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Development and performance evaluation of bioenzyme-responsive temporary plugging materials

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Abstract:
Ocean gas hydrate is a potentially efficient and clean oil and gas alternative energy resource. Wells with complex structure, such as horizontal wells, can improve the extraction efficiency; however, drilling operations face challenges such as wellbore instability and reservoir damage due to the complex interaction between drilling fluids and hydrate reservoirs. This work presents a ceramsite temporary plugging microcapsule that uses ceramsite modified by 3-aminopropyltriethoxysilane as the core material and chitosan and sodium alginate as shell materials. It exhibits high strength during drilling and excellent plugging effects. After the action of bioenzymes, it can easily be dissolved, leading to high permeability post-drilling. The analysis and performance evaluation of ceramsite microcapsules show that their particle size is generally 40 μm, which can match the pore size of the hydrate reservoir depending on the number of encapsulation layers. Bioenzyme optimization at 15 °C yields the best permeability recovery of 74.5% for the low-temperature composite enzyme. As the temperature rises, the permeability recovery rate of ceramic microcapsules gradually increases and the difference in permeability recovery rate between 5 and 25 °C becomes more significant. With a longer degradation time, the permeability recovery rate of ceramsite microcapsules gradually enhances and the difference in permeability recovery rate becomes smaller after 12 h. The microcapsules exhibit a specific inhibitory effect on the decomposition of hydrates. Utilizing bioenzyme-responsive ceramsite microcapsules as temporary plugging materials can establish an "isolation barrier" around the wellbore, effectively sealing off the interaction between the wellbore and the gas hydrate reservoir during the drilling process. Re-opening the flow path around the well by bio-enzymatic unblocking at the end of drilling proves to be effective in solving the problem of balancing the stability of the well wall and protecting the reservoir.

1. Introduction

Oil and gas are among the most important energy sources worldwide, with great significance to the economy, energy security and national security (Mahmood and Guo, 2023). Natural gas hydrate, which has enormous resource potential, is a kind of ice-like cage-shaped crystalline substance formed by the combination of water molecules and gas molecules under conditions of low temperature and high pressure (Li et al., 2021; Shaibu et al., 2021; Zhang et al., 2022). This compound is widely distributed in nature, mainly in submarine sediments at the bottom of the ocean and permafrost zones on land (Yang et al., 2022; Lu et al., 2023; Wang et al., 2023a). As a new type of gas energy, natural gas hydrate exhibits apparent advantages regarding gas content and storage capacity per unit area (Makogon, 2010; Song et al., 2021; Liao et al., 2023). The development and utilization of natural gas hydrate may also play essential roles in mitigating the problem of climate change (Chen et al., 2020, 2022).

The drilling process for natural gas hydrate is non-adiabatic, and the formation where the hydrate is located is

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mostly a porous medium, which leads to heat and mass transfer between the drilling fluid and the hydrate formation (Yan et al., 2020; Li et al., 2023). The penetration of drilling fluid into the formation around the wellbore causes the decomposition of natural gas hydrate (Cai et al., 2020a, 2020b; Shaibu et al., 2021). Natural gas hydrate has a cementing solid effect in the reservoir and its decomposition will lead to mechanical destabilization of the well wall, which will in turn severely impact normal drilling operations (Sun et al., 2018). Therefore, the well wall and the formation around the wellbore are often blocked during drilling to minimize the interference of drilling fluids with the reservoir. Conventional plugging agents are tricky to remove after blocking the formation, which affects subsequent construction operations (Zhao et al., 2021). A temporary plugging agent can block the well wall during drilling so that the drilling fluid will not enter the formation and protect the oil and gas reservoir (Li et al., 2021; Wang et al., 2023b). After the end of the operation, the well wall can be automatically unblocked to restore the permeability of the formation and reduce damage to the oil and gas reservoir (Zhou et al., 2022). Conventional preformed particle gels can selectively penetrate high-permeability channels to form effective plugs and transfer chased injection fluids to low-permeability oil zones not invaded by the replacement fluid. To cope with the various characteristics of deep oil and gas reservoirs, the use of high temperature-resistant and high-strength degradable nanometer ester, as a temporary plugging material, can enhance the reservoir yield and the production enhancement effect, reducing the difficulty and increasing the safety of operation (Xiong et al., 2018). This is a thermo-responsive temporary plugging agent that can be used to plug and unblock strata depending on the temperature. At low temperatures, this material is in a sol-gel state, while at higher temperatures, it forms a stable gel that transforms into a sol-gel upon further heating (Du et al., 2017). With the development of biotechnology, bioenzymes have been gradually applied to petroleum engineering. The use of polymer degradation in the temporary plugging agent has a two-fold beneficial effect: it can perfectly restore the permeability of the formation and reduce the damage to the oil and gas layer.

