methanol and ethanol with a thickness of 50 mm at 20°C were tested (this thickness is adequate to guarantee nearly all fringe field energy is enclosed in the measured materials) and thus the effect of the thickness was excluded. The numerical model was established 1:1 to the real experimental equipment, and the S11 was obtained and experimental and simulated curves are shown in Figure 5. In addition to the resonating frequency, the other key parameter of the resonator is the Q-factor, which indicates the damping and bandwidth of the resonant cavity. In the frequency domain, the S11 parameter decreased as the Q-factor rose. When the frequency was close to the resonating points, the S11 curve approached the specific trough. When the frequency matched the resonating point, S11 reached the bottom. By appropriately setting up some electric and magnetic field monitors in the simulation, it was determined that there were four resonating modes in the specific band with the recorded EM field distribution. With frequencies from low to high, they are TM010, TM011, TM020, and TM021. Higher Q-factors can produce a larger energy intensity inside the cavity. However, the critical broad bandwidth of the TM011 mode makes the energy intensity significantly low. To optimize the measuring mode, TM011 is obviously so weak that the precision and detection depth cannot be guaranteed, and the situation was analogous in the TM020 mode. As a consequence, the remaining two modes TM010 and TM021 were then selected as the sensing modes in the following studies. There are some discrepancies between the simulated and experimental S11 curves as shown in Figure 5, but the trends of the curves are approximately consistent.

The exact resonating points at the two modes TM010 and TM021 are illustrated in Figure 6, when four kinds of samples with a thickness over 50 mm were placed over the vessel wall. Different materials are distinguished with colored symbols in Figure 6, and from left to right they are air, ethanol, methanol, and deionized water, as their dielectric constant successively increase. Results obtained with simulation and experiments present a synchronized tendency. Because of the dispersion in dielectric properties of these three liquids, their data points are not vertically aligned at the two different resonating modes. The resonating frequencies decreased as the dielectric constant rose, and the relationships remained monotonous at the two modes. The slopes of them are both larger when the dielectric constant was not too big, for example, the differences in resonating points between water and methanol were significantly smaller than those between the other two media. The dielectric constants of hydrate layers and hydrate/liquid mixture were always smaller than methanol, and hence, the designed resonator sensor can provide adequate sensitivity for hydrate layer detection.

There are differences between experiments and simulated S11 curves that were primarily shown in Figure 5, and this phenomenon can be observed more clearly in Figure 6. It can be attributed to the differences in the permittivity of real and simulated materials, such as the PTFE that filled the cavity, and a similar phenomenon can be found in other studies.17 The relative deviation is obtained by: $\left| \frac{f_{\text{simulated}} - f_{\text{experimental}}}{f_{\text{simulated}}} \right| \times 100\%$. 

---

**Figure 5** Experimental and simulated S11 curves of the cavity resonator with methanol and ethanol layers, the four most dominant resonating frequencies are outlined with blue frames.

**Figure 6** Experimental and simulated resonant frequency of TM010 and TM021 mode with some known dielectric constant materials. The TM010 data points are presented with colored square symbols, and the TM021 data points are presented with colored rhombus symbols. Data for air, ethanol, methanol, and deionized water are, respectively, colored as purple, green, blue, and red.
Seeing the error analysis in Table 2, the deviation in both modes is significantly small (<1.5% in TM010 and <5% in TM021), and thus it can be concluded that the simulation and experiments matched well. These differences between $f_{\text{experimental}}$ and $f_{\text{simulated}}$ are basically constant for each resonating mode. No matter which material is measured, it can be reasonably generalized that the deviation of the numerical simulation for each resonating mode is approximately a fixed value. This fixed value or the relative deviation is bigger for mode TM021, which is located in a higher frequency range, but it is also independent of the measured materials. In other words, the deviation between experimental and simulated resonating frequencies has no concern with the equivalent wavelength or sensor design itself. Therefore, we speculated that those deviations come from the precision limitation of numerical simulation or the accuracy of prototype manufacturing. The numerical simulation will be used as a basic reference, and a corresponding relationship between the simulation and experimental data was used when this method was used to evaluate the composition of THF layers.

