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Invited review

Recent advances in phase change microcapsules for oilfield applications

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Abstract:
Unconventional oil and gas reservoirs have become a new focus of energy development due to their wide distribution and abundant reserves. However, the exploitation of these reservoirs is often accompanied by varying temperatures, which impose higher requirements for novel material, equipment, and technology. Recently, phase change microcapsules have been attracting increasing attention in oilfield applications, because they can absorb or release considerable latent heat during the phase change process, enabling stable temperature control. Herein, the current status and future development trend of phase change microcapsules in oilfield applications are reviewed. The classification of phase change materials, including solid-solid, solid-liquid, solid-gas, and liquid-gas phase change materials, is introduced, with an emphasis on their advantages and disadvantages. Then, the microencapsulation methods for phase change materials are presented. Next, the critical thermophysical properties of phase change microcapsules relevant to oilfield applications, including melting and freezing points, latent heat capacity, thermal conductivity, and cycling stability, are discussed. Subsequently, the specific applications of phase change microcapsules in oilfields, including temperature regulation of drilling fluid, thermal management of cement paste, thermal protection of drilling equipment, and thermal insulation of submarine oil and gas pipelines, are thoroughly overviewed. Finally, the critical challenges and future perspectives are outlined. This review highlights the critical role of phase change microcapsules in advancing thermal management solutions for the efficient development of oil and gas from high- and low-temperature reservoirs, guiding future research and development efforts.

1. Introduction

With the continuous growth of energy demand and the gradual depletion of traditional energy sources, the oil and gas industry is facing unprecedented challenges (Li et al., 2023). Traditional oil and gas reservoirs are no longer sufficient to meet the increasing energy demand, prompting a shift towards the development of unconventional reservoirs such as shale gas, tight oil, ultra-deep oil, and natural gas hydrates (Sun et al., 2024c). However, there are many challenges in the exploitation of oil and gas from unconventional reservoirs, e.g., high temperature in deep and ultra-deep formation, as well as low temperature in gas hydrate formation, which place higher demands on oilfield working fluids, equipment, and pipelines. For instance, under high-temperature conditions,

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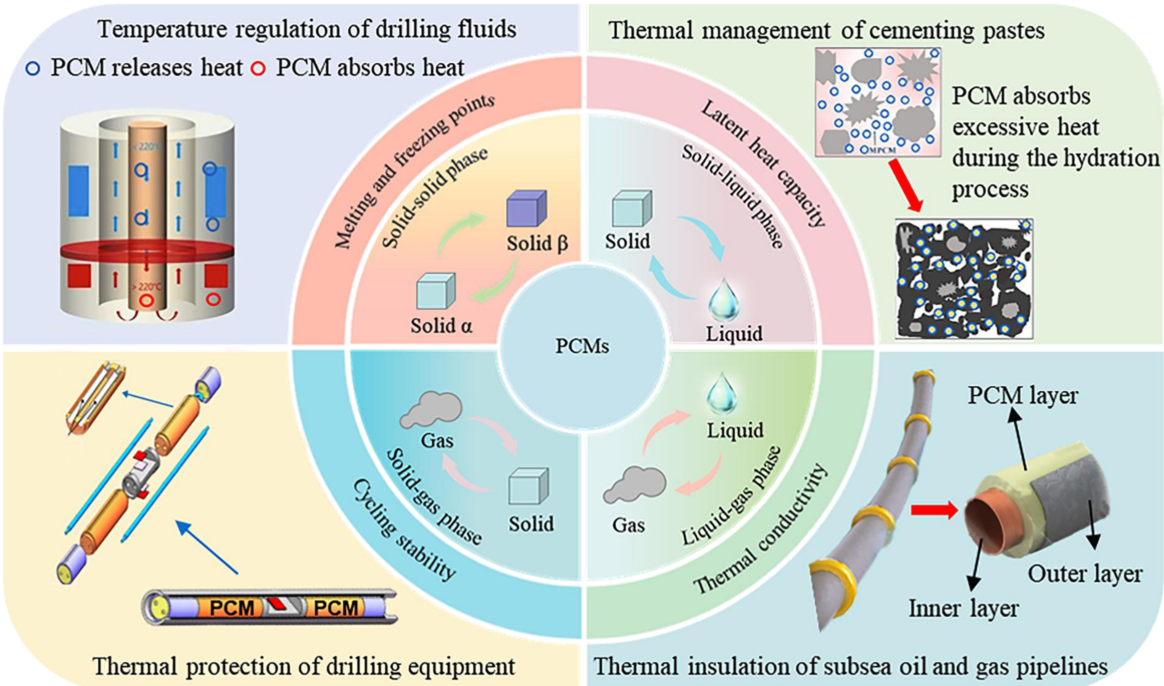

Fig. 1. The overview of the topic of this review, including the classification, microencapsulation method, thermophysical properties, and emerging application of MPCMs in oilfields.

drilling fluids may fail, increasing the risk of drilling accidents (e.g., wellbore collapse, lost circulation, and blowouts). In low-temperature conditions, the rheology of drilling fluids and the phase of gas hydrate may be affected, resulting in impaired operational efficiency.

Phase Change Materials (PCMs) provide significant advantages in addressing these challenges by absorbing or releasing large amounts of latent heat during phase transitions, enabling stable temperature control without requiring additional energy input (Zhang et al., 2023c). PCMs come in a variety of types, each with unique properties and promising applications. Organic PCMs are favored for their high latent heat values and minimal supercooling, whereas they may encounter issues with low thermal conductivity and chemical stability at high temperatures (Lin et al., 2023). In contrast, inorganic PCMs, while having high melting points, low costs, and good thermal stability, may suffer from phase separation and corrosiveness (Man et al., 2023). The selection of PCM types depends on the phase change temperature, latent heat capacity, thermal conductivity, and cycling stability needed for the specific oilfield application.

PCMs are prone to leakage during phase transitions, which can compromise their efficiency and usability in practical applications. To address this issue, microencapsulation techniques have been developed and widely reported to produce Microencapsulated Phase Change Materials (MPCMs), offering a protective barrier that prevents leakage while maintaining the material's thermal storage capabilities (Zhang et al., 2023d). Recently, the application of MPCMs in the oilfield has been increasing. For instance, Zhao et al. (2023b) used MPCMs to intelligently regulate the temperature of drilling fluids, effectively suppressing the decomposition of gas hydrates while ensuring good compatibility with the drilling fluids. Guo et al. (2024b) applied silicon dioxide coated binary nitrate as MPCMs to a high-temperature drilling fluid system. MPCMs melted at high temperature to absorb heat in deep wells and solidified at shallow layers through heat release, which further improved the applicability of temperature-resistant drilling fluid in extremely high-temperature formation environments. Ma et al. (2024) used MPCMs to provide thermal protection for electronic components (i.e., pulse power sources) in the development of shale oil from high-temperature reservoirs, and further studied the thermal protection capabilities of different structures (i.e., single-layer array, staggered stacking, and double-layer stacking). The staggered stack structure showed the best thermal protection performance, and the phase transition duration was 14.1% longer than that of the double stack structure. Despite the broad application prospects of MPCMs in oilfields, to the best of our knowledge, an overview on this topic is missing.

This review article systematically overviews the current state and future development trends of MPCMs in the oilfields. The article first provides a comprehensive classification, microencapsulation method, and thermophysical performance analysis of MPCMs, including their advantages and limitations (Fig. 1). Then, the specific applications of MPCMs in oilfield, such as temperature regulation of drilling fluids, thermal management of cementing pastes, thermal protection of drilling equipment, and thermal insulation of submarine oil and gas pipelines, are documented. It is expected that this work will provide insight on the application of MPCMs in oilfields, promoting the development of oil and gas from unconventional

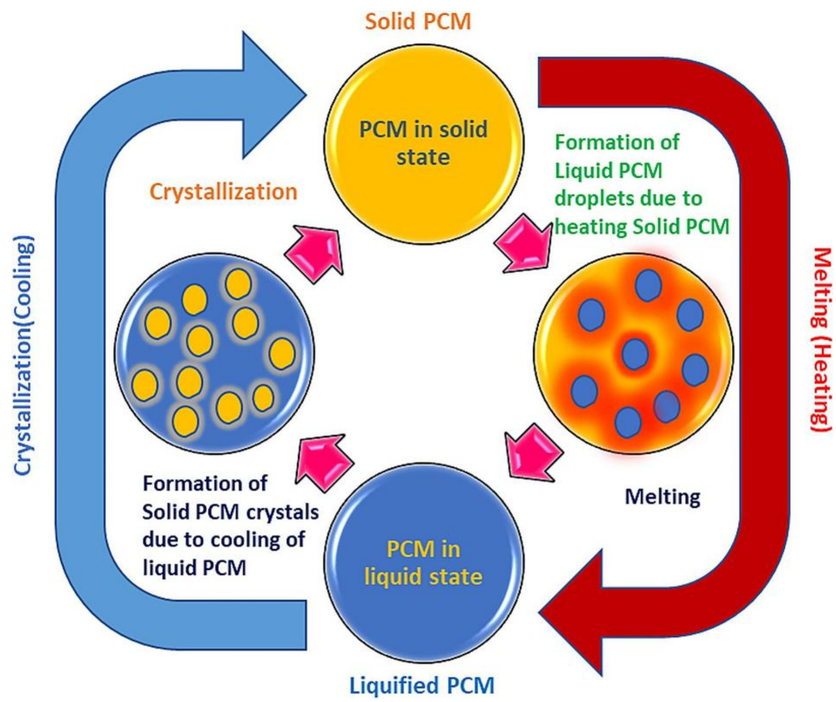

Fig. 2. Mechanism of PCMs (Reddy et al., 2024).

reservoirs more efficiently and sustainably.