Microencapsulation technology involves the encapsulation and wrapping of a functioning substance by an inert material to form particles with a core-shell structure, with the final particle size of microcapsules typically ranging from 2 to 1,000 μm (Gouin, 2004; Nazzaro et al., 2012). This microcapsule structure is usually core-shell-shell, where the substance in the center of the core is called the core material and the outer shell consisting of an encapsulated membrane material is called the wall material (Peng et al., 2023). The choice of core material can be solid, liquid or gas, with important implications on the effect upon degradation of the shell material (Sawalha et al., 2011). The thickness of the wall material usually ranges from 0.5 to 150 μm, and the outer layer can be realized as non-permeable, lowly permeable or highly permeable (Lopez-mendez et al., 2021). At present, microcapsules are widely used in the chemical industry, such as for medicine, coatings, food transportation, energy, construction, and other important fields (Li et al., 2023; Liao et al., 2023; Liu et al., 2023; Yin et al., 2023).

As a petroleum fracturing proppant, ceramsite is highly uniform in shape (Bechteler et al., 2020). It has high chemical stability, thermal stability, sphericity, and compressive strength (Szymanska et al., 2016; Man and Wong, 2017). Furthermore, it can form fracture channels and improve the reservoir permeability during hydraulic fracturing (Assem and Nasr-El-Din, 2017; Yang et al., 2022). Thus, it is an optimal choice as a temporary plugging microcapsule core material. In this paper, we utilize the layer-by-layer self-assembly and coupling agent modification methods to combine ceramsite with polysaccharide materials to form temporary plugging materials. This method can play the role of sealing off a geological stratum during drilling and unblocking the stratum after drilling for hydrate reservoirs. It is demonstrated that developing bioenzyme-responsive ceramsite temporary plugging microcapsules is advantageous for safe and efficient drilling for the extraction of natural gas hydrates.

2. Materials and methods

2.1 Materials

All commonly used reagents and solvents were purchased from commercial suppliers and did not require further purification. Anhydrous ethanol, chitosan and sodium were of analytical grade. Dichloromethane (specification: 99.9%), chitosan, sodium, and 3-aminopropyltriethoxysilane (specification: 97%) were obtained from Macklin. Anhydrous ethanol was acquired from Aladdin.

2.2 Synthesis method and principle

The primary methods chosen for the synthesis of bioenzyme-responsive ceramsite temporary plugging microcapsules (BCTM) in this experiment were the condensation polymerization method and the coupling agent modification method (Meng et al., 2023; Wani et al., 2023). The ceramsite was selected as the core material, while chitosan and sodium alginate acted as the shell material, and aqueous dichloromethane solution was the solvent. The surface of ceramsite was modified by a coupling agent to connect ceramsite and chitosan, and chitosan and sodium alginate were self-assembled by electrostatic action to BCTM.

In order to better elaborate the synthesis mechanism of BCTM, the synthesis route of BCTM was shown in Fig. 1. First, the alkoxy group in the silane coupling agent is hydrolyzed to form Si-OH, then via -OH reaction, the silane coupling agent is connected to the surface of the ceramsite as a modification. The silane coupling agent modification for the ceramsite provides amino groups and hydroxyl groups on the surface of chitosan to form hydrogen bonds with amino groups in the modified ceramic granules, enabling chitosan to wrap up the modified ceramsite. The amino group of chitosan is positively charged in the weakly acidic environment of dichloromethane solution to form a capsule with positively charged surfaces. This and sodium alginate are formed by ionic complexation to form polyelectrolyte complexes, yielding the formation of multilayer microcapsule shells.