### 3.2 Application in detection of hydrate layers with different thicknesses

By setting the target temperature of the thermotank to $-12^\circ$C, the hydrate was prepared as mentioned in Section 2 and it was cold enough to guarantee that the hydrate layer quickly agglomerated and with no solution left. THF with purity > 99.9% was mixed with deionized water at a mass ratio of 1:4.25 as a solution to guarantee that no liquid remains after hydrate forming is complete. Combined with the recorded temperature curves, it can be confirmed that there is no ice formed throughout the whole experiment. When the temperature is monitored near the target, the formation of the hydrate is certainly complete.23

In this part, hydrate layers of thickness covering the range from 0 to 30 mm with a 2-mm interval step were prepared as the measured samples, and the resonance frequencies at the TM010 and TM021 modes are correspondingly shown in Figure 7. For both modes, there is a turning point as the thickness of $h_3$ increases, before which the two resonating frequencies both monotonically decreased with increasing thickness. Turning points in the TM021 mode arose “earlier” than in the TM010, and the corresponding thickness was approximately half of it with the TM010 mode. Referring to the features of the resonating points, these two specific thicknesses were obtained at roughly the same ratio of wavelengths at the two resonating modes ($\lambda_{TM010}/\lambda_{TM021} = 7.33 \text{ GHz}/2.73 \text{ GHz} = 2.68 = 2.67 = 20 \text{ mm}/7.5 \text{ mm}$). When the thickness was larger than 24 mm, it can be observed in Figure 7 that the relationship between the resonating frequency of the TM010 and thickness also monotonously decreases.

| Mode | Air | Ethanol | Methanol | Deionized water |
|------|-----|---------|----------|-----------------|
| TM010 |     |         |          |                 |
| $\epsilon'$ | 1   | 6       | 19.5     | 78.4            |
| Experimental (GHz) | 2.924 | 2.896   | 2.822     | 2.78            |
| Simulated       | 2.946 | 2.925   | 2.862     | 2.799           |
| Relative deviation | 0.75% | 0.99%   | 1.4%      | 0.68%           |
| TM021 |     |         |          |                 |
| $\epsilon'$ | 1   | 4.8     | 9        | 68              |
| Experimental (GHz) | 7.599 | 7.462   | 7.378     | 7.324           |
| Simulated       | 7.923 | 7.783   | 7.699     | 7.65            |
| Relative deviation | 4.1%  | 4.12%   | 4.17%     | 4.26%           |

TABLE 2 Experimental and simulated resonant frequency of TM010 and TM021 mode, and relative error.

![Figure 7](image-url) Relationship between the thickness of hydrate layers and the resonating frequencies of TM010 and TM021 modes.
decreases. We speculate that the variation of the resonating frequency with thickness is periodic. Nevertheless, because the penetration depth of the electromagnetic wave decreased with frequency, the testing precision of S11 is limited by the dynamic range of the VNA, and the experimental results were abandoned when the hydrate layer thickness was “overlarge.” Thus, the resonating frequencies of a layer thickness bigger than 30 and 12 mm for TM010 and TM021 mode, respectively, are not presented.

Considering that the sensing characteristic should be at least a monotone function and best to be linear, the measuring ranges of the proposed resonator at TM010 and TM021 are, respectively, 20 and 8 mm, and they are predominately decided by the resonating frequency as well as the operating wavelength. It can be deduced that the detecting range of the resonator-type sensors with open ends depends on monotone features when they are used to detect layer thickness.

### 3.3 The effects of the vessel wall thicknesses

The wall thickness of the oil and gas transportation pipeline is always different, the effects of the vessel thickness were further determined in this study. The experimental measured S11 curves of different vessel wall thicknesses are shown in Figure 8. To exclude the influence of the thickness of the materials under test, the water and THF hydrate layer of 30-mm thickness guaranteeing to cover almost all field energies were prepared on the vessel bottom, and another experiment group with the empty vessel (actually the vessel was filled with air) was set as the control group. Thus the thickness of the vessel wall was installed as the only variable, and its influence on the two concerned modes was distinctly illustrated. Four vessel walls with different thicknesses from 2 to 5 mm were selected, and for the TM010 mode, the resonance frequencies were almost unchanged for each same tested material layer. It means that the fringe field for TM010 with a longer wavelength can hardly be affected by the vessel wall thickness, while the changes crucially appeared as the wavelength decreased for the TM021 mode. Therefore, the resonant frequencies of TM021 are not only material-dependent but also related to the thickness of the vessel wall. For water and THF hydrate, the influences of the vessel wall thickness are reinforced.