2. Mechanism and classification of PCMs

PCMs are a class of materials that exhibit the ability to store and release latent heat within specific temperature ranges through phase transition processes (Shen et al., 2024). When the external temperature exceeds the phase transition temperature of PCMs, they absorb energy from the environment to store latent heat. Conversely, when the ambient temperature falls below the phase transition temperature, PCMs release their stored energy, maintaining a stable temperature (Fig. 2). According to the states of matter involved their phase transitions, they can be divided into solid-solid, solid-liquid, solid-gas, and liquid-gas PCMs (Zhou et al., 2012). These classifications cover most traditional PCMs, but some new materials may involve intermediate states or multiple phase transition stages, which are difficult to be strictly classified, and are no longer described in detail in this paper.

2.1 Solid-solid PCMs

Solid-solid PCMs realize phase change through crystal structure transformation, with small volume change and no need for encapsulation, and are mainly classified into inorganic, organic, organometallic, and polymeric PCMs. Inorganic salt solid-solid PCMs (e.g., Li_2SO_4, KHF_2, and NH_4SCN) have high energy storage densities but are low in thermal conductivity, costly, and potentially corrosive. Organic solid-solid PCMs (e.g., polyols) have good chemical stability and high latent heat values, but have low thermal conductivity and are volatile. Metal-organic PCMs (e.g., layered chalcogenides) have high enthalpy changes and reversible solid-solid phase changes, but low thermal conductivity. Polymer-based solid-solid PCMs (e.g., polyethylene glycol, polyurethanes, etc.) have high energy densities, no liquid problems, and are environmentally friendly, but have low latent heat, a narrow range of phase change temperatures, and high costs.

2.2 Solid-liquid PCMs

Solid-liquid PCMs can be classified into three categories: organic, inorganic, and composite solid-liquid PCMs. These materials are capable of absorbing or releasing energy, thereby converting between solid and liquid states. This process involves large latent heat and is characterized by a stable phase change. Organic solid-liquid PCMs, which include paraffin, fatty acids, and polyalcohols, possess a stable phase change process and undergo a small volume change. However, they are also volatile and possess low thermal conductivity, which renders them unsuitable for applications requiring high temperatures. Inorganic solid-liquid PCMs (e.g., hydrated salts) possess high energy storage densities and high thermal conductivity; however, they are prone to phase separation and supercooling. Composite solid-liquid PCMs enhance performance by combining different components, such as blending alkanes, fatty acids, and polyols to obtain low eutectic mixtures, thereby expanding the range of applications.

2.3 Solid-gas PCMs

The essence of solid-gas PCMs is to undergo solid-gas sublimation or gas-solid condensation process at a specific temperature, enabling efficient storage and release of energy. Common solid-gas PCMs include some metal oxides, such as zirconia and alumina, as well as some organic compounds, such as benzophenone and naphthalene. These materials usually have a high latent heat value, but the gas generated during

Table 1. Applicable conditions, advantages, and disadvantages of different preparation methods for MPCMs.

Method	Advantages and disadvantages	Oilfield-specific suitability
Spray drying	High production efficiency, low cost Thin shells, prone to breakage under shear forces	Subsea pipeline insulation
Microfluidics	Precise control over capsule size, uniformity Low production rate, high cost	High-value applications and research
Solvent evaporation	Good encapsulation efficiency Requires organic solvents, limited mechanical strength	Limited use due to environmental concerns
Interfacial polymerization	Dense polymer shells, high mechanical and thermal stability Complex process, may involve toxic reactants	High-pressure, high-temperature drilling fluids
In-situ polymerization	Strong adhesion to host materials, excellent shell integrity Requires precise control over reaction conditions, potential toxicity	Cement slurries and wellbore treatments
Emulsion polymerization	Stable microcapsules, good dispersion Requires surfactants, possible rheology issues	Downhole applications
Suspension polymerization	High encapsulation efficiency, good mechanical stability Needs stabilizers, can affect drilling fluid rheology	High-shear environments like drilling fluids
Sol-gel	Inorganic shells with excellent strength and stability Complex process, high cost	Ultra-deep, high-temperature wells
Complex coacervation	Thick and flexible shells, high encapsulation efficiency Sensitive to pH and ionic strength changes	Long-term stability in drilling fluids

the phase transition process occupies a larger volume, resulting in relatively low thermal conductivity and high costs, which limits their oilfield use.

2.4 Liquid-gas PCMs

Liquid-gas PCMs are substances that can change from liquid to gas or from gas to liquid at a specific temperature. Liquid-gas phase transitions usually involve evaporation and condensation processes, such as the boiling and condensation of water. Common liquid-gas PCMs include water, alcohols (such as ethanol and isopropyl alcohol), ketones, ammonia aqueous solutions, and some organic compounds. Water is the most common liquid-gas PCMs, because it has a high latent heat value, moderate phase change temperature, non-toxic nature, and easy to obtain. However, it undergoes significant volume change in the process of phase transformation, limiting its oilfield application.

2.5 Suitability of PCMs for different oilfield applications

The suitability of different types of PCMs for oilfield applications depends on various factors such as the temperature range, stability, and the specific requirements of the reservoir or operation. Solid-solid PCMs undergo a phase transition between two solid states without changing their volume. They are highly suitable for applications where volume change and leakage are critical concerns, such as in deepwater gas hydrate reservoirs and high-pressure deep wells. Solid-liquid PCMs undergo a phase transition from solid to liquid, storing and releasing a significant amount of latent heat during the phase change. With their high latent heat and broad phase change temperature range, they are effective for temperature regulation in most of oilfield applications. However, the leakage risk as well as low thermal conductivity should be addressed. Liquid-gas and solid-gas PCMs are less commonly used due to issues with volume expansion and pressure constraints.

3. Microencapsulation of PCMs

The direct application of PCMs in oilfield may result in a multitude of issues caused by the leakage of PCMs (Xu et al., 2022). In drilling fluids, PCM leakage can lead to contamination of the wellbore, reducing drilling fluid stability and performance while increasing disposal challenges. Within cement pastes, PCM leakage can weaken the mechanical properties of the cement, resulting in reduced structural stability and potential failure of wellbore integrity. In drilling equipment, leaked PCMs may cause fouling, blockages, or corrosion, leading to decreased equipment reliability and costly maintenance. Similarly, in pipelines, PCMs leakage can contribute to clogs, reduced flow efficiency, and potential chemical reactions with transported substances, compromising pipeline performance and safety. Moreover, leaked PCMs, especially those composed of hydrocarbons or other environmentally sensitive materials, pose a risk of environmental contamination, necessitating stringent mitigation and containment measures. To address the leaking issues, microencapsulation technology is frequently employed to produce MPCMs. This microencapsulation treatment has two primary benefits. First, it prevents PCMs from leaking and protects the oilfield working fluid, equipment, and pipelines. Second, it improves heat transfer efficiency and the stability of MPCMs.

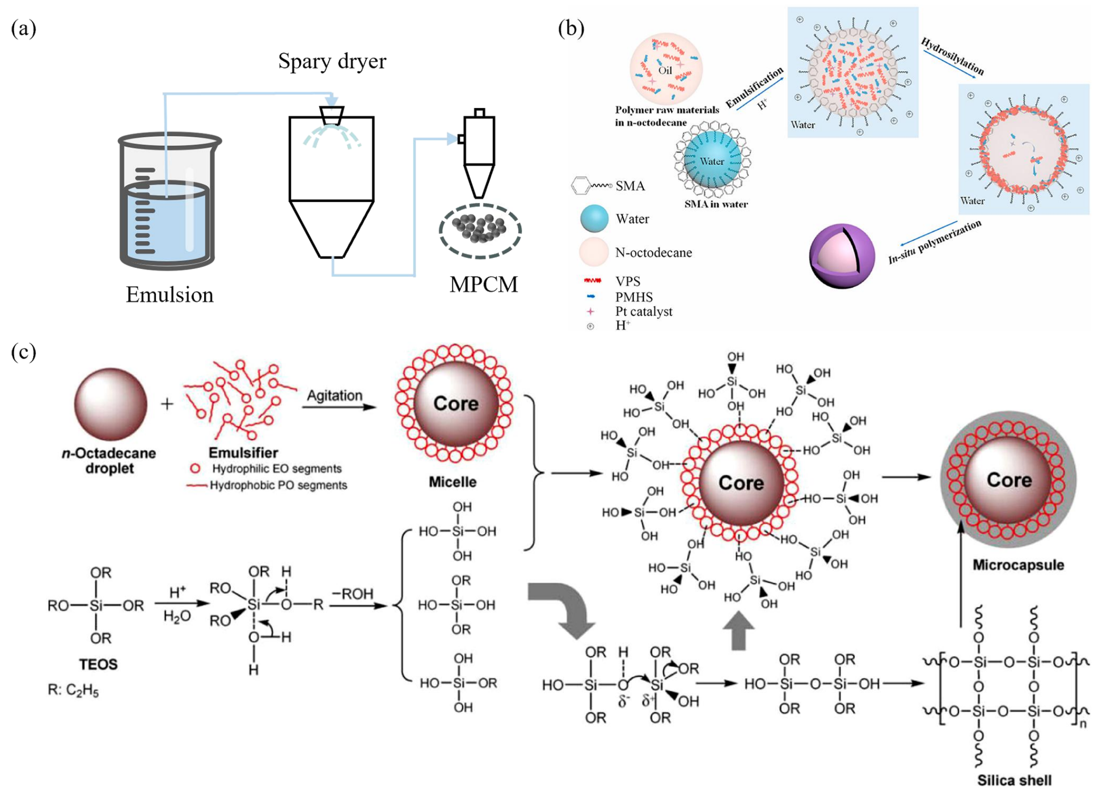

Fig. 3. Schematical illustration of the preparation of MPCMs using different methods: (a) Spray drying, (b) emulsion polymerization (Guo et al., 2022), and (c) sol-gel (Chang et al., 2022).