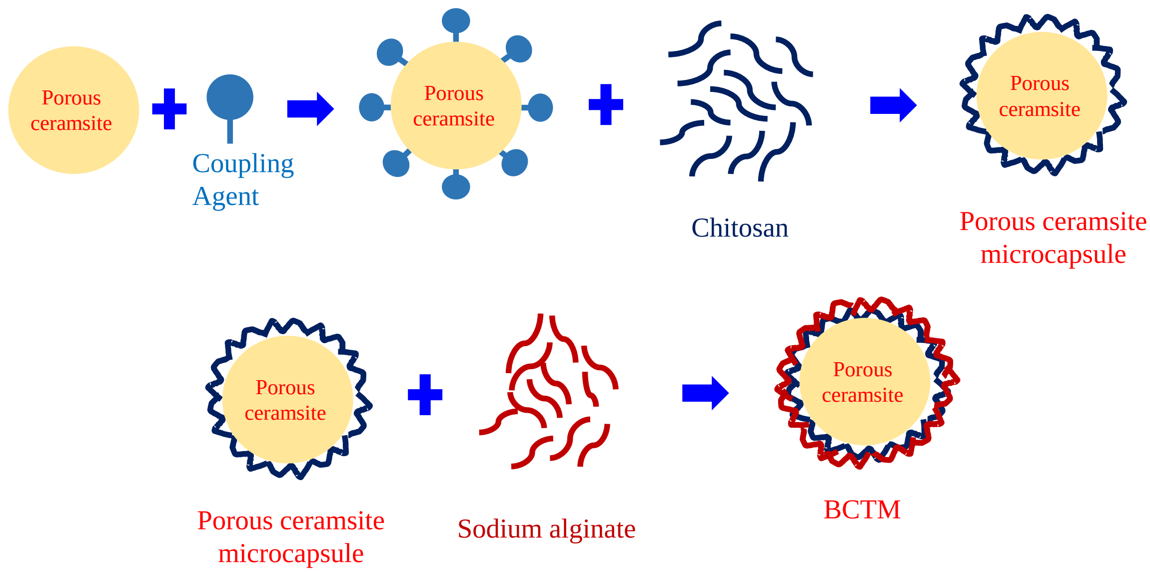

Fig. 1. Schematic diagram of the synthesis mechanism of BCTM.

2.3 Synthesis process

In order to obtain a silane coupling agent solution, 0.95 g of 3-aminopropyltriethoxysilane was first mixed with 100 g of deionized water. Next, 20 g of ceramsite (ceramsite size: 20-30 μm) was thoroughly dispersed in the silane coupling agent solution and the reaction was stirred for 50 min at room temperature at 250 r/min. Subsequently, the dispersion was dried at 60 °C for 10 h to obtain the modified ceramsite.

Then, 5 g of chitosan was dissolved in 100 g of mixed solvent (the mixed solvent was obtained by mixing methylene chloride and water according to the mass ratio of 1 : 1), followed by stirring for 30 min at room temperature at 250 r/min. 20 g of the resulting modified ceramsite was added and stirred for 30 min at room temperature at 200 r/min. Finally, 2.5 g of sodium alginate was added and the reaction was warmed up to 45 °C with a stirring rate of 200 r/min for 30 min at room temperature. Heating was next performed to 45 °C for the mixture to react for 2 h to evaporate the organic solvent. During this step, the stirring rate was set to 200 r/min. Once the reaction ended, the solution obtained was filtered, the obtained solids were washed with ionized water three times and then dried at 85 °C for 15 h to obtain BCTM.

2.4 Evaluation methods

The morphology of the microcapsules was observed under a scanning electron microscope, and the chemical structures of the microcapsules were analyzed using a Fourier transform infrared spectrometer. The blocking performances of BCTM, modified ceramsite and chitosan microcapsules were tested, the effect on core permeability under laboratory conditions was observed and their blocking rate was calculated. Then, we carried out experiments on the degradation rate of temporary plugging materials by different bioenzymes (cellulase, low-temperature composite enzyme and amylase) to study the influence of different bioenzymes on the temporary plugging materials with degradation time. We tested the changes in the permeability of the temporary plugging materials under the action of bioenzymes to evaluate the degradation performance at different temperatures. Permeability and permeability recovery were determined by an LDY50-180A core flow tester (Jiangsu Hongbo Machinery Manufacturing Co., Ltd.). Different combinations of experimental materials and artificial cores were placed in a core holder, and core expulsion experiments were conducted under the same backpressure and peripheral pressure conditions. Permeability and permeability recovery were calculated based on the experimental results. Finally, a phase equilibrium test was carried out to investigate the influence of BCTM on the hydrate decomposition process by the hydrate automatic evaluation reactor (Beijing Shijisenlang Co., Ltd.).

3. Results and discussion

3.1 Characterization test

3.1.1 Morphological characteristics

The observations showed that the whole ceramsite microcapsule is approximately spherical, the surface is relatively smooth, and most of the ceramsite microcapsule particle size is 40 μm. Fig. 2 presents the results of the scanning electron microscope observation of BCTM. The hydrate reservoir pore size is mainly distributed between 10 and 100 μm. In the field application process, according to the pore structure of the hydrate reservoir, the pore size of ceramsite size parcel layers is under reasonable control, with an ability to achieve the grain size with the reservoir to match, support the rock substrate, and stabilize the well wall.

