International Journal Of Engineering Research And Development
e- ISSN: 2278-067X, p-ISSN: 2278-800X, www.ijerd.com
Volume 21, Issue 4 (April 2025), PP 268-274

Review of Technical Research on Long-acting Hyperosmotic Sealing Fluid for High Permeability Channels in Hydrogel Layer Openhole Sections

Yuchen Wang[1,2,3,*](王雨晨) Sui Jin [1,2,3,*](金穗) Bo Sun[1,2,3](孙波)
Xinyang Wei[1,2,3](魏鑫漾) NasiWang[1,2,3](王娜斯)

[1] *Cooperative Innovation Center of Unconventional Oil and Gas, Yangtze University, Wuhan 430100, China*
[2] *Hubei Key Laboratory of Oil and Gas Drilling and Production Engineering, Yangtze University, Wuhan 430100, China*
[3] *National Engineering Research Center for Oil & Gas Drilling and Completion Technology, School of Petroleum Engineering, Yangtze University, Wuhan 430100, China*

Abstract: *This review summarizes the advancements in long-term sealing fluid technology for high-permeability channels in uncased sections of hydrate layers, focusing on three key technologies: microcapsule solid acid, sodium alginate microcapsules, and high-permeability cement. China has abundant natural gas hydrate resources, but ensuring the stability of high-permeability channels in the uncased section during extraction is a critical challenge. Microcapsule solid acid technology, prepared through interfacial polymerization and in-situ polymerization methods, offers slow-release acid and improved acidizing efficiency, though issues with wall material mechanical strength and large-scale production need addressing. Sodium alginate microcapsules, known for their natural polysaccharide properties and mild gelation ability, excel in drug release and material encapsulation, but require optimized preparation processes to enhance mechanical strength. High-permeability cement, designed with pore structures via foaming and pore-forming agent methods, combines high permeability and mechanical strength, suitable for applications such as oil and gas well cementing. Experiments show that adding aluminum powder and silicon powder significantly increases the compressive strength and elastic modulus of the cement. Future research should further optimize the controlled release performance of microcapsules and the pore structure design of high-permeability cement to advance the industrial application of natural gas hydrate extraction technology.*

Key words: *microcapsule solid acid；sodium alginate；high-strength cement; compressive strength; porous structure*

Date of Submission: 13-04-2025 Date of acceptance: 28-04-2025

I. Introduction

China has enormous potential for natural gas hydrate resources, primarily concentrated in the South China Sea and the permafrost areas of the Qinghai-Tibet Plateau. Areas such as the Shenhu region and the Pearl River Mouth Basin in the South China Sea have resource quantities estimated at around 800 billion tons of oil equivalent. In recent years, China has made significant breakthroughs in the exploration and development of natural gas hydrates. In 2017, China became the first globally to achieve test production from mudstone and fine sand reservoirs. By 2020, during the second round of test production, daily gas output reached 28,700 cubic meters, setting a new world record, which fully demonstrates that China has reached a leading position in this field. However, the industrial development of natural gas hydrates still faces key technological challenges, particularly in creating more efficient extraction processes. Specifically, how to effectively construct high-permeability flow channels in the uncased wellbore section of natural gas hydrate reservoirs is a critical issue that needs to be addressed. Therefore, in-depth research on the destruction process and long-term stability of high-permeability channels in hydrate layers is required.

1. Microcapsule solid acid

1.1 The principle of solid acid acidification of microcapsules

The acid liquid technology of encapsulating solid acid involves first wrapping the solid acid with specific materials and then injecting it into the opened fractures with water-based liquid. When the microcapsules are immersed in the aqueous solution, the external water will penetrate into the interior of the microcapsules through

the tiny channels on the coating, dissolving the solid acid into a solution. Subsequently, hydrogen ions will diffuse outward along the water-filled microchannels, thereby being released from the microcapsules. According to Fick's diffusion law, the thicker the coating of the microcapsules, the slower the diffusion rate of hydrogen ions and the longer the delayed release time; while when the temperature rises, the diffusion rate increases and the delayed release time shortens.

1.2 Research progress of microcapsule solid acids

In recent years, significant achievements have been made in the research of microcapsule solid acids, with major breakthroughs in preparation techniques, performance improvement, and expansion of application scope. In terms of preparation methods, technologies such as interfacial polymerization, in-situ polymerization, and sol-gel have been continuously optimized.