The encapsulation methods for MPCMs can be categorized into three main groups, i.e., physical, chemical, and physicochemical methods. Physical methods include spray drying, microfluidics, solvent evaporation, and so on. Chemical methods comprise interfacial polymerization, *in-situ* polymerization, emulsion polymerization, and suspension polymerization. Physicochemical methods involve processes such as sol-gel and complex coacervation. Table 1 provides an overview of the application conditions, advantages, disadvantages, and oilfield-specific suitability of different microencapsulation methods.

3.1 Physical methods

3.1.1 Spray drying

Spray drying is simple operation and high yield, but there are some problems such as agglomeration between particles, partial PCMs may not be completely coated by wall materials. As shown in Fig. 3(a), the fundamental principle underlying the spray drying method entails the dissolution of the shell material into an aqueous solution, followed by the incorporation of an oil-soluble core material. This mixture is subsequently introduced into a spray drying apparatus, where it undergoes solidification through high-temperature atomization, resulting in the formation of microcapsules. Methaapanon et al. (2020) encapsulated methyl palmitate and n-octadecane in separate silica shells by spray drying. The results demonstrated that the optimal surfactant concentration was conducive to maintaining emulsion stability and enhancing encapsulation efficiency.

3.1.2 Microfluidics

Microfluidics involves the precise manipulation of fluids at the microscopic scale, where different fluids are combined in a controlled manner. This process relies on the systematic control of fluid interfaces, ensuring their formation and stability. By managing the interaction or solidification at the external interfaces of liquids and within laminar fluid flow, MPCMs with highly controllable characteristics are fabricated (Fig. S1). The microfluidic method has many advantages over traditional manufacturing methods, such as simple preparation process, better monodispersity of microspheres, and uniform and adjustable size, but the fabrication cost of microfluidic chips is high, and it is difficult to realize large-scale industrialized production. Li et al. (2022) prepared monodisperse MPCMs with sodium alginate as shell material and paraffin wax as core material by microfluidic technique, demonstrating their potential for thermal energy storage in buildings.

3.1.3 Solvent evaporation

The solvent evaporation method involves the removal of volatile solvents from the dispersed phase of an emulsion, typically derived from Water-in-Oil (W/O), Oil-in-Water (O/W), Water-in-Oil-in-Water (W/O/W), and Oil-in-Water-in-Oil (O/W/O)-type emulsion systems. Heating, continuous stirring, and other techniques are utilized to facilitate the diffusion of organic solvents into the continuous phase, resulting in the formation of microspheres (Fig. S2). Advantages of the solvent evaporation method include high yield, low cost and easy operation; however, commonly used solvents such as acetone and trichloromethane are highly volatile and toxic, and can easily pollute the environment (Ahangaran, 2023). The physical appearance of microcapsules is affected by a number of factors, Amberkar and Mahanwar (2023) investigated the effect of parameters such as core (beeswax) shell (ethyl cellulose) ratio, PVA concentration, solvent type and evaporation temperature on the physical morphology of microcapsules, which showed better thermophysical properties at a core/shell ratio of 60:40, a PVA concentration of 2%, and evaporation temperature of 40 °C.

3.2 Chemical methods

3.2.1 Interfacial polymerization

Interfacial polymerization involves preparing microcapsules by forming an oil/water emulsion or a water/oil emulsion using an emulsifier. Reactive monomers are added to the emulsion, undergoing rapid reactions at droplet interfaces to form a shell (Fig. S3). A variety of core materials were encapsulated by interfacial polymerization, including alkanes, fatty acids, salt hydrate, and pigments, and the microcapsules prepared by this method had a regular spherical morphology, a compact and smooth surface, and a uniform distribution of particle sizes, mostly of micrometer size, as well as a high encapsulation rate. Chen et al. (2025) synthesized methyl palmitate-polyurethane phase-change microcapsules, with a phase-change temperature and enthalpy of 27.2 °C and 160.5 J/g, respectively, and the encapsulation rate of 72.42%.

3.2.2 *In-situ* polymerization

In-situ polymerization involves a reaction between a monomer and catalyst located outside the core material droplets. The monomer, soluble in the continuous phase, undergoes polymerization on the surface of the droplets, gradually forming a shell through cross-linking (Fig. 3(b)). If there is only one hydrophilic or lipophilic monomer for the preparation of the shell material, *in-situ* polymerization is more suitable for the preparation of this phase change microcapsule compared to interfacial polymerization, with a simple preparation process, a higher encapsulation rate, and a better thermal stability. MPCMs with Melamine resin (MF) as shell, particle size of 4 μm, MF shell with adjustable thickness, core material content of 87.0% , were prepared by Zhang et al. (2022c), after 200 heating-cooling cycles, the retention rate of enthalpy is 99.7% (Zhang et al., 2022c).

3.2.3 Emulsion polymerization

The emulsion polymerization method involves mixing the PCMs with the reacting monomer, the initiator is dissolved in the aqueous phase, but the monomer is insoluble or insoluble in the aqueous solvent. The monomers are emulsified in the polymerization medium with the help of a surfactant. A water/oil emulsion is formed, which is polymerized in the presence of the initiator. Finally, the microcapsules are isolated by repeated washing to remove the oil phase (Fig. S4). The advantages of this method are stability, high encapsulation rate and low energy consumption. The disadvantages are the complexity of the process, the need to purify the polymer from the surfactant, and the possibility of oil residues. Zhang et al. (2022a) used this method to synthesize microcapsules with a paraffin wax as the nucleus and a boron nitride nanosheets-modified polystyrene as the shell. It was found that the modified microcapsules showed 63.8% higher thermal conductivity, 166.3 J/g enthalpy of melting, and 80.8% encapsulation rate compared to pure paraffin.

3.2.4 Suspension polymerization

As shown in Fig. S5, suspension polymerization is a process in which monomers are dispersed into droplets within a stabilized medium consisting of a small amount of suspension, a dispersant, and water. Under the action of an initiator, which is continuously deposited on the surface of the droplets to form a polymer shell, a polymerization reaction occurs to form a polymer (Sánchez-Silva et al., 2010). The merits of this method include its cost-effectiveness, high utilization, and encapsulation rates. The preparation of MPCMs by means of suspension polymerization is influenced by several variables, including the stirring rate, the reaction temperature, and the ratio of shell material (Jamekhorshid et al., 2014). Zhao et al. (2023a) employed this method to prepare microencapsulated phase-change n-octadecane, which exhibited the optimal enthalpy of melting of 111.5 J/g and encapsulation rate of 51.4% at a core-to-shell ratio of 2:1.

3.3 Physicochemical methods

3.3.1 Sol-gel

The sol-gel method involves the dissolution of ester compounds or metal-alcohol salts in an organic solvent to form a homogeneous solution. Water is then added to initiate a hydrolysis reaction, generating reactive monomers. These monomers are subsequently polymerized to form a sol, which is then aged to form a gel. The final step involves drying and heat-treatment to prepare MPCMs. Fig. 3(c) showed the sol-gel preparation of MPCMs. The process is characterized by its stability and controllability, and it is carried out at low temperatures, a common practice in the preparation of inorganic shell materials. Among these materials, SiO_2 and TiO_2 have garnered significant attention due to their exceptional stability and high thermal conductivity. However, the cost is substantial, and the applications are somewhat limited. Li et al. (2018) used the sol-gel method and yielded SiO_2-TiO_2 encapsulated paraffinic microcapsules. The experimental findings indicated a phase transition temperature of 29 °C for the microcapsules, along with a melt enthalpy of 62.6 J/g and an encapsulation rate of 39.8%.

3.3.2 Complex coacervation

Complex coacervation relies on the interaction of oppositely charged aqueous polyelectrolytes, a process that is highly susceptible to a number of factors in the media environment (e.g., ionic strength, temperature, solubility, and pH). Due to its high payload efficiency and adaptability to ambient temperatures, complex coacervation is a desirable