3.1.2 Chemical structure characterization

The shell materials chitosan, sodium alginate and BCTM were tested in infrared mode using an infrared spectrometer. Fig. 3 shows the infrared spectra of the microcapsule shell materials and BCTM. The characteristic peaks of the function-

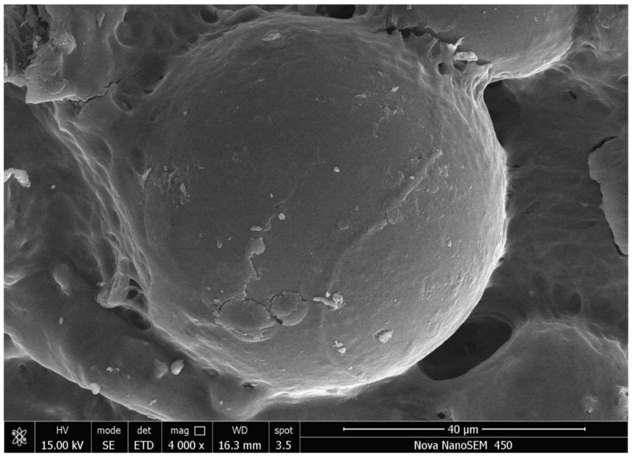

Fig. 2. Scanning electron microscope view of the BCTM.

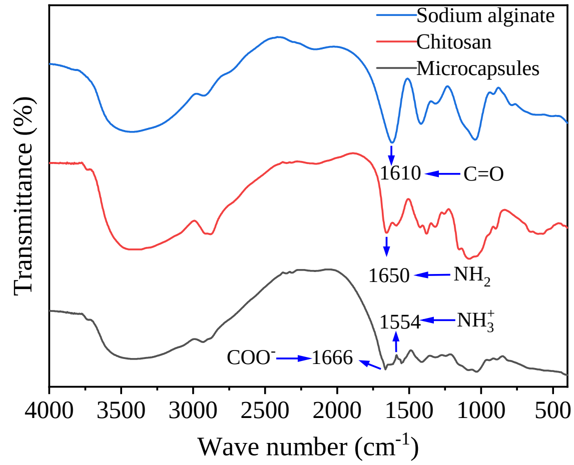

Fig. 3. Infrared spectra of the shell material and BCTM.

al groups in the test samples indicate the molecular structure of the microcapsules. The core material ceramsite is inorganic and the characteristic peaks of the functional groups are outside the detection range. The test results were identical for the background samples, so infrared testing was not performed for these.

In the infrared spectrum of sodium alginate, 1,610 cm^{-1} is the characteristic absorption peak of the carbonyl group. In the infrared spectrum of chitosan, 1,650 cm^{-1} corresponds to the symmetric bending vibrational absorption peak of the amino group. In the infrared spectrogram of microcapsules, 1,666 cm^{-1} appears as the symmetric telescopic vibrational absorption peak of the carbonyl group, and at the same time, 1,554 cm^{-1} appears as the $-NH^{3+}$ antisymmetric deformation vibrational absorption peak. It could be proved that the amino group in chitosan reacted with $-COO^{-}$ in sodium alginate by electrostatic interaction and the microcapsule shell was composed of chitosan and sodium alginate.

3.2 Performance evaluation

3.2.1 Encapsulation testing of BCTM

Chitosan microcapsules are ceramsite microcapsules synthesized using only chitosan as the shell material. According to the experimental results, it could be obtained that the permeability of the core blocked by modified ceramic granules was 0.334 mD after blocking, and the blocking rate was 40.88%. The permeability after blocking by microcapsules prepared from chitosan encapsulation was 0.278 mD, with a blocking rate of 51.4%. Some improvement in the blocking rate could be detected, but the magnitude was small. BCTM was found to have a 100% blocking rate for cores. Fig. 4 shows the results of the blocking performance tests on BCTM, modified ceramsite particles and chitosan microcapsules. It can be seen that BTCM has a noticeable blocking effect, and under the experimental setting conditions, it can block the core nearly perfectly. Using only chitosan as shell material weakens its resistance to external pressure changes. However, utilizing chitosan in combination with sodium alginate can stop the fluid more efficiently.

3.2.2 Permeability with different biological enzymes

The degradation process of polysaccharides chitosan and sodium alginate by biological enzymes mainly includes first hydrolyzing the glycosidic bond, then cutting the resulting long-chain oligomers into short-chain oligomers, and finally hydrolyzing the products into monosaccharides. In this experiment, the enzyme solution degraded chitosan and sodium alginate, exposing the ceramic grains and restoring permeability. The degradation effect of the enzyme solution is closely related to the enzyme type, activity and degradation time.

The results of BCTM degradation by different bioenzymes are shown in Fig. 5. The process was carried out at 15 °C because the average temperature of the general natural gas hydrate reservoir is around this value. According to the experimental results, the core permeability after BCTM degradation by amylase and cellulase is 0.265 and 0.23 mD, respectively. In contrast, the core permeability after the degradation of BCTM by the low-temperature complex enzyme is 0.395 mD and its permeability recovery rate is 74.5%. It could be obtained that the degradation of ceramic microcapsules by low-temperature complex enzymes is better, followed by cellulase, while amylase is less effective.