In practical applications, microcapsule solid acids have been successfully applied in fields such as organic synthesis catalysis, biodiesel production, slow-release fertilizers, and self-healing materials. Currently, research efforts are mainly focused on overcoming the challenges of insufficient mechanical strength of the wall material, acid leakage, and high production costs during large-scale manufacturing, while also exploring the design concepts and preparation methods of stimulus-responsive microcapsule systems.

1.2.1 Microcapsules by interfacial polymerization method

Interfacial polymerization is an efficient and controllable technique for preparing microcapsules. The principle is that in the reaction system, both immiscible phases contain reactive monomers, but the generated polymer is insoluble in both phases. Therefore, the reaction occurs at the interface between the two phases. As the reaction proceeds, different reactive monomers in the two phases move towards the interface, eventually completely encapsulating the dispersed phase to form phase-change microcapsules[1]. This method has many advantages. On the one hand, the reaction conditions are mild and can be carried out at room temperature, and the resulting polymer has a high molecular weight. The purity and ratio of the monomers are not strictly required and are not the key factors for the molecular weight of the polymer. Moreover, no extraction or devolatilization processes are needed, and the condensation reaction can be made irreversible. However, it also has certain disadvantages. Often, some monomers cannot participate in the film-forming reaction and remain in the microcapsules. Therefore, when preparing water-containing microcapsules, non-toxic ethylene glycol or glycerol is usually added as a film-forming monomer to play a corresponding role and can also act as a water retarding agent to inhibit water activity [2]. This method plays an important role in the preparation of microcapsule solid acids.

1.2.2 Microcapsules by in-situ polymerization

In-situ polymerization refers to a process where monomers or monomers along with catalysts are provided to form oligomers or initial condensation polymers, and then under specific conditions, a condensation reaction takes place on the surface of the core material to achieve the preparation of microcapsules[3]. The difference is that in interfacial polymerization, the reaction of wall material monomers occurs at the interface of two phases, while in in-situ polymerization, the wall material monomers and catalysts are dissolved in the same phase, and the polymerization reaction also takes place within this phase, with the resulting wall material polymer being insoluble in the entire reaction system. During the in-situ polymerization reaction, the molecular weight of the pre-polymer continuously increases, the molecular[4] chains keep elongating, and they continuously aggregate and precipitate on the surface of the core. Then, through cross-linking and curing, a capsule membrane is formed to completely enclose the core, ultimately successfully preparing microcapsules. In-situ polymerization can be further classified into three types: chemical polymerization, thermal polymerization, and photo-induced polymerization[5][6][7]. Regardless of the specific method used in in-situ polymerization, the basic principle of the reaction is based on the principle of three-dimensional condensation polymerization. The first step is to allow the raw material monomers to react under the action of various catalysts until a certain extent is reached, thereby generating reactive macromolecular linear and branched oligomers. The second step is to promote the continuous reaction of the potential, unreacted functional groups or double bonds in the oligomers, ultimately forming three-dimensional structured high polymers. Using epoxy resin and benzyl alcohol as the core material and styrene-divinylbenzene as the capsule wall, microcapsules with self-healing function were successfully prepared through in-situ polymerization. This product has shown broad application prospects in many fields such as medicine, food, textiles, coatings, and printing, and has become a new direction for the development of microcapsule technology.

1.2.3Preparation of microcapsules by sol-gel method

When preparing microcapsules of solid acid using the sol-gel method, first evenly distribute the solid acid within the sol formed by the hydrolysis of metal alkoxides such as TEOS. Then, by altering the pH value or adjusting the temperature, induce the sol to undergo polycondensation, forming a gel state where the acid particles

are encapsulated within the three-dimensional network structure. Finally, after drying and curing, porous microcapsules are obtained.

2. Sodium alginate microcapsules

2.1 The structure and properties of sodium alginate

Sodium alginate is a natural anionic polysaccharide extracted from brown algae, formed by the alternating links of the two structural units, β -D-manuronic acid (M) and α -L-guluronic acid (G), through 1, 4-glycosidic bonds. Its unique "egg box" structure can rapidly cross-link with divalent cations (such as Ca^{2+}) to form hydrogels. This biopolymer has excellent biocompatibility, degradability and mild gel formation characteristics. Its solution shows the behavior of pseudoplastic fluid, and the viscosity will increase significantly with the increase of concentration and molecular weight.