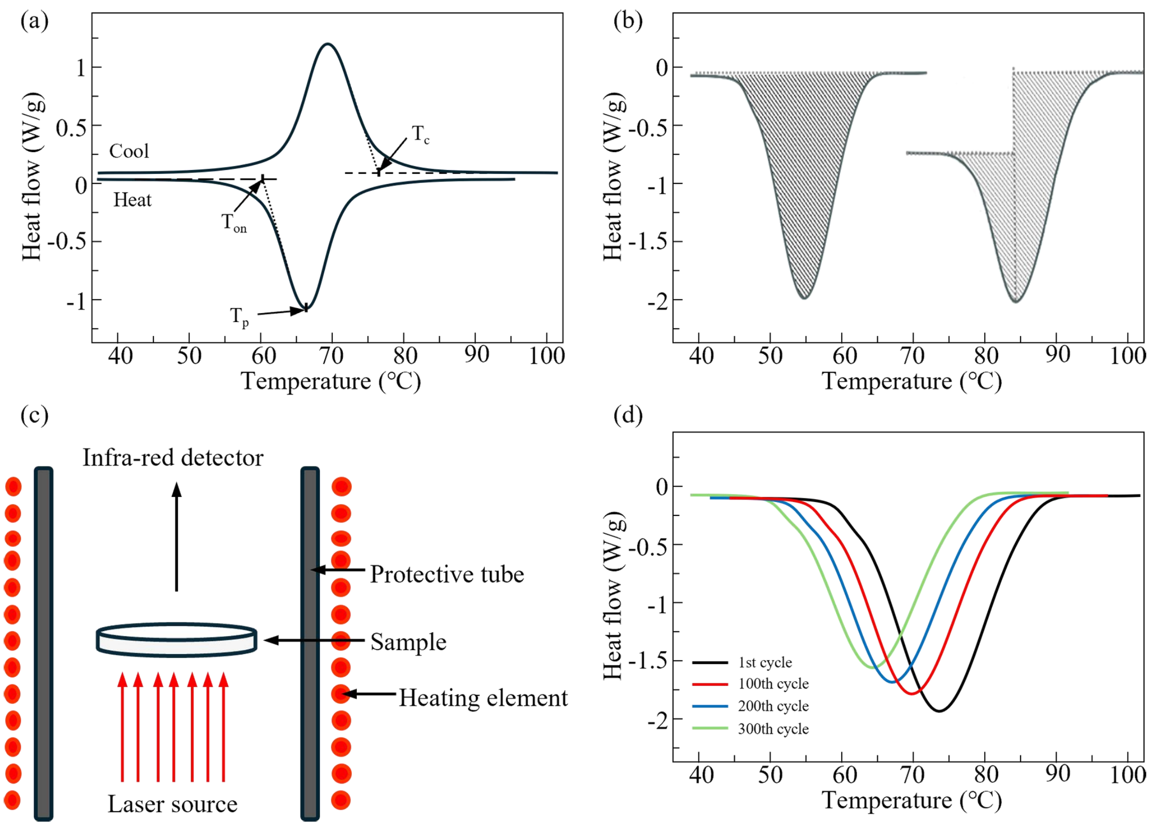

Fig. 4. Thermophysical properties of MPCMs: (a) Melting and crystallization points, (b) latent heat, (c) thermal conductivity, and (d) cycling stability.

alternative in the field of microencapsulation. However, one of the major limitations of this technology in commercial applications is its sensitivity to pH and ionic strength. Tian et al. microencapsulated paraffin waxes with gelatin (GE) and gum arabic (SA) complexes as wall materials by the complex coalescence method. It was found that the encapsulation rate of microcapsules could be as high as 82.1% and the leakage rate was significantly reduced under the optimized conditions, i.e., the mass ratio of GE to SA was 3:0.75, the core-to-shell mass ratio was 1.5:1, the dosage of $CaCl_2$ solution was 50 mL, the pH value was 4.5 and the emulsification time was 60 min (Tian et al., 2020).

3.4 Mitigation of leakage risks by microencapsulation

Microencapsulation techniques play a crucial role in preventing leakage, ensuring the stability and durability of the microcapsules over extended operational periods. For example, the microcapsules developed by Yan et al. (2023) demonstrated remarkable resilience, with no breakage or core material leakage observed even after 200 thermal cycles, highlighting the potential of advanced microencapsulation techniques in enhancing the longevity of MPCMs in oilfield conditions. Moreover, the likelihood of leakage is influenced by the mechanical properties of the shell material, which are particularly critical in determining the capsule's ability to withstand shear forces and pressure fluctuations during operation. Chemical microencapsulation methods, such as interfacial polymerization and *in-situ* polymerization, are commonly used to produce denser and more cohesive polymer shells, such as melamine-formaldehyde or polyurethane. These shells offer strong structural integrity and resistance to fracture, significantly reducing the risk of leakage under shear forces (e.g., melamine-formaldehyde or polyurethane) (Wang et al., 2023). In contrast, physical methods like spray drying typically generate thinner or more porous shells, which may be more susceptible to mechanical stress and prone to fracture under challenging field conditions. Physicochemical methods, especially sol-gel processes, have gained attention for producing inorganic shells, such as SiO_2 or TiO_2, which possess high hardness and strength. These materials offer excellent mechanical stability and are less likely to break under the pressure and thermal cycling encountered in oilfield applications (Qian et al., 2019).

4. Characteristics of MPCMs

When selecting and applying MPCMs in oilfield applications, it is crucial to consider their inherent properties related to the specific application environment. These properties include melting and freezing temperatures, latent heat capacity, thermal conductivity, and cycling stability (Fig. 4). The phase change temperature is the primary factor in selecting MPCMs, as it determines whether the MPCMs can effectively absorb or release heat under specific reservoir conditions. The latent heat capacity, thermal conductivity, and cycling stability of the MPCMs also influence its efficiency and durability. A MPCM with a high latent heat capacity can store or release more energy, while high thermal conductivity ensures rapid heat transfer, and good cycling stability guarantees long-term performance. Therefore, the selection of MPCMs should consider all these properties in a balanced manner to achieve optimal thermal management results.

4.1 Melting and freezing points

The melting and freezing points of MPCMs are the specific temperatures at which the phase transition occurs. In oilfield applications, the selection of a MPCM with the appropriate melting and freezing points is essential to ensure the effective operation of the thermal energy storage system. Different oil and gas reservoirs, due to their varying formation, depths and temperature conditions, have specific requirements for the phase change temperature of MPCMs. For example, in ultra-deep oil and gas reservoirs, the wellbore temperatures typically exceed 150 °C, requiring MPCMs capable of absorbing latent heat at high temperatures. In contrast, for natural gas hydrates, MPCMs with a lower phase change temperature of around 10-20 °C are needed to match the reservoir temperature. Such MPCMs help stabilize the wellbore walls and prevent instability caused by the decomposition of hydrates during the drilling process.

Differential scanning calorimetry (DSC) is a prevalent technique for measuring the melting and freezing points of MPCMs. Conducted under programmed temperature control and in a specific atmosphere, DSC assesses the thermal properties of a sample by measuring the rate of heat flow into the sample and a reference material as a function of temperature or time (Zhang et al., 2023a). DSC is characterized by automated temperature control, ease and speed of operation, minimal human error influence, and high repeatability.

The DSC curve reflects the characteristic temperatures of the sample during the melting and crystallization processes, enabling the precise determination of the sample's melting and crystallization points. In heat-flow type DSC, the vertical axis represents the heat flow, and the horizontal axis represents temperature. The melting temperature of MPCMs typically corresponds to the extrapolated onset temperature on the curve, which is the temperature at the intersection of the tangent to the initial linear part of the peak with the extended baseline (Fig. 4(a)). Occasionally, the peak temperature is also considered as the melting point. Similarly, the crystallization point of MPCMs can be obtained by analyzing the extrapolated onset temperature of the peak on the cooling crystallization curve.

4.2 Latent heat capacity

The latent heat of a phase transition is the ability of a MPCM to absorb or release heat during its transition from one phase state to another, usually expressed in J/g or kJ/kg . A MPCM with high latent heat capacity is able to store or release more energy during phase transitions, which is very beneficial for improving the energy efficiency of thermal energy storage systems.

The latent heat value (Δh) of MPCMs is measured using the DSC technique, which can be expressed in (Harvey et al., 2018):

$$\Delta h = A\frac{\Delta(T)}{m} \tag{1}$$

where A is the area of the endothermic peak, $\mathrm{mW\cdot{}^\circ C}$; m is the sample mass, g; and $\Delta(T)$ is the instrument sensitivity function, $\mathrm{J/(mW\cdot{}^\circ C)}$, which relates a known enthalpy change to a measured peak area. The DSC curve records the variation of heat flow over time, and the area enclosed by the curve and the baseline (A) is usually proportional to the change in enthalpy (Fig. 4(b)). For example, Lazaro et al. (2013) conducted a comparative test of enthalpy values of PCMs by DSC method, Su et al. (2021) introduced n-eicosane to evaluate the accuracy of temperature and latent heat measurement of DSC. A normal DSC curve is shown in the first subfigure of Fig. 4(b). However, when the heat capacity of the sample differs before and after the phase transition, it may lead to inconsistencies in the baseline on either side of the peak (as illustrated in the second subfigure of Fig. 4(b)). In such cases, it is critical to select an appropriate baseline to prevent baseline shift from blurring the peak boundaries, which could result in incorrect integration intervals and ultimately affect the accurate measurement of latent heat values. Therefore, specialized software is usually employed to assist in the calculation, allowing the computer to directly analyze the data.

4.3 Thermal conductivity

Thermal conductivity determines the heat transfer efficiency of MPCMs and affects the speed of heat storage and release. MPCMs with high thermal conductivity allow for faster heat exchange, which is essential in oilfield applications where rapid temperature control is needed. During the drilling process, high thermal conductivity allows MPCMs to transfer heat rapidly and efficiently. This means that the MPCMs can quickly absorb or release heat from the surrounding environment, maintaining the desired temperature and preventing localized overheating or cooling. To enhance the efficiency of heat transfer, the geometric structure of MPCMs can be optimized, such as using layered, porous, or fibrous structures, which increase the pathways for heat transfer and the contact area. Additionally, through microencapsulation technology, PCMs can be encapsulated in shells made of materials with high thermal conductivity, such as graphite or carbon-based materials. MPCMs typically have uniform particle sizes, which can be well dispersed in the drilling fluid, thereby increasing the contact area with the drilling fluids and increasing the overall heat transfer rate.