A preferable low-temperature composite enzyme can be active at 5 °C, while low temperature can still degrade the temporary blocking material, realizing the effect of unblocking. At the same time, this enzyme can be used in the temporary plugging material preparation process and added to the shell of biological enzymes to avoid the influence of the surrounding environment. Enzyme activity decreases at low temperatures and fluid enters the temporary plugging material after the temporary plugging material has sealed the stratum. Under prolonged action, the bioenzyme starts to degrade the shell material and the amount of bioenzyme is controlled according to the required blocking time.

3.2.3 Permeability at different degradation temperatures

According to the results of bioenzyme preference test, the degradation temperature test of the low-temperature composite enzyme was carried out by dissolving the bioenzyme in pure water solution at 5, 10, 15, and 25 °C. Fig. 6 presents

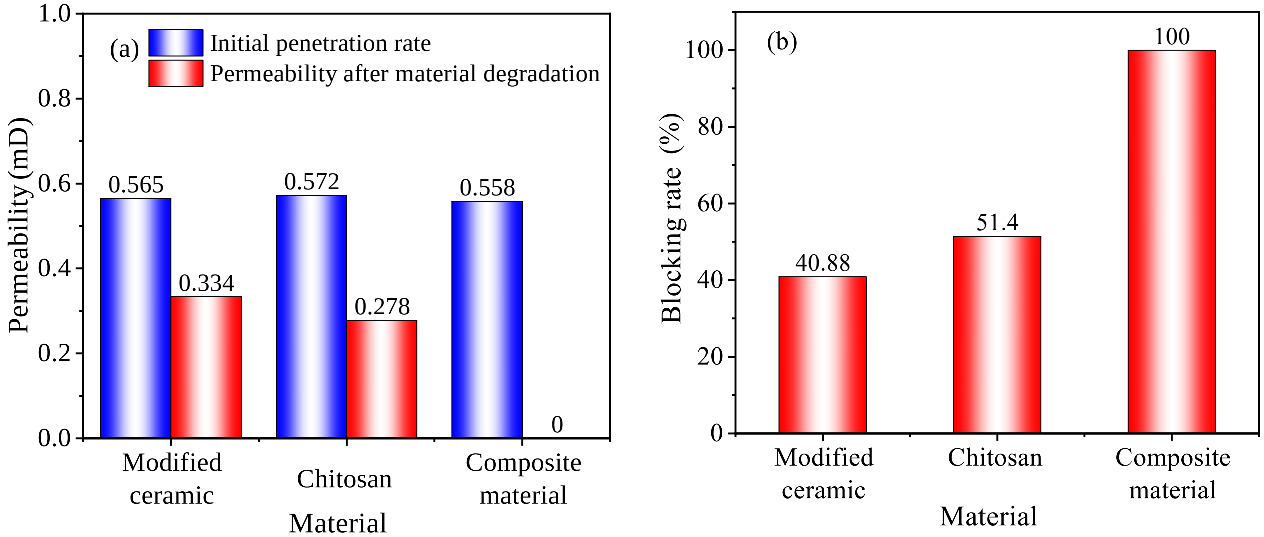

Fig. 4. Blocking test charts for microcapsules: (a) permeability and (b) blocking rate.

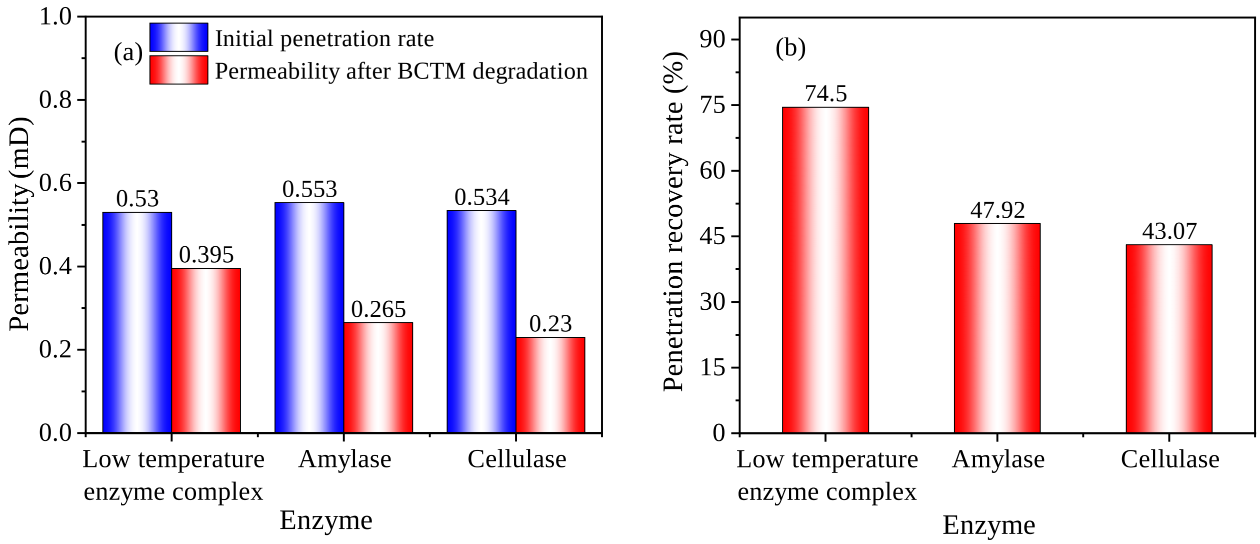

Fig. 5. Permeability test charts for different biological enzymes: (a) permeability and (b) penetration recovery rate.