The physicochemical properties of sodium alginate are affected by the M/G ratio. Sodium alginate with a high G type can form a stronger and more stable gel, while sodium alginate with a high M type will produce a more flexible structure. Due to its excellent film-forming performance, controlled-release ability and biosafety, sodium alginate is widely used in fields such as the food industry, drug delivery, tissue engineering and microencapsulation technology.

2.2 Preparation of Sodium Alginate Composite Gel Microspheres

2.2.1 Preparation of Sodium Alginate Gel Microspheres

Sodium alginate gel microspheres are typically prepared by ionic cross-linking: Sodium alginate solution is dripped into a coagulation bath containing divalent cations (such as Ca^{2+}). Through ion exchange between Na^{+} and Ca^{2+}, sodium alginate molecular chains form a 'cage' structure, leading to immediate gelation and the formation of spherical microspheres with controllable particle size. This preparation method is convenient and simple, and parameters such as sodium alginate concentration, Ca^{2+} concentration, needle diameter, and dripping rate can be adjusted to regulate the particle size of the microspheres[8].

2.2.1.1 Ionic emulsification cross-linking method

The ionic emulsification cross-linking method involves first thoroughly mixing sodium alginate solution with specific drugs, then gradually adding it into an oil phase system containing emulsifiers to produce W/O (water-in-oil) emulsions. Subsequently, multivalent cations are added and continuous stirring is maintained until the cross-linking reaction proceeds for a certain period. After separation, drug-loaded microspheres are obtained. The key factor affecting the shape of the microspheres is the ratio of the oil phase to the water phase. Sodium alginate can cross-link with multivalent cations such as Ca^{2+} to form a 'egg-box' structure. This process occurs under mild conditions and rapidly induces gelation, making sodium alginate commonly used as a raw material for preparing drug-loaded microspheres[9].

2.2.1.2 Drip method

Currently, droplet injection is the most widely used method[10]. Typically, sodium alginate solution is injected at a constant speed into a solution containing cations using a syringe. However, due to inconsistent needle diameters and varying distances of liquid drop descent, combined with the viscosity of the sodium alginate solution, it often leads to microspheres sticking together. As a result of these factors working together, the final prepared microspheres may have different shapes.

2.2.2 Preparation of Sodium Alginate Composite Gel Microspheres

In the preparation of sodium alginate composite gel microspheres, a co-mixing and cross-linking method is typically used. First, sodium alginate is mixed with functional materials such as chitosan, gelatin, nanoclay, or carbon materials to form a composite sol. Then, using electrostatic spraying or microfluidic technology, the mixed solution is precisely droplet into a coagulation bath containing Ca^{2+}/Ba^{2+}. At this point, ion cross-linking and intermolecular interactions (hydrogen bonds, electrostatic interactions) occur simultaneously, constructing a dual-network structure[11][12].

2.3 The process of making sodium alginate composite gel beads

2.3.1 Prepare a 1% sodium alginate solution

Add 1 gram of sodium alginate powder to 99 grams of water, maintaining a temperature of 65 degrees Celsius while stirring continuously. Stir for 40 minutes until the sodium alginate powder is fully dissolved, then stop heating and let it sit until it reaches room temperature.

2.3.2 Prepare emulsion

Add 3 grams of calcium chloride to 97 grams of water and stir for 15 minutes until the calcium chloride is fully dissolved[13][14][15]. Then, take 72.2 grams of the mixture and add 27.8 grams of 30% hydrochloric acid, stirring until uniform. This forms the aqueous phase. In another step, mix 10 grams of white oil with 1 gram of Tween-80 and stir at 25° C for 100 minutes to form the oil phase. Once both phases are prepared, allow the oil phase to cool to room temperature. Mix the two phases in a 2:1 ratio (oil to water), adding 5.5 grams of the aqueous phase to 11 grams of the oil phase and stir at room temperature until a uniform and stable oil-in-water emulsion is formed.