Laser flash analysis (LFA) is a transient thermal conductivity measurement technique used to determine the thermal conductivity coefficient of materials. The fundamental principle of this method involves using a laser as an instantaneous heat source to rapidly heat the lower surface of a sample under adiabatic conditions. This causes the surface layer of the sample to quickly absorb energy, leading to a sharp increase in temperature. The energy then propagates upward from the heat source end to the upper surface in a one-dimensional heat conduction manner. By measuring the temperature change on the upper surface of the sample with an infrared detector (Fig. 4(c)), a curve of temperature versus time can be obtained. Specifically, the time $t_{1/2}$ required for the upper surface temperature to rise to half of its maximum value T_m is measured. Using Fourier's law of heat conduction (Eq. (2)) (Parker et al., 1961), the thermal diffusivity α of the material can be calculated:

$$\alpha = \frac{1.388L^2}{\pi^2 t_{1/2}} \tag{2}$$

where α represents the thermal diffusivity of the material, m^2/s; L is the thickness of the sample, m; and $t_{1/2}$ denotes the half-temperature rise time, s. The thermal conductivity coefficient λ of the material can be further calculated (Zhao et al., 2016):

$$\lambda = \alpha \rho c \tag{3}$$

where λ is the thermal conductivity coefficient, W/(m·K); ρ is the material density, kg/m^3; and c is the specific heat capacity of the material, J/(kg·K).

4.4 Cycling stability

Cyclic stability is a critical parameter that assesses a MPCM's capacity to retain its phase transition characteristics through successive cycles of heating and cooling. In practical scenarios, MPCMs are subjected to numerous melting and crystallization cycles, making robust cyclic stability imperative for the enduring reliability and efficacy of MPCMs in sustained operations. When integrating MPCMs into drilling fluids, it is essential to find an economic equilibrium between the higher costs associated with MPCMs and the more cost-effective nature of the drilling fluid. Achieving economic feasibility depends on the MPCMs' superior recyclability. This entails ensuring that the MPCMs are not only physically and chemically robust to withstand repetitive use, phase transitions, and harsh drilling condition, but also incorporated in a manner that optimizes their quantity and application strategy to achieve maximum cost-effectiveness. Refining the integration of MPCMs involves a strategic approach to material selection and usage to ensure long-term operational success while managing costs effectively. This includes the continuous assessment of the MPCMs' performance over time and the adaptation of their use based on the evolving demands of the drilling process. Emeema et al. (2024) evaluated the thermal cycling stability of the material through the thermal cycling system, and tested the latent heat and thermal stability of the paraffin-based composite MPCMs. The experimental results showed that after 300 thermal cycles, the paraffin-based composite MPCMs still showed good phase changing stability.

The thermal cycling test is a pivotal procedure for assessing the cyclic stability of MPCMs, which is typically conducted within a high-low temperature test chamber (Miró et al., 2016). This chamber, composed of a robust enclosure and an exquisite temperature controller, operates on the principle of strong convection to ensure uniform temperature distribution. It utilizes liquid nitrogen for achieving low temperatures and resistive heating elements for high-temperature generation, guaranteeing precise control over the temperature spectrum. The chamber features a door with an observation window, facilitating the monitoring of the test conditions while maintaining the integrity of the testing environment. The interior and exterior walls of the chamber are crafted from stainless steel, known for its corrosion resistance and high-temperature endurance, thereby ensuring the longevity and safety of the test chamber. After a certain number of cycles, the phase change temperature and latent heat value of MPCMs after each cycle are measured by DSC, and the curves are plotted to show how these characteristics change with the number of thermal cycles. By scrutinizing these curves, the trend of melting temperature and latent heat value changes over time can be discerned, providing an assessment of the MPCMs' cyclic stability (Fig. 4(d)). This evaluation is crucial for determining the suitability of MPCMs for long-term cycling applications, as it directly pertains to their reliability and performance sustainability in practical scenarios. Through a detailed analysis and evaluation of the cyclic stability of MPCMs, appropriate MPCMs can be selected for oilfield applications such as drilling fluids and optimize their usage strategies to achieve optimal performance and economic benefits.

4.5 Health, safety, and environment standards of MPCMs

When selecting and preparing MPCMs, it is important to consider their environmental impact throughout their lifecycle. Organic PCMs, such as paraffin wax and fatty acids, may release volatile organic compounds at high temperatures, posing a health risk. Inorganic salts are generally chemically stable and non-toxic; however, certain salts, such as magnesium chloride and magnesium nitrate, are corrosive, while barium hydroxide is corrosive to the respiratory system, eyes, and skin and is considered a moderate hazard (Nartowska et al., 2023). Therefore, strict sealing designs and emergency handling measures are necessary. During microcapsule preparation, solvents such as methylene chloride and acetone can volatilize, potentially affecting the health of workers (Satturwar et al., 2002). In the future, the use of renewable or bio-based materials and the development of degradable shell materials will help mitigate the environmental impact.

5. Emerging oilfield application of MPCMs

In the oilfield, effective thermal management is crucial for ensuring the efficiency and safety of various operations. Temperature fluctuations can significantly impact the performance of drilling fluids, equipment longevity, and the overall productivity of extraction processes. Traditionally, managing these temperatures has relied on conventional methods (e.g., drilling fluid ground cooling system) that may not always provide the desired efficiency. Therefore, recent advancements have introduced MPCMs with the capability to revolutionize thermal management practices. MPCMs are demonstrating significant emerging potential in oilfields, primarily due to their unique properties in downhole cooling capacity and precise temperature regulation. These characteristics enable more efficient temperature management, which is critical for optimizing processes and enhancing the overall performance of oilfield operations. Particularly, MPCMs have potential applications in many oilfield areas, including the temperature regulation of drilling fluids, thermal management of cement slurry, thermal protection of downhole electronics, and thermal insulation of submarine oil and gas pipelines (Table S1).

5.1 Drilling fluids

Drilling is a critical component of the oil and gas industry, serving as the primary method for extracting hydrocarbons from beneath the Earth's surface. Drilling fluids, often referred to as the "blood" of drilling, are complex fluid systems composed of various chemicals and additives (Li et al., 2021). These fluids can be categorized into water-based, oil-based, and synthetic-based drilling fluids, depending on different dispersion phases (Liu et al., 2023, 2024). Each type of drilling fluid has unique properties suited to specific scenarios. The main functions of drilling fluids include cooling and lubricating the drill bit to reduce wear and extend its lifespan, carrying rock cuttings to the surface to keep the bottom of the well clean, maintaining the stability of the wellbore wall to prevent collapse, controlling the formation pressure to prevent blowouts or leaks, and providing information about the formation.

The good compatibility between MPCMs and drilling fluids, as well as the prevention of leakage, are prerequisites for the application of MPCMs. Therefore, the encapsulation of PCMs have been extensively conducted, producing a wide spectrum of MPCMs. Various PCMs, e.g., paraffin wax and certain salts, are used as the core, and polymers, silica, and expanded graphite are employed as the shells for different reservoir applications. In particular, for drilling the natural gas hydrate reservoirs, MPCMs can impart temperature stability, leading to the prevention of the dissociation and formation of natural gas hydrates, thereby maintaining the stability of the wellbore. For drilling the deep oil and gas reservoirs, MPCMs can help remove heat from the bottom of the well through the circulation of drilling fluids, reducing the wellbore temperature and preventing high-temperature failure of the drilling fluid and downhole instruments. Therefore, due to their unique thermophysical properties and multifunctionality, the application of MPCMs in drilling fluids has attracted significant attention. Their integration provides tailored solutions to the temperature fluctuation challenges in different reservoirs, leading to their wider application in the oil and gas industry. Table S1 presents the recent application of MPCMs in drilling fluids.

5.1.1 Natural gas hydrate reservoirs

Natural gas hydrates are cage crystalline compounds formed by water and natural gas molecules (mostly methane) at specific temperatures, pressures, and other conditions. They are widely distributed in permafrost soil layers and seabed deposits. Recent estimates suggest that the resource volume of marine natural gas hydrates is approximately 2×10^{16} m^3, while that of permafrost areas is about 7.4×10^{14} m^3. Natural gas hydrates, in contrast to traditional fossil energy, are solid substances typically found on the sea floor under conditions of high pressure (over 10 MPa) and low temperatures (2-20 °C), whereas the depth of deposition in the permafrost is relatively shallow (100-600 m). Low-temperature, low-pressure environments in shallow water layers are conductive to the formation of gas hydrates. A key characteristic of gas hydrates is their tendency to undergo thermal degradation.

Although gas hydrates are a potential energy source, preventing hydrate decomposition and reforming, as well as maintaining wellbore stability are key technical challenges during the drilling of gas hydrate reservoirs. In gas hydrate drilling, the drilling fluid is in direct contact with the hydrate reservoir, resulting in the impact of phase of gas hydrates. The temperature, liquid column pressure, and chemical properties of the drilling fluid are decisive factors to maintain the stability of the hydrate. Conventional drilling fluids often lack the ability to effectively control downhole temperature, resulting in hydrate instability during drilling, which can lead to wellbore collapse and fluid blockage (Sun et al., 2024a). By mixing MPCMs with drilling fluid, intelligent temperature control during drilling can be achieved, thus inhibiting the decomposition and regeneration of hydrate, and enhancing the thermal stability and rheological properties of drilling fluid.

For instance, Zhao et al. (2023b) successfully prepared a new type of MPCMs using an in situ polymerization method, with dodecane as the core substance and melamine-urea-formaldehyde resin as the shell material. The phase transition temperature of MPCMs is 6.7 °C, the latent heat is 116 kJ/kg, and the particle size is concentrated in the range of 0.7-10 μm. In the simulation experiment, the addition of 10 wt% MPCMs reduced the drilling fluid temperature by 5.4 °C (Fig. 5(a)). Through the calculation and analysis of a thermal fluid-solid coupling numerical model, it was found that adding 5%, 8% and 10% MPCMs by weight to drilling fluid significantly reduced the well wall expansion rate, reaching reductions of 23.51%, 51.57% and 89.72%, respectively (Fig. S6). In addition, the temperature regulation performance of the MPCMs remained stable even after 15 heating/cooling cycles, showing good cycle stability.