the tests performed at different degradation temperatures. When the temperature is 25 °C, the difference between the initial permeability and that after plugging is slight and the permeability recovery rate is 90.2%. With the decrease in temperature, the gap between the initial permeability and that after plugging increases gradually. When the temperature is lowered to 5 °C, the initial permeability is 0.504 mD. After plugging, the permeability is 0.267 mD and the permeability recovery rate becomes 53%. According to the experimental results, the permeability recovery rate of the core increases gradually with the increase in temperature. As the temperature rises, the enzyme molecules move more actively, making the shell material more susceptible to destruction. It also leads to easier fluid intrusion into the microcapsules and higher permeability recovery.

3.2.4 Penetration under different degradation durations

The degradation of BCTM was tested at 15 °C using a low-temperature enzyme complex, and the degradation results at different time durations are shown in Fig. 7. The degradation lengths are 6, 12 and 24 h. When the degradation length is 6 h, the initial permeability is 0.619 mD, and the permeability after blocking is 0.347 mD. When the degradation length is increased to 12 h, the permeability after blocking is 0.395 mD and the permeability recovery increases from 56.06% to 64.86%. However, when the degradation duration is 24 h, the permeability recovery rate is 67.48%, which is not much different from the data for the degradation duration of 12 h. Therefore, it is concluded that the permeability recovery rate gradually increases with the increase in degradation duration, but when the degradation duration exceeds 12 h, the increase in permeability recovery rate becomes smaller.

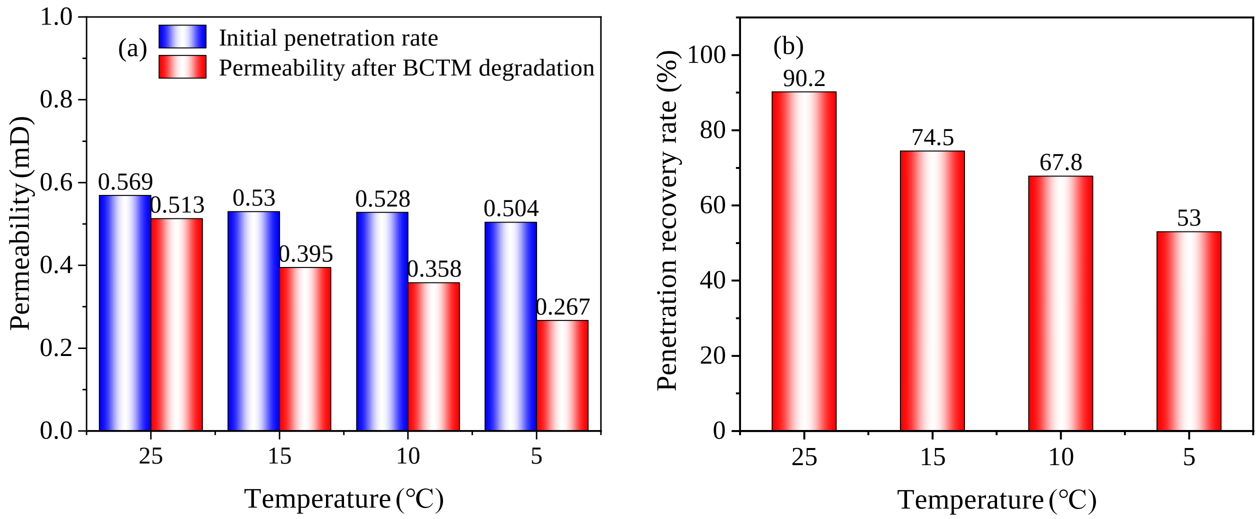

Fig. 6. Permeability test charts for different degradation temperatures: (a) permeability and (b) penetration recovery rate.