2.3.3 Form cross-links

Use sodium alginate solution as the solvent and the emulsion as the solute. Slowly add the emulsion to the sodium alginate solution. If the emulsion cannot be fully encapsulated due to buoyancy, switch to injecting it drop by drop into the sodium alginate solution with a syringe. This allows the sodium alginate solution to encapsulate the emulsion and form cross-links.

3. High-penetration cement preparation method

High-permeability cement technology is a new type of cement-based material developed through material composition and pore structure design. Materials produced using this technology have controllable high permeability, with permeability coefficients ranging from 10^-2 to 10^-4 cm/s, while also maintaining good mechanical strength, with compressive strength between 5 and 30 MPa. This technology uses graded aggregate particle sizes, incorporates high-molecular permeability enhancers or foaming agents to create interconnected pore networks, and employs fiber reinforcement or nanomaterial modification methods to ensure structural stability. In practical applications, high-permeability cement technology is widely used in ecological slope protection projects, groundwater remediation, sponge city construction, and oil and gas well cementing processes.

3.1 Material selection

3.1.1 Cement

High-fineness cement, such as ultra-fine cement, is typically chosen because its particles are small and have a large specific surface area, which increases the contact area between cement and water, facilitating the formation of more penetration channels.

3.1.2 Surfactant

A composite of oil-soluble resins and inorganic fiber materials is commonly used as a permeability enhancer. The oil-soluble resin dissolves under the action of crude oil, forming continuous oil flow channels; the inorganic fiber material improves the connectivity of pores in cement stone, significantly enhancing its permeability.

3.1.3 Other additives

Dispersants can evenly disperse cement particles in the slurry, preventing agglomeration and improving the fluidity and permeability of the slurry. Retarders extend the setting time of the cement slurry, ensuring sufficient time for operations during construction.

3.2 Preparation process

3.2.1 Mixing ingredients

Add cement, penetrant, dispersant, retarder, and other materials in specific proportions to the mixing equipment, dry mix evenly to ensure thorough blending of all ingredients.

3.2.2 Add water and stir

Add an appropriate amount of water to the mixed dry ingredients and stir. The stirring speed and duration must be strictly controlled to ensure that the cement slurry has good uniformity and fluidity. Typically, start with low-speed stirring to initially mix the materials, followed by high-speed stirring to fully disperse and evenly distribute the slurry.

3.2.3 Molding and curing

Pour the mixed cement slurry into the mold to shape it, and then cure it under specific temperature and humidity conditions. The curing conditions significantly impact the structure and performance of the cement stone. Proper curing conditions facilitate adequate hydration reactions, forming stable pore structures and enhancing permeability.

3.3 Performance features

High permeability: This is the main feature of high-permeability cement, with its permeability adjustable within a certain range to meet different engineering requirements for cement permeability. Adequate strength: Although the addition of permeability enhancers may reduce the strength of the cement stone, by properly adjusting the formulation and preparation process, high-permeability cement can still have sufficient compressive strength to meet the basic mechanical performance requirements of some projects. Good construction performance:

The high-permeability cement slurry has good fluidity and pumpability, allowing it to smoothly pass through pipes, gaps, and other narrow spaces.

3.4 Preparation method

3.4.1 Foaming method

3.4.1.1 Foaming agent type

Currently, domestic foaming agents mainly include rosin-based foaming agents, foaming agents made from waste animal hair, resin soap foaming agents, foaming agents made from hydrolyzed blood gel, aluminum petroleum sulfonate foaming agents, as well as lignin sulfonates, protein hydrolysates, and high-molecular surfactants. Overall, the foaming agents produced in China have relatively few functions, poor stability, and the strength of the products made from them is not high. In contrast, most foaming agents in Japan and Italy are protein-based, offering better foaming ratios and stability.

3.4.1.2 The principle of foaming method

Using a foaming agent to create numerous uniform small bubbles in the cement slurry, a porous structure is formed when the cement hardens. In the specific experimental process, cement, water, and additives are first mixed into a uniform slurry, then a foaming agent solution is added and stirred to produce bubbles, which are then poured into molds for curing and shaping. The experiment shows that this method can precisely control porosity and pore size, with a uniform distribution of pores. It can produce high-porosity cement with a porosity of up to around 80%. However, improper selection and use of the foaming agent may affect the performance of the cement, and this method requires a high level of precision in the mixing process.