The use of melamine-urea-formaldehyde resin as the shell material, although providing good protection, may have limitations in terms of thermal conductivity. Compared with melamine-urea-formaldehyde resin material, inorganic materials exhibit higher thermal conductivity. Zhang et al. (2021) prepared nano-silica/modified n-paraffin microcapsules by interfacial polymerization using modified n-paraffin as the core material and nano-silica as the shell material. The median particle size of microcapsules is 10.34 μm, with most particles distributed in the range of 5.32   28.05 μm, which meets the requirements for offshore drilling recovery screening (i.e., 106 μm). The melting temperature is 14.06 °C, the latent heat is 136.8±2.0 kJ/kg, and the encapsulation rate and encapsulation efficiency are 63.3±0.9% and 62.6±0.8%, respectively. In a simulated hydrate temperature experiment, the temperature of the solution with 5 wt% MPCMs decreased by 1.8 °C compared to the pure solution (Fig. S7). To further enhance the latent heat value and thermal conductivity of MPCMs, Zhang

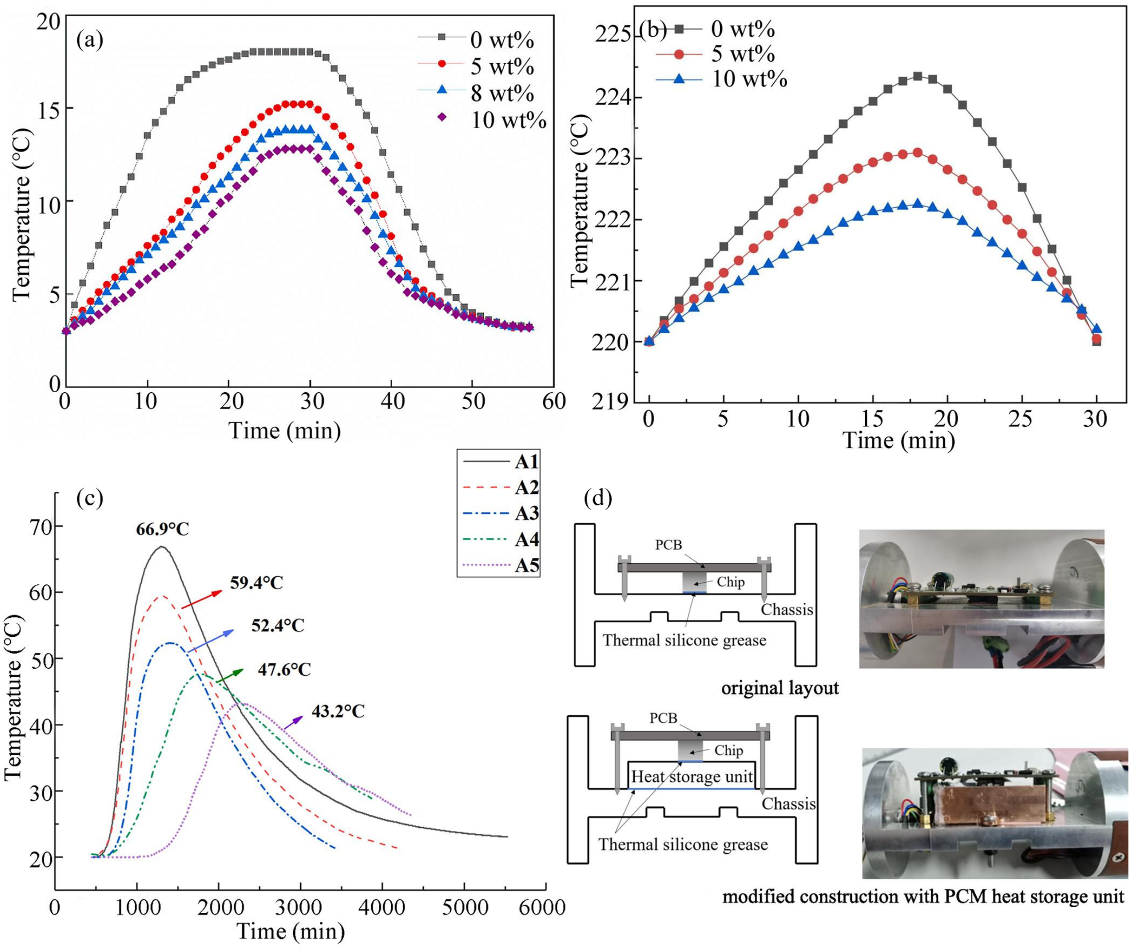

Fig. 5. Application of MPCMs in different oilfields: (a) Drilling fluid for natural gas hydrate reservoir (Zhao et al., 2023b), (b) drilling fluid for deep oil reservoir (Guo et al., 2024b), (c) oilwell cement slurry (Bu et al., 2021), and (d) drilling equipment (He et al., 2022).

et al. employed nano-silicon and nano copper (nano-Cu) as shells and mixed alkanes as cores. The results showed that the phase transition temperature of the composite MPCMs is 16.43 °C, the latent heat is 163.3 kJ/kg, and the particle size is concentrated in 20.32 μm. Once the phase transition temperature is reached, the composite MPCM solution can effectively control the temperature. Adding 5 wt% of MPCMs reduced the maximum temperature by 2.12 °C, while adding 10 wt% of composite MPCMs delayed the decomposition time of hydrate and reduced the average decomposition rate by about 34% (Zhang et al., 2022b).

The MPCMs mentioned above were primarily prepared using in situ polymerization and interfacial polymerization methods, which have been shown to effectively produce microcapsules with robust shells and controlled release characteristics. However, these methods often involve complex procedures, require specific chemical reagents, and may face limitations in scalability. In contrast to in situ and interfacial polymerization, Guo et al. (2024a) used a new method of electrostatic spraying and physical crosslinking to prepare MPCMs. The MPCMs prepared through this method utilize n-tetradecane and n-hexadecane as the core materials and sodium alginate as the shell material. Experimental measurements reveal that the phase change temperature of the MPCMs is 13.72 °C, with a latent heat value of 161.63 kJ/kg and a thermal conductivity of 0.38 W/(m·°C). In hydrate decomposition experiments, the suspension containing 8 wt% MPCMs was found to reduce the decomposition rate of natural gas hydrate (NGH) by 15.25% (Fig. S8), with the inhibitory effect on hydrate decomposition increasing as the MPCM concentration increases.

Although MPCMs have demonstrated the ability to effectively inhibit hydrate decomposition and enhance wellbore stability when incorporated into natural gas hydrate drilling fluids, several challenges remain in their practical application. First, the high cost of MPCMs poses a significant barrier to their widespread adoption in large-scale applications. Moreover, traditional organic PCMs, such as paraffin wax, suffer from low thermal conductivity, which restricts their efficiency in rapid energy storage and release, a critical factor in dynamic drilling environments. Second, the performance and effectiveness of MPCMs are highly dependent on the chosen preparation method, each of which comes with its own set of advantages and drawbacks. For example, interfacial and in situ polymerization can produce MPCMs with optimal shape and size distributions, leading to improved latent heat, thermal efficiency and consistency. However, this method requires precise process control and involves complex chemical reactions, which may pose challenges for large-scale production. In contrast, spray drying is a relatively straightforward and scalable method. However, this method often results in MPCMs with larger particle sizes. These larger particles are more prone to thermal degradation, negatively impacting their thermal properties and stability. Therefore, future research should focus on developing cost-effective MPCM formulations, improving the thermal conductivity of organic PCMs through composite or hybrid materials, and optimizing synthesis methods to balance performance, scalability, and cost.

5.1.2 Deep oil reservoirs

As shallow reservoirs are increasingly depleted, exploration and production activities are shifting toward deep oil reservoirs. The temperature of these deep reservoirs typically exceeds 150 °C. Excessively high bottom hole temperatures often lead to drilling fluid failure, downhole tool malfunctions, and various other issues, increasing the frequency of lifting up drilling pipes and reducing drilling efficiency (Sun et al., 2024b). Therefore, reducing the high temperature of wellbore during the drilling process has always been one of the key technical challenges in the deep oil and gas development. MPCMs can store energy through phase transition when entering the high temperature reservoirs and release it during circulation to the surface, achieving intelligent temperature control of drilling fluids.

For example, Monteiro et al. (2012) investigated the application of solid-liquid PCMs in drilling fluids through experiments and mathematical modeling to reduce the temperature of circulating fluids in the wellbore. A variety of PCMs, including cholesterol stearate and zinc stearate, as well as other organics such as waxes and thermoplastic polymers, were measured. The experimental results showed that the addition of PCMs significantly reduced the temperature of drilling fluid in the bottom hole assembly. When a wax with a melting point of 90 °C and a latent heat of 300 kJ/kg was used as PCMs, the addition of 5% and 10% wax reduced the temperatures by 2.5 °C and 5.5 °C, respectively. The research conducted by Zhang et al. (2023b) building upon the foundational work of Monteiro, developed an advanced computational model to analyze the temperature field of drilling fluids incorporating MPCMs (Zhang et al., 2023b). This model was applied to evaluate the cooling performance of MPCMs in drilling fluids for ultra-deep and high-temperature wells. The MPCM studied exhibited a phase transition temperature range of 120-130 °C and a latent heat of 264.15-265.53 kJ/kg. The results showed that the addition of 12% MPCMs had the best cooling effect, reducing the bottom hole temperature by 12.3 °C and extending the horizontal section by 700 m (Fig. S9).In a more recent study, Guo et al. (2024b) prepared MPCMs through sol-gel interfacial polymerization, using binary eutectic nitrate as the core material and SiO_2 as the shell material. The as-prepared MPCMs exhibited a phase transition temperature of up to 225.43 °C (Fig. S10) and average particle size of 7.79 μm. The experiment showed that MPCMs still maintained good compatibility with drilling fluid at high temperatures. After 50 cycles, MPCMs still possessed an enthalpy retention rate of up to 96.7% (Fig. S11). Additionally, the presence of 10 wt% MPCMs reduced the maximum temperature of drilling fluid by 2.1 °C (Fig. 5(b)) (Guo et al., 2024b).