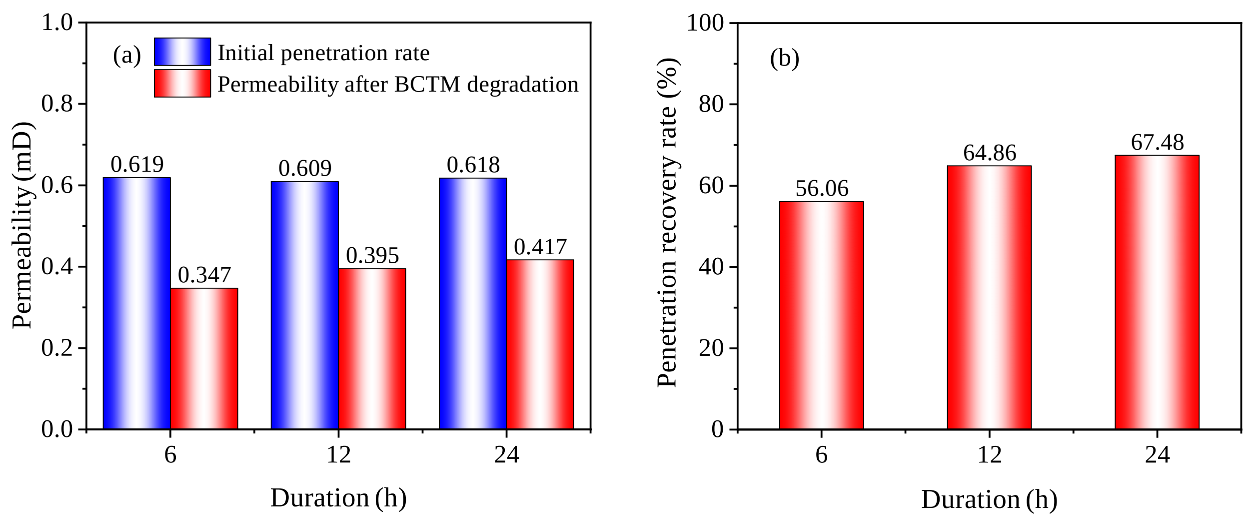

Fig. 7. Penetration tests chart for different degradation durations: (a) permeability and (b) penetration recovery rate.

3.2.5 Phase equilibrium of natural gas hydrates

In order to investigate the effect of BCTM on the hydrate decomposition process, its phase equilibrium test on natural gas hydrates was carried out using a hydrate phase equilibrium reactor. Fig. 8 shows the temperature and pressure curves of the hydrate decomposition experiments. The tested base stock solutions are 4% drilling fluid and 3% microcapsule solution. It takes 8 h for hydrate to go from decomposition to equilibrium when only base slurry is added, while the time required for hydrate to shift from decomposition to equilibrium after adding microcapsules is 10 h. It could be obtained that the microcapsules have a specific decomposition inhibition property.

3.2.6 Temporary plugging mechanism of BCTM

Natural gas hydrate reservoirs are characterized by shallow burial, weak cementation and non-rock-forming characteristics, while the BCTM can be tightly arranged on the surface of the well wall. Fig. 9 is a schematic diagram of the temporary plugging mechanism of BCTM. The BCTM of the surface layer of natural polymers can be grouped to stop the drilling fluid infiltration into the reservoir, which prevents well wall destabilization due to hydrate decomposition. The BCTM shell is made of natural polymer material and can be biodegraded by enzymes. Once the shell material has degraded, the enclosed ceramsite becomes exposed. Ceramsite can also utilize the adhesive effect of degraded shell materials to stabilize the well wall; it belongs to a porous medium with high permeability. After the degradation of shell materials, the reservoir permeability is restored, which will not affect subsequent construction operations. This renders BCTM high strength, great plugging effect during drilling and easy unblocking after biological enzyme action.

4. Conclusions

During the extraction of natural gas hydrates, the drilling fluid penetrates into the formation around the wellbore, causing gas hydrate decomposition. This leads to mechanical