3.4.2 Drilling agent method

Porogen rules involve adding decomposable or soluble porogens to the cement matrix. After the cement hardens, the porogens are removed to create pores. During experiments, the porogens must be mixed and stirred with the cement, then poured and cured. The porogens are subsequently removed using methods such as heating or dissolving. This method allows for flexible control over pore shape and size, making it suitable for special pore structures. The porosity can be adjusted between 30% and 70%, making it ideal for preparing high-porosity cement with specific pore requirements. However, the removal process may cause some damage to the cement matrix, and some porogens can be expensive.

3.4.3 Fiber reinforcement method

Fiber reinforcement involves creating a three-dimensional network of fibers within the cement matrix, which prevents cement particles from clumping together and forms pores around the fibers. This method increases porosity, enhances material toughness, and improves crack resistance. Porosity can typically be increased by 10% to 30%. However, due to difficulties in controlling fiber dispersion, uneven distribution can lead to inconsistent pore distribution, affecting material performance.

3.4.4 Template method

The template method involves using a template with a specific pore structure to restrict the formation of cement slurry, resulting in high-porosity cement with a similar pore structure. This method allows precise control over pore shape, size, and distribution, enabling the preparation of materials with regular pore structures. The porosity can be determined by the template's porosity, typically ranging from 40% to 80%. Permeability is relatively high and stable, depending on the connectivity and size of the template pores. At a porosity of 70%, permeability may reach 3 to 8 darcies. However, the cost of the templates is high, and the removal process can be complex, potentially causing damage to the cement products.

It is important to note that the permeability of high-porosity cement is influenced by various factors, such as porosity, pore size distribution, and pore connectivity. In actual production, it is necessary to select appropriate methods based on specific requirements and material performance criteria, and optimize process parameters through experiments to achieve the desired high-porosity cement material.

4. Conclusion and Prospects

4.1 Conclusion

（1）Microcapsule solid acid technology enhances the stability, recyclability, and reaction controllability of solid acid catalysts by encapsulating them in high polymer or inorganic wall materials. Using sodium alginate composite gel microspheres can produce relatively complete microcapsules, but it is important to note the concentration of the sodium alginate solution and the stirring degree of the oil phase in the emulsion. During the experiment, various concentration ratios should be tried and thoroughly stirred.

（2）High-porosity cement, with its unique pore structure and properties, is widely used in fields such as

construction, environmental protection, and biomedical engineering. During preparation, factors like raw material selection, mix design, and manufacturing process significantly impact its porosity, strength, and durability. Currently, high-porosity cement faces challenges in balancing strength and porosity, as well as insufficient durability, requiring constant adjustments in water-to-cement ratio and additives to achieve suitable strength.

4.2 Prospects

（1）Microencapsulation technology is currently a key area of development. Sodium alginate microcapsules have great potential for future advancements. However, this technology still has many shortcomings, such as deficiencies in mechanical strength and limitations in controlled release. Further research based on existing literature is needed to develop microcapsules that better meet requirements.

（2）In the future, the performance of high-porosity cement is expected to be further optimized. This can be achieved by improving raw materials and processes to enhance strength while maintaining high porosity, and by developing new additives to improve the durability and water resistance of the cement.

Acknowledgements

The authors are sincerely grateful for the support of the following funds:

1.Open Foundation of Cooperative Innovation Center of Unconventional Oil and Gas, Yangtze University (Ministry of Education & Hubei Province), Grant No. UOG2024-05.

2.Hubei Province Science and Technology Plan Project (Key R&D Special Project), China, Grant No. 2023BCB070.

3. Key R&D Program Project in Xinjiang, China, Grant No.2022B01042.

4. Guiding Project of Scientific Research Program of Education Department of Hubei Province, China, Grant No. B2023024.

5. Open Fund of National Key Laboratory of Oil and Gas Reservoir Geology and Exploitation (Southwest Petroleum University), Grant No. PLN2023-03.

Author declarations

The authors have no conflicts to disclose.