It is worth noting that debris during drilling may damage the microcapsule shells. Therefore, it is essential to produce mechanically robust shells. The mechanical properties of the shell material can also be optimized by introducing wear-resistant materials and self-healing functional polymers. For example, adding nanoparticles such as Al_2O_3, CuO, ZnO, TiO_2, SiO_2, ZrO_2 can improve the wear performance of polymer shell materials (Shi et al., 2019). White et al. (2001) encapsulated cyclopentadiene in urea-formaldehyde resin . The addition of cyclopentadiene microcapsules and catalysts enhanced the toughness of the epoxy, enabling it to exhibit good self-healing properties. In addition, the addition of MPCMs to drilling fluids may affect the rotational speed of the drill bit due to changes in fluid viscosity and flow characteristics. Dutkowski and Fiuk (2018) reported that as the mass fraction of MPCMs increased from 10% to 90%, the shear rate rose from 0.0132 to 132.00 s^{-1}. Moreover, the dynamic viscosity of the aqueous slurry increased with the rising concentration of MPCMs, with only 10% MPCM slurry exhibiting Newtonian behavior. Zhang and Zhao (2011) further indicated that larger MPCM particles result in higher slurry viscosity. High viscosity, in turn, increases the flow resistance of the drilling fluid, reduces the rotational speed of the drill bit, and consequently leads to higher energy consumption and decreased drilling efficiency.

Overall, the application of MPCMs in deep oil reservoirs remains limited, potentially due to the high temperatures of deep oil reservoirs and the low latent heat of conventional MPCMs. The high-temperature formation conditions necessitate MPCMs with appropriately high phase transition temperatures to effectively manage heat. Many conventional MPCMs are also unable to maintain stability at such high temperatures, leading to thermal degradation or loss of functionality. Finding materials that can both withstand these extreme conditions and perform reliably during phase transitions remains a significant challenge. Additionally, the latent heat of MPCMs determines its capacity to store and release thermal energy during phase transitions. Conventional MPCMs typically have low latent heat values, limiting their ability to absorb and release sufficient energy to manage the thermal loads encountered in deep reservoirs. This limitation is particularly problematic in ultra-deep wells, where efficient heat absorption and dissipation are critical to maintaining wellbore stability and preventing thermal damage to drilling fluids and tools. To overcome these challenges, research should focus on developing composite or hybrid MPCMs with enhanced thermal stability and latent heat capacity.

5.2 Oilwell cement slurry

In oil well cementing, temperature management of cement slurry is vital for proper thickening, operational efficiency, and long-term wellbore stability. Traditional cement generates significant heat during hydration, raising formation temperatures and affecting well stability. This is especially problematic in permafrost or gas hydrate zones, where excessive temperatures can destabilize formations, leading to severe geological consequences. For example, cement slurry in deepwater wells can reach over 60 °C during hydration, causing hydrate decomposition. Minor decomposition may lead to wellbore instability, while extensive decomposition can cause well blowouts and formation. To address this, researchers have explored methods to regulate cement slurry temperature, including the use of supplementary cementitious materials and PCMs. Table S1 summarizes the recent applications of MPCMs in oil well cement slurry.

For instance, Huo et al. utilized an *in-situ* polymerization method to fabricate MPCMs with a urea-formaldehyde resin shell and a paraffin core. The melting point was determined to be 35.85 °C, with a latent heat value of 85.69 kJ/kg and an average particle size of 5.74 μm (Fig. S12). After 100 thermal cycles, there was no significant change in the melting point and latent heat, demonstrating excellent thermal reliability. Additionally, the incorporation of inorganic materials such as slag and fly ash effectively reduced the heat released during the cement hydration process. Compared to the pure cement samples, the maximum temperature and temperature rise were reduced by 35.9 °C and 36.0 °C, respectively (Huo et al., 2019). Although alkali-activated materials such as fly ash and slag, which partially replace cement particles, reduced heat release, the presence of resin-coated MPCMs and alkali-activated materials significantly lowered the initial strength of the cement sheath, posing a risk to the stability of the wellbore structure (Sun et al., 2022). In addition, Liu et al. investigated polymethyl methacrylate as a shell to encapsulate paraffin, creating MPCMs for phase change thermal energy storage, and studied the effects of these MPCMs on the well cementing slurry system (Liu et al., 2017). MPCMs with a particle size of 200-250 μm exhibited high encapsulating efficiency and exceptional thermal energy retention, maintaining stability up to 120 °C. Incorporating 5-10 wt% of these MPCMs significantly mitigated heat dissipation during hydration.

The majority of MPCM research has focused on organic polymers as shell materials, but these polymer shells have certain limitations, such as poor thermal conductivity, inferior mechanical properties, and poor compatibility with cement slurries. Bu et al. (2021) explored a novel MPCM using high-strength hollow microspheres derived from metakaolin. The inclusion of up to 20% MPCMs did not adversely affect the strength and other fundamental properties of the cement, such as density, sedimentation stability, and rheological performance. The addition of 30% MPCMs lowered the peak temperature of conventional cement by 23.7 °C (Fig. 5(c)). However, the MPCMs were prone to leakage, requiring further encapsulation with resin.

SiO_2, as a promising inorganic material, has good mechanical properties, superior thermal conductivity, and excellent leakage resistance. Feng et al. (2022) prepared MPCMs with silica as shell material and paraffin as core material for cementing operations in deepwater natural gas hydrate reservoirs. The phase change temperature of the MPCMs is 30.52 °C, the enthalpy is 72.4 kJ/kg, and the encapsulation rate is 66.4%. Experimental tests showed that the maximum temperature of cement slurry was reduced by 4.5 °C after adding 6% MPCMs to cement slurry, while the early strength of cement slurry was improved. Binary core materials offer more sensitive hydration heat control than a single core material, and binary or multi-component MPCMs have been investigated extensively to absorb heat and store energy (Liao et al., 2023). Cai et al. (2023) prepared MPCMs with a shell of silica and a core of decanoic acid and dodecanol through interfacial polymerization. The MPCMs have a phase change temperature of 24.31 °C and a latent heat value of 150.64 kJ/kg, with a microsphere diameter of 200 nm (Fig. S13). Yang et al. (2024) synthesized MPCMs with a $BaCO_3$ shell and a core of low-melting point binary PCM using a self-assembly method. The results confirmed that the MPCMs have two phase change temperature points, 3.5 °C and 13.9 °C, effectively reducing the hydration heat in the cement slurry, thereby reducing the disturbance to the stability of the natural gas hydrate layer. In addition, the influence of cement slurry hydration heat on the stability of natural gas hydrates was directly analyzed through a laboratory simulation device, providing theoretical guidance and experimental data for the application of cement slurry in natural gas hydrate layers (Fig. S14).

At present, the application of MPCMs in cementing cement still faces several challenges. Although studies have shown that the thermal behavior of cement slurry during cementing can be effectively controlled by encapsulating PCMs in different shell materials, in complex environments, the cement grout may set prematurely, which can not only lead to blockages during pumping, but can also negatively affect the pore structure within the cement sheath. In addition, research on deep, high-temperature wells is relatively insufficient, which limits the application potential of phase change microspheres under these conditions. Further research and technical development are needed to realize their wide widespread use in complex environments, such as deep and high-temperature wells.

5.3 Drilling equipment

In the process of unconventional energy development, such as ultra-deep oil and gas exploration, the extremely high temperatures pose severe challenge to drilling equipment, as well. To meet the diverse functional demands of downhole equipment, a large number of heat-sensitive electronic components must be integrated, ensuring they can operate stably in harsh underground environments under high temperatures. Consequently, the use of passive cooling technology containing PCMs have become an effective mean to maintain the electronic components within a safe operating temperature range.

The use of PCM-filled thermal storage units for internal thermal management has attracted considerable interest. This PCM-based strategy not only effectively controls internal heat generation but also releases heat during equipment rest periods, significantly enhancing stability and reliability in extreme environments. A well-designed PCM unit can precisely control the internal thermal flow of electronic equipment, ensuring it remains within a safe operating temperature range even under prolonged high-temperature conditions. He et al. (2022) evaluated the performance of pulse power supplies using paraffin and Low Melting Point Alloys (LMTA) as PCMs (Fig. 5(d)). The study found that paraffin wax had a higher latent heat value than LMTA, but its thermal conductivity was only 0.2 W/(m·K), while the thermal conductivity of LMTA-1 was 26.1 W/(m·K) and that of LMTA-2 was 20.1 W/(m·K) (Fig. S15). Fig. S16, S17 showed the temperature transient changes of different PCMs under vertical and horizontal layout. Compared with paraffin wax, both LMTA showed a longer flat region above their melting point, significantly reducing the temperature rise trend of the chip. As a result, the safe working time was extended by more than 1.5 times. To address the thermal management issue of high-power downhole electronic equipment used in oil and gas exploration under high-temperature environments, Peng et al. proposed a thermal management method combining liquid cooling with PCMs, and validated its effectiveness through numerical simulation. The results showed that compared with traditional thermal management, the heat source heating rate of the new method is only 1.8 °C/ h, much lower than the conventional 11.9 °C/ h, the final temperature of the heat source is 29 °C lower than the traditional thermal management, and the average equivalent thermal resistance is reduced from 0.76 °C/W to 0.25 °C/W, the utilization rate of PCMs increased from 73.5% to 75.4% (Peng et al., 2022).