The wall thickness of oil and gas transportation pipelines is different, and it is undoubtedly one of the critical factors to influence the sensing result. As shown in Figure 9, the resonant frequency of the TM010 mode corresponding to different layers was independent of the vessel wall thickness; however, for TM021 mode, the tendency of the resonant frequencies to vary with the wall thickness was more complicated. The resonating
points decreased with the thickness rising when the vessel was empty, while the tendency was reversed when there are water or hydrate layers. For both situations, the relationship between the vessel wall thickness and the resonance frequency were monotonous, respectively.

### 3.4 Monitoring the dissociation process of hydrate layers

To study the sensor’s response to the phase changes of the hydrate layer, dissociation experiments of a hydrate layer with a thickness of 2 mm were conducted. Initially, the vessel containing the THF solution was fixed on the resonator, and they were cooled down to −12°C. The temperature was maintained for more than 6 h to guarantee that all the solution was converted to hydrate. Thus, the preparation of the hydrate layer was completed. Then, the hydrate dissociation experiment began by setting the target temperature to room temperature (about 20°C), and the temperature was recorded with a resistance thermometer during the whole process. As shown in Figure 10, the S11 curves were recorded every minute, and the resonating frequency change with time of the TM010 mode is shown in Figure 11. The relationship between \( f_r \) and time was kept monotonously decreasing. Concerning the inclination of the curve, the whole process can be roughly divided into three stages: (a) 0–4 min; (b) 5–12 min; (c) 13–16 min. For the three stages, the slope of each curve was reduced in turn. Specifically, as shown in Figure 6, the resonating frequency in TM010 mode is sensitive to the dielectric constant of the detecting layers, and the assumption can be made that Stage a is the early stage of the dissociation, and zigzags are found in this section of the curve. In Stage b, the dissociation occurred at a relatively even speed, and the slope of the stage is relatively stable. Finally, in Stage c, the \( f_r \) was almost stable, so it can be deduced that dissociation is completed in Stage c.

Nevertheless, the details of the dissociation process were still not clear, and numerical simulation and the recorded temperature were integrated to help to evaluate the phase change process in the experiment. First, numerical models with layer samples of 2-mm thickness were simulated with the FDTD method, and six different layer samples with various component proportions were installed in these models to imitate the real situations during the hydrate dissociation process. Layer samples are defined as two phases, with a volumetric fraction of liquid solution of 0%, 20%, 40%, 60%, 80%, and 100%, respectively, and the materials of the numerical models were all homogeneous. The total thickness of the layer samples keeps constant at 2 mm during the whole process.
The dissociation process. The permittivity of the mass mixture was calculated with the complex refractive index method.

\[
\sqrt{\varepsilon^*} = V_{\text{solution}} \sqrt{\varepsilon^*_{\text{solution}}} + (1 - \varphi_{\text{solution}}) \sqrt{\varepsilon^*_{\text{hydrate}}},
\]

where \(\varepsilon^*\), \(\varepsilon^*_{\text{hydrate}}\), and \(\varepsilon^*_{\text{solution}}\) are the complex permittivity of the mass mixture, hydrate, and solution, respectively, and \(\varphi_{\text{solution}}\) is the volumetric fraction of the solution.

As shown in Figure 12, the simulated resonating frequencies of the TM010 mode \(f_s\) varied with the volumetric fraction of the THF solution. The relationship was approximately linear, and a first-order fitting was further conducted to eliminate the fluctuation of the simulation data, which was attributed to the numerical dispersion.