Author contributions

Yuchen Wang: Conceptualization(lead); Data Curation(equal); Methodology(lead); Project Administration(lead); Writing/Original Draft Preparation(equal). Sui Jin: Data Curation(lead); Investigation (lead); Methodology(equal); Validation(lead); Writing/Review & Editing(equal). Bo Sun: Investigation(supporting); Project Administration(equal); Supervision(supporting); Visualization(supporting). Xinyang Wei: Conceptualization(supporting); Formal Analysis(supporting); Visualization(supporting). NasiWang: Data Curation(supporting); Investigation (supporting).

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

References

[1]. Shaoxian Wang, Xue Chen, Wengang Wu, et al. Experimental Study on Microcapsule Solid Nitric Acid Acidification Solution [J]. Journal of Southwest Petroleum University (Natural Science Edition), 2008, (05): 129-132+4.

[2]. Xiaoyun Zhu. Research on Phase Change Capsules Prepared by Interfacial Polymerization and Their Applications [D]. Guangdong University of Technology, 2022. DOI:10.27029/d.cnki.ggdgu.2022.001096.

[3]. Tianqiang Jiang, Hongtian Zhao, Pan Liu, et al. Advances in the application of microcapsules prepared by in-situ polymerization in functional materials [J]. Applied Chemical Industry, 2023, 52(01): 199-204. DOI: 10.16581/j.cnki.issn1671-3206.20221117.012.

[4]. Xiangchun Cai. In Vitro and In Vivo Studies on the Promotion of Osteogenic Differentiation by Sodium Alginate-Chitosan-Tannic Acid Composite Hydrogel Microspheres [D]. Nanchang University, 2023. DOI: 10.27232/d.cnki.gnchu.2023.000867.

[5]. Xiao Zhang. Study on the Repair Effect of Graphene Oxide-Alginate-Chitosan Composite Scaffold for Cranial Defects [D]. Jilin University, 2022. DOI: 10.27162/d.cnki.gjlin.2022.005652.

[6]. Qinglin Zou. Preparation and Study of the Hemostatic and Wound Healing Promoting Properties of β-Glucan-Sodium Alginate-Polyglutamic Acid Composite Microspheres [D]. Qilu University of Technology, 2024. DOI: 10.27278/d.cnki.gsdqc.2024.000485.

[7]. Qingkun Zhong. Preparation and Hemostatic Performance Study of Chitosan Oligosaccharide/Carboxymethyl Chitosan/Alginate/Saussurea Inulae Methylester Composite Sponge [D]. Guangdong Ocean University, 2019. DOI: 10.27788/d.cnki.ggdhy.2019.000109.

[8]. Qingkun Zhong, Sitong Lu, Zhang Hu, et al. Study on the Preparation Process of Carboxymethyl Chitosan/Sodium Alginate Composite Hemostatic Microspheres [J]. Applied Chemical Industry, 2018, 47(03): 501-504. DOI: 10.16581/j.cnki.issn1671-3206.2018.03.014.

[9]. Sha Li, Xinhao Zhang, Rui Jia, et al. Preparation of Polypyrrole/Chitosan-Alginate Composite Microspheres and Their Drug Sustained Release Performance [J]. Journal of Composite Materials, 2024, 41(07): 3756-3763. DOI: 10.13801/j.cnki.fhclxb.20231123.001.

[10]. Messaoud G B, Sánchez-González L, Probst L, et al. Influence of internal composition on physicochemical properties of alginate

aqueous-core capsules[J]. Journal of colloid and interface science, 2016, 469: 120-128.
[11]. Chachanidze R, **e K, Lyu J, et al. Breakups of Chitosan microcapsules in extensional flow[J]. Journal of Colloid and Interface Science, 2023, 629: 445-454.
[12]. Gåserød O, Sannes A, Skjåk-Bræk G. Microcapsules of alginate‐chitosan. II. A study of capsule stability and permeability[J]. Biomaterials, 1999, 20(8): 773-783.
[13]. Ji M, Liu S, **ao H, et al. Investigation on tribological performance of Ionic liquid filled microcapsules as additives under water-based drilling mud conditions[J]. Tribology International, 2023, 184: 108439.
[14]. Frent O D, Vicas L G, Duteanu N, et al. Sodium alginate—natural microencapsulation material of polymeric microparticles[J]. International journal of molecular sciences, 2022, 23(20): 12108.
[15]. Pereda M, Poncelet D, Renard D. Characterization of core-shell alginate capsules[J]. Food biophysics, 2019, 14(4): 467-478.