However, effective integration of PCM-based thermal management systems with existing electronic equipment, especially in high-temperature environments like downhole applications, poses technical challenges. Ensuring compatibility with liquid cooling systems, minimizing energy losses, and maintaining the long-term reliability of PCM units in these harsh environments require further optimization and fine-tuning of both the PCM material and system design. Future designs could incorporate multi-layered or modular PCM units, combining PCMs with high latent heat and thermal conductivity enhancements to optimize both heat storage and dissipation.

5.4 Submarine oil and gas pipelines

During the extraction and transportation of deep-sea natural gas, the formation and deposition of natural gas hydrates (NGH) have become significant bottlenecks, restricting efficient development. Due to the low-temperature and high-pressure conditions of the deep-sea environment, natural gas hydrates are highly prone to formation and deposition in submarine pipelines, leading to flow obstruction and equipment damage. Currently, the industry primarily mitigates NGH formation by injecting hydrate inhibitors. However, the processing and separation costs of these inhibitors are high. The application of PCMs for thermal insulation in submarine pipelines offers a promising solution by effectively reducing heat exchange between the fluid and the surrounding environment. This approach helps maintain the fluid temperature above the critical threshold for hydrate formation, thereby preventing NGH generation.

Wang et al. (2023) investigated the effects of PCM content on the thermal storage performance, effective thermal conductivity, and insulation capacity of PU-PCM composites through experimental studies and numerical simulations. PU-PCM was prepared by embedding PCMs into a polyurethane (PU) matrix, which is applied to insulate subsea oil and gas pipelines and prevent hydrate blockages. The relative effective enthalpy coefficients of the prepared PU-MPCM composites exceeded 80%. Notably, PU-PCM24, with a melting enthalpy of 35.95 kJ/kg and an effective thermal conductivity as low as 0.16 W/(m·K), increases heat preservation time by 229.79% compared to pure PU.

However, the phase change temperature, latent heat, and thermal conductivity of microcapsules often struggle to meet the complex working conditions of the seabed. Additionally, the corrosive nature of seawater and the high pressures of deep-sea environments severely affect their structure and performance. Long-term stability is another concern, as repeated phase change cycles and aging can gradually deteriorate performance. In the future, research should focus on developing novel PCMs and optimizing their preparation processes. Further in-depth studies are needed to understand their behavior in complex seabed environments, enhance environmental adaptability, and improve long-term stability. Overcoming these application bottlenecks will promote the widespread use of PCMs for submarine pipeline insulation, supporting the steady growth of the marine oil and gas industry.

6. Conclusions

In this article, the current status and future development trends of MPCMs in oilfield applications are reviewed. The main conclusions are outlined as follows:

1) Solid-liquid and solid-solid PCMs are the most widely studied, offering stable phase transitions and minimal leakage risks. Techniques such as interfacial polymerization, sol-gel, and spray drying effectively mitigate PCM leakage risks while improving their compatibility with oilfield applications. However, challenges such as high costs, particle uniformity, and precise control of particle size remain, necessitating further optimization of encapsulation technology.
2) Key thermophysical properties of MPCMs include phase change temperature, latent heat, thermal conductivity, and cyclic stability. The required properties vary depending on reservoir conditions, and selecting appropriate thermophysical characteristics is crucial for effective thermal management. Characterization techniques such as differential scanning calorimetry and laser flash analysis can be employed to evaluate MPCM suitability.
3) Existing research highlights the significant potential of MPCMs in the oilfield sector. In drilling fluids, their heat storage and release properties enable intelligent temperature control. In natural gas hydrate layers, MPCMs with low phase change temperatures (6-16 °C) can reduce hydrate decomposition risks; while in high-temperature deep reservoirs, MPCMs with high phase change temperatures (120-225 °C) can lower bottom-hole temperatures

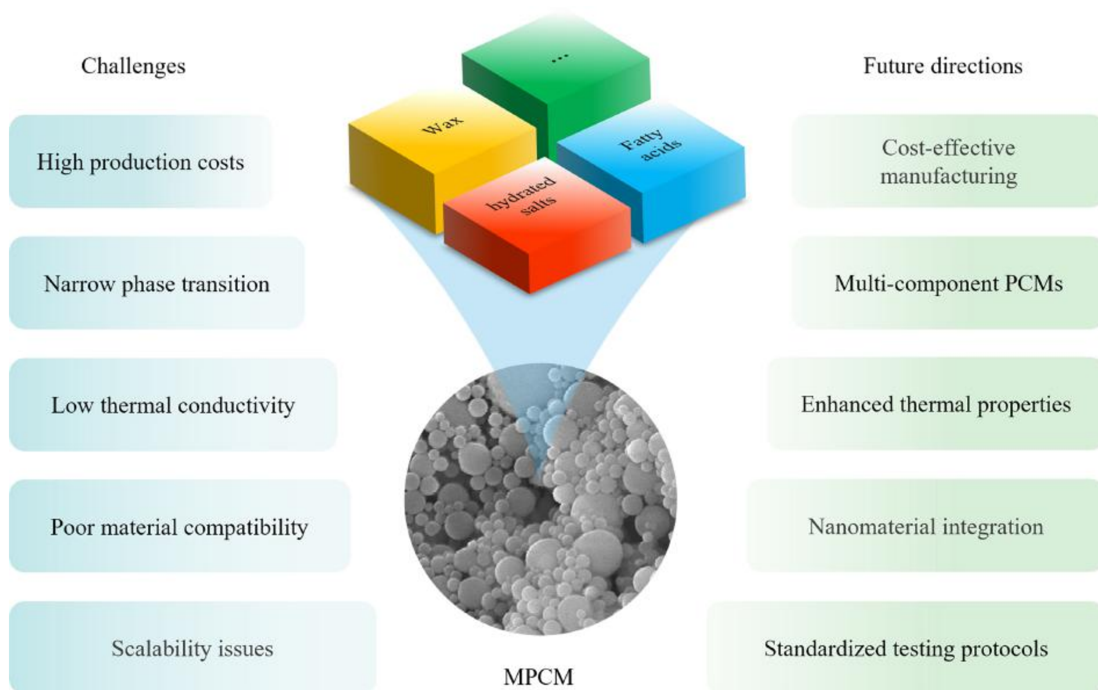

Fig. 6. Challenges and future directions of MPCMs in oilfield applications.

by 2-12 °C. Incorporating MPCMs into cement slurry can reduce the hydration heat peak by 4-36°C. For high-temperature drilling equipment, low-melting-temperature alloys as PCMs with high thermal conductivity can extend the lifespan of electronic components by 1.5 times. In subsea pipelines, PCM-PU composite materials can enhance thermal insulation duration by up to 230%.

7. Challenges and future perspectives

Despite significant advancements in oilfield applications, the large-scale adoption of MPCMs remains hindered by both economic and technical challenges (Fig. 6). Overcoming these barriers is crucial for integrating MPCM-based thermal management solutions into routine oilfield operations and ensuring their feasibility across different oilfield sizes and production stages. The key challenges are outlined as follows:

1) The use of high-purity raw materials, complex microencapsulation techniques, and multi-step chemical synthesis processes significantly drive up production costs, making MPCM-based solutions considerably more expensive than traditional thermal management methods. Existing encapsulation techniques, such as interfacial polymerization and sol-gel processes, are often slow, energy-intensive, and unsuitable for continuous large-scale production. Additionally, ensuring uniform particle size, shell stability, and high encapsulation efficiency remains challenging.
2) MPCMs face several inherent thermal performance challenges, including a narrow phase transition range, low latent heat, and poor thermal conductivity. Expanding the phase transition range and increasing latent heat capacity are essential for improving the adaptability and efficiency of MPCMs in oilfield thermal management. Additionally, enhancing thermal conductivity through nano-additives (e.g., carbon nanotubes, graphene, and boron nitride) can improve heat transfer efficiency.
3) The incorporation of MPCMs into drilling fluids and cement slurries presents significant challenges related to rheology, stability, and overall performance. PCMs must not negatively impact critical drilling fluid properties such as viscosity, filtration behavior, and thermal stability, nor should they interfere with cement slurry setting time, compressive strength, or long-term durability. Currently, there is a lack of standardized protocols for assessing MPCM compatibility with oilfield fluids, making it difficult to ensure consistent performance under varying field conditions.

To address these challenges, the following future directions are proposed:

1) Future research should focus on cost-effective and scalable MPCM manufacturing. Developing continuous large-scale manufacturing using spray-assisted techniques can improve production efficiency while maintaining the uniformity and stability of MPCMs.
2) Expanding the phase transition temperature range through the design of multi-component or eutectic PCMs can improve adaptability across different reservoir conditions, from gas hydrate layers to high-temperature deep wells. Increasing latent heat storage capacity through molecular modifications and hybrid composite structures can further enhance heat storage efficiency. Improving thermal conductivity by incorporating high-conductivity nanomaterials, such as graphene, carbon nanotubes, boron nitride,

and metal nanoparticles, is essential for effective heat transfer.

3) Maintaining an appropriate particle size and surface chemistry is important to prevent adverse effects on drilling performance. Functional coatings on MPCMs could prevent chemical interference with cement hydration reactions. Standardizing MPCM compatibility testing and formulation design through industry-wide protocols will help ensure reliable performance across various oilfield conditions.

Overall, by addressing these research directions, MPCM technology can transition from laboratory-scale development to widespread industrial implementation, providing efficient and sustainable thermal management solutions for the oil and gas industry.

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Supplementary file

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Conflict of interest

The authors declare no competing interest.

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