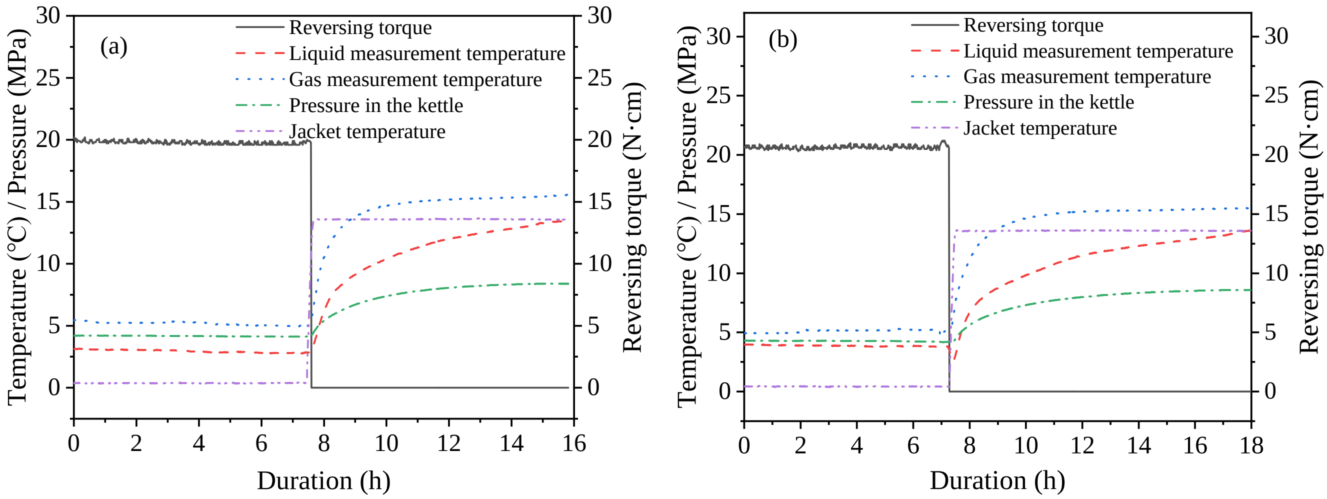

Fig. 8. Temperature-pressure profiles of hydrate decomposition experiments: (a) 4% base slurry and (b) 3% BCTM.

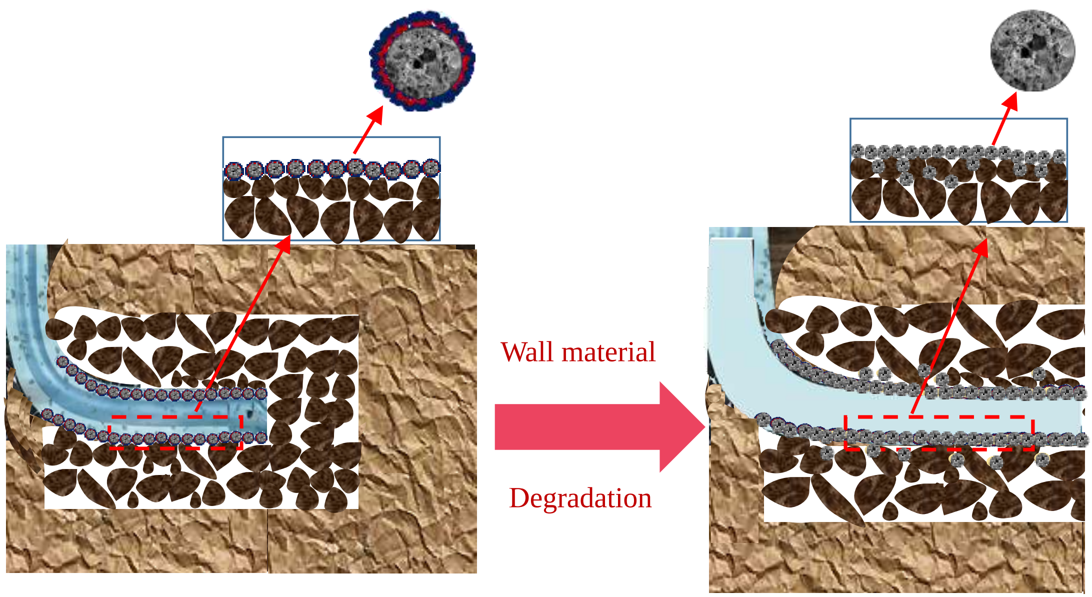

Fig. 9. Schematic diagram of the mechanism of BCTM.

destabilization of the well wall, with serious impacts on normal drilling operations. To address this issue, this work proposes a temporary plugging microcapsule material for sealing the formation, which can be degraded by biological enzymes. The prepared microcapsules are further subjected to characterization tests and performance evaluation. The following contributions are made in this study:

1) The ceramsite is wet-modified by 3-aminopropyltriethoxysilane as a coupling agent. The BCTM is prepared by the solvent evaporation method using chitosan and sodium alginate as wall materials.
2) Characterization experiments on BCTM reveal that the overall approximation is spherical, the surface is relatively smooth and the particle size is 40 μm, which can match the pore size of the hydrate reservoir according to the number of wrapped layers. The chemical structure is in line with the preparation mechanism.
3) The BCTM has a good sealing effect, with no fluid passing through the core under the experimental conditions. The degradation effect of low-temperature complex enzyme on BCTM is enhanced and more prominent, and the permeability recovery rate is 74.5%. The permeability recovery rate of the core increases gradually with rising temperature, which is 90.2% at 25 °C.
4) With the progression of degradation time, the degradation effect of the enzyme is more significant and the permeability recovery rate is 67.48% at 24 h. However, above 12 h, the increase of degradation effect is slower. In the case of only adding the base slurry, it takes 8 h for the hydrate to go from the decomposition to equilibrium, while after adding the microcapsules to the base slurry, this period becomes 10 h. It can be obtained that the microcapsules have a certain inhibitory effect on decomposition.

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Conflict of interest

The authors declare no competing interest.

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