As demonstrated in Figures 5 and 6, there was a regular deviation between the experimental responses and simulated results. The resonating frequencies at the 0th and 17th minute were obtained with a 2-mm layer of 0% and 100% THF solution volume ratio, and then these two points were selected as upper and lower limits of experimental data, respectively. As described above, the deviation between numerical simulation and experiments at a specific resonating mode is a fixed value, so a linear relationship between simulated and experimental results can be established as:

\[
f_s = 1.08811 \times f_e - 0.2194. \tag{6}
\]

Combined with the linear fitting result as shown in Figure 12, the relative expression between the resonating frequencies \(f_e\) and the volumetric fraction of the THF solution \(V_{\text{solution}}\) is modified as:

\[
V_{\text{solution}} = -11.576 \times f_e + 33.143. \tag{7}
\]

All the parameters in (6) and (7) are dimensionless. Then by applying (7) to the experimental data shown in Figures 10 and 9, the variation curves of the solution fractions were obtained. The calculated \(V_{\text{solution}}\) are synchronously presented with real-time temperature in Figure 13. The \(V_{\text{solution}}\) had an analogous change tendency with \(f_e\), which is shown in Figure 11, and the three stages are still applicable to the curve of \(V_{\text{solution}}\). The dissociation process seemed more perspicuous when the temperature curve was taken as the reference. In the first stage, the temperature kept rising, until it reached the point around 4.4°C, which is the phase equilibrium temperature of the
THF hydrate. The rising slope of both the $f_e$ and the $V_{\text{solution}}$ in this stage is steep and can reveal that melting has occurred in the initial temperature rising period. Then the temperature was kept at 4.4°C for about 9 min (4th–13th minute), and also, the $V_{\text{solution}}$ increased from 45% to 90% at a basically constant rate, which corresponds to Stage b in Figure 11. Because the hydrate dissociation is an endothermic process, the persistent melting exhausted the absorbed heat, and thus the temperature did not continue to rise until the melting was completed at the 14th minute. In the final stage, $V_{\text{solution}}$ was always 100%, which indicated no solid hydrate existed, and it was simply a temperature-rising process. The hydrate layer ultimately developed into a liquid layer. Although there was a tiny variation in thickness because of the density difference between the hydrate and solution, compared with the influence of the phase change on the resonating frequency, the thickness change was negligible.

**FIGURE 15** Intensity of the E-field at the vertical section. The field intensities are presented in absolute value. The stainless-steel shell of the resonator is contoured with a gray solid line, and the boundary of the open end is represented with a solid red line. The area between the solid red line and the dotted line is the bottom wall of the polytetrafluoroethylene vessel, and the area between the dashed line and the dotted line is the measured layers. (A) 2-mm layer with 100% hydrate, (B) 2-mm layer with 100% solution, (C) 4-mm layer with 100% hydrate, (D) 4-mm layer with 100% solution.
A comparative experiment of a 4-mm layer sample was conducted, and some differences can be found between Figures 13 and 14. First, the total time that the dissociation process consumed for the 4-mm layer was about two times longer than that for the 2-mm layer. It is reasonable that a thicker layer absorbs more heat, and for the same temperature setting, the melting time increases with the thickness. Second, in Stage b, the $V_{\text{solution}}$ rose staircase-like, which can be observed in the gray area in Figure 14, and this was distinct from the gray area in Figure 13. The main reason for the difference is the thickness increase, which affects two aspects: on the one hand, the total quantity of hydrate was doubled, and it made the composition more inhomogeneous during the melting process. For example, the solution may stream along hydrate cracks and holes, and these micromechanisms cause further structure collapse, which results in the step-like curve in Figure 14 Stage b. On the other hand, the sensor obtains the best sensitivity and resolving ability in the region adjunct to the open end, and the sensitivity gradually decreased with the distance from the open end. These jointly resulted in the zigzags in the $V_{\text{solution}}$ curve in the gray area in Figure 13.

As shown in Figure 15, the E-field intensity was obtained with FDTD simulation, which belongs to the TM010 mode. From Figure 15A–D, the simulated frequencies are 2.87, 2.77, 2.84, and 2.75 GHz. Based on the results in Figures 13 and 14, layer samples with pure hydrate and solution of 2- and 4-mm thickness were, respectively, set as the measured objects, and the complex permittivity in the numerical models was calculated with (5). It was illustrated in Figure 1 that the dielectric constants of the THF solution are close to water’s, which possesses high dielectric loss in the sensing frequency range. On the contrary, the THF hydrate has relatively low loss factors and was non-dispersive. The field distribution after melting was completed is shown in Figure 15B,D, and the layers with a high dielectric constant make the boundary conditions mismatch. The majority of electromagnetic power was reflected at the interface between the measured layer and the PTFE wall, and also, compared to Figure 15A,C, the part of the electromagnetic power which has penetrated the measured layers was crucially attenuated. In contrast, the diffuse field outside the open end of the resonator is more evident as shown in Figure 15A,C. The differences between the dielectric constant of PTFE and epoxy are inconspicuous, so no matter in which condition, a mass of electromagnetic power smoothly penetrates into the PTFE wall. Hence, the depth of the PTFE wall does not make a significant difference in the measurement, and this feature makes it possible to realize the noncontact monitoring of the hydrate layers. In addition, the influence of the thickness of the layer can also be revealed in Figure 15. Concerning the field in free space over the measured layer, it is not only affected by constituents of the layer, but also is impacted by the layer thickness, and this phenomenon is more notable when the solution fraction increases. For example, the intensity of the E-field in Figure 15D where the y-axis is greater than 20 mm is critically weaker than in the same area of Figure 15B. The composition of the two layers is the pure solution; however, the thickness was the prominent affecting factor. Thus, the fundamental relationship between the sensor’s responses and layer’s properties can be approximately built through the analysis of field distributions.

4 | CONCLUSION

A method for noncontact evaluation of the thin hydrate layer at the vessel wall with an open-ended cylindrical cavity resonator was presented. Through our study, it was found that in the frequency range of 1–8 GHz, the spectral response of the TM010 and TM021 modes can both reflect the thickness of the hydrate, and the TM010 mode can provide a deeper detection range. The resonance frequency of the TM010 mode is applicable for measuring the thickness of hydrates within 20 mm, while the TM021 mode is only suitable for 8 mm, and the detection ranges depend on the monotonous relationship of thickness and resonating frequency for each mode.

Through the combination of experimental and simulation study, the dynamic process of volume fraction change of the hydrate/solution during the dissociation of the hydrate layer was quantitatively analyzed. By applying the method, the volume fraction of the two components during the whole dissociation process of different thicknesses can be evaluated in real time with a time step of 1 min. Compared with other designs, this method also has a simple structure and easy implementation in in-situ and noncontact detection scenarios of oil/gas transportation applications.

ACKNOWLEDGMENTS

The authors thank Dr Edward C. Mignot, Shandong University, for linguistic advice. The authors would like to express sincere thanks for the financial support from the National Natural Science Foundation of China (42174141, 41704124), Fundamental Research Funds for the Central Universities (20CX05005A and 18CX02112A), the Major Scientific and Technological Projects of CNPC (ZD2019-184-001), PetroChina Innovation Foundation (2018D-5007-0214), and Shandong Provincial Natural Science Foundation (ZR2019MEE095, ZR2017BEE026).
REFERENCES

1. Makogon YF. Hydrates of natural gas. PennWell Books; 1981.
2. Sa J-H, Zhang X, Sum AK. Hydrate management in deadheads: effect of driving force on hydrate deposition. Fuel. 2020;279:118481.
3. Zhao Y, Wang Z, Yu J, et al. Hydrate plug remediation in deepwater well testing: a quick method to assess the plugging position and severity. Paper presented at: SPE Annual Technical Conference and Exhibition. Society of Petroleum Engineers; 2017.
4. Grasso GA, Sloan ED, Koh CA, Sum AK, Creek JL, Kusinski G. Hydrate deposition mechanisms on pipe walls. Paper presented at: Offshore Technology Conference; 2014.
5. Li X, Liu Y, Liu Z, et al. A hydrate blockage detection apparatus for gas pipeline using ultrasonic focused transducer and its application on a flow loop. Energy Sci Eng. 2020;8(5):1770-1780.
6. Kippersund R, Lunde P, Frøysa K. Hydrate deposit detection in pipes using ultrasonic guided waves. Paper presented at: Proceedings of the 34th Scandinavian Symposium on Physical Acoustics; 2011.
7. Zhou X, Fan S, Liang D, Wang D, Huang N. Use of electrical resistance to detect the formation and decomposition of methane hydrate. J Nat Gas Chem. 2007;16(4):399-403.
8. Longo JPN, Galvao JR, Antes T, et al. Sensing hydrates in pipes by a combined electrical and optical fiber sensor. IEEE Sens J. 2020;20(9):5012-5018.
9. Bouat S, Pinier L, Sebastian X, et al. Detection of hydrate plugs inside submarine pipelines using neutrons. Nondestruct Test Eval. 2022;37:245-257.
10. Folgerø K, Haukalid K, Kochach J, Peterson AS. Combined thickness and permittivity measurement of thin layers with open-ended coaxial probes. Sensors. 2019;19(8):1765.
11. Haukalid K, Folgerø K. Broad-band permittivity measurements of formation of gas hydrate layers using open-ended coaxial probes. Energy Fuels. 2016;30(9):7196-7205.
12. Nyfors EG. Cylindrical Microwave Resonator Sensors for Measuring Materials Under Flow. Dissertation. Helsinki University of Technology; 2000.
13. Nyfors E. Industrial microwave sensors—a review. Subsurf Sens Technol Appl. 2000;1:23-43.
14. Abd Rahman N, Zakaria Z, Abd Rahim R, Dasril Y, Mohd Bahar AA. Planar microwave sensors for accurate measurement of material characterization: a review. Telkomnika. 2017;15(3):1108-1118.
15. Zarifi MH, Rahimi M, Daneshmand M, Thundat T. Microwave ring resonator-based non-contact interface sensor for oil sands applications. Sens Actuators B Chem. 2016;224:632-639.
16. Yang Y, Xu Y, Yuan C, et al. Superficial dielectric constant (SDC) model of gas-water flow in resonant cavity sensor (RCS) based on flow regimes. J Nat Gas Sci Eng. 2021;88:103849.
17. Sharma P, Lao L, Falcone G. A microwave cavity resonator sensor for water-in-oil measurements. Sens Actuators B Chem. 2018;262:200-210.
18. Mao YJ, Zhang YJ, Chen ZR, Tong MS. A noncontact microwave sensor based on cylindrical resonator for detecting concentration of liquid solutions. IEEE Sens J. 2020;21(2):1208-1214.
19. Li Z, Haigh A, Wang P, Soutis C, Gibson A. Characterisation and analysis of alcohol in baijiu with a microwave cavity resonator. LWT. 2021;141:110849.
20. Li Z, Meng Z, Haigh A, Wang P, Gibson A. Characterisation of water in honey using a microwave cylindrical cavity resonator sensor. J Food Eng. 2021;292:110373.
21. Hejazi S, Pahlavanzadeh H, Manteghian M. Experimental study and kinetic modeling on THF hydrate formation under a static electric field. J Nat Gas Sci Eng. 2021;95:104162.
22. Santamarina J, Francisca F, Yun T-S, Lee J-Y, Martin AI, Ruppel C. Mechanical, thermal, and electrical properties of hydrate-bearing sediments. Paper presented at: AAPG Hedberg Conference “Gas Hydrates: Energy Resource Potential and Associated Geological Hazards”; 2004.
23. Wang B, Zhang Z, Xing L, Lao W, Wei Z, Ge X. Integrated dielectric model for unconsolidated porous media containing hydrate. IEEE Trans Geosci Remote Sens. 2020;59(7):5563-5578.
24. Critchfield FE, Gibson JA Jr, Hall JL. Dielectric constant and refractive index from 20 to 35° and density at 25° for the system tetrahydrofuran–water. J Am Chem Soc. 1953;75(23):6044-6045.
25. Gough SR, Hawkins RE, Morris B, Davidson DW. Dielectric properties of some clathrate hydrates of structure II. J Phys Chem. 1973;77(25):2969-2976.
26. Waldron R. Perturbation theory of resonant cavities. Proc IEE C Monographs. 1960;107(12):272-274.
27. Korostynska O, Mason A, Al-Shamma’a A. Microwave sensors for the non-invasive monitoring of industrial and medical applications. Sens Rev. 2014;34:182-191.
28. Ni E, Ni Y. Extended cavity perturbation method for the measurement of dielectric resonator materials. Rev Sci Instrum. 1997;68(6):2524-2528.
29. Binshen M, Booske J, Cooper R. Extended cavity perturbation technique to determine the complex permittivity of dielectric materials. IEEE Trans Microw Theory Tech. 1995;43(11):2633-2636.

How to cite this article: Wang B, Li X, Xing L, et al. Noncontact monitoring of thin hydrate layers with microwave cavity resonator. Energy Sci Eng. 2022;10:4136-4149. doi:10.1002/es3.1279