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Advances in Nano-Scale Plugging Agents for Water-Based Drilling Fluids: Mechanisms and Applications

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Abstract:
During drilling operations, the efficient sealing of nano- to micro-scale fractures effectively mitigates the invasion of the fluid phase, ensures the long-term structural stability of shale formations, and suppresses hydration swelling together with associated wellbore-instability phenomena. Consequently, determining how to seal nano- and micro-scale fractures in shale reservoirs has become a prominent and intensively studied topic within the domain of water-based drilling-fluid research. Nano-sealing materials, characterized by their ultra-fine particle dimensions together with their distinctive physical and chemical properties, demonstrate pronounced potential for improving fluid-loss control as well as for enhancing overall wellbore stability. Building upon this foundation, the present study systematically classifies the nano-plugging agents that have been reported in recent years, conducts a detailed analysis of their respective sealing mechanisms, and explores the prospective developmental trajectories of nano-plugging agents, thereby offering new and valuable insights for subsequent investigations focused on water-based drilling-fluid plugging agents. Nano-emulsion plugging agents possess multifunctional, high-efficiency, low-cost, safe, and environmentally friendly characteristics, and the related research holds substantial engineering significance and practical value.

Keywords: nano; emulsion; plugging agent; high-performance water-based drilling fluid

Introduction

Water-based drilling fluids can, during drilling activities conducted within complex geological formations such as shale, infiltrate along micro-fractures and pores situated within the wellbore wall, ultimately leading to the occurrence of wellbore instability. Consequently, enhancing the sealing capacity of water-based drilling fluids with respect to pores and micro-fractures constitutes one of the principal technical measures employed to prevent wellbore instability [1]. Shale formations contain highly developed micro-fractures that demonstrate the coexistence of both micron- and nanometer-scale features, with nanometer-scale fractures being predominant. Conventional sealing particles, because of their comparatively larger particle size together with their irregular and uneven morphology, struggle to penetrate nanometer-scale fractures effectively, resulting in continuous drilling-fluid loss and in the ineffective sealing of microporous throats. In recent years, significant advancements achieved within the fields of nanotechnology and materials science have facilitated the development of nano-sized sealing materials that exhibit high specific surface area, elevated surface energy, and excellent chemical stability. These nano-sized materials are capable of improving rheological properties, enhancing inhibitory effects, and significantly increasing sealing efficiency, thereby markedly enhancing the stability and operational efficiency of wellbores located within complex geological formations. Owing to their ability to penetrate both micro- and nano-pores/fractures, nano-particles can form dense and stable sealing layers through the combined actions of physical blocking, chemical adsorption, and interfacial synergy, thereby comprehensively enhancing the sealing capability of drilling fluids and contributing to improved wellbore stability [2].This paper comprehensively analyzes domestic and international nano-plugging agents and summarizes their advantages and disadvantages, providing guidance for future research and development of plugging agents.

Solid Nanoparticle Plugging Systems

Based on their physical state, nano-plugging agents can be broadly categorized into two main types: solid particle plugging agents, which include nano-silica, alumina, nano-clay, nano-lapis, and nano-graphene oxide, and emulsion plugging agents.

Solid particle plugging agents

Nano-particles exist in a thermodynamically unstable state as a direct consequence of their extremely high surface energy, which significantly enhances their chemical activity and renders them prone to agglomeration within drilling fluids, thereby inhibiting the full realization of their performance potential. Existing research has predominantly concentrated on single nano-systems, whereas comparatively limited discussion has been devoted to composite nano-materials [3]. By integrating the rigidity, dimensional stability, and heat resistance of inorganic phases with the resilience, processability, and interfacial bonding efficiency of organic polymers, it is possible to prepare high-performance nanocomposites utilizing the synergistic complementary effects of both. To improve the dispersion of nanoparticles, inorganic/organic composite systems typically undergo chemical modification of their surfaces using coupling agents, halogenated hydrocarbons, or polymer By integrating the inherent rigidity, dimensional stability, and heat resistance of inorganic phases with the flexibility, processability, and interfacial bonding efficiency of organic polymers [4]. Hao et al.[5] capitalized upon the bridging functionality of inorganic nanoparticles in conjunction with the deformation capability of organic particles to prepare a nano-plugging agent exhibiting a core–shell structure via emulsion polymerization. The polymer shell is capable of undergoing deformation under applied pressure, thereby enabling penetration into shale micro-pores and micro-fractures to achieve effective sealing and to form a high-strength sealed zone. Cui [6] designed and synthesized a stable organic/inorganic composite membrane plugging agent that employs modified nano-rigid SiO_2 as the core and flexible-chain polymers as the shell. This plugging agent demonstrates strong interfacial adsorption on shale and clay mineral surfaces, rapidly spreading to form a dense and uniform thin film. High-modulus SiO_2 nanoparticles function as rigid bridging centers, creating mechanical blockages within micro-fractures, while the flexible polymer shell leverages its reversible deformation capability to penetrate and fill nanometer-scale pores, thereby achieving multi-scale sealing of the micro-fracture–nanopore throat network. Nevertheless, long-term thermal ageing of such systems leads to a significant increase in both apparent viscosity and plastic viscosity, indicating that there remains considerable scope for further improvement in terms of temperature stability and rheological control capabilities. LI D[7] functionalized the surface of nano-SiO_2 with the silane coupling agent A-1891 and subsequently grafted temperature-sensitive poly(N-isopropylacrylamide) onto the outer layer of the particles to produce temperature-responsive nano-blocking particles; these particles are non-toxic and environmentally friendly, while maintaining excellent dispersion and blocking performance across a wide temperature range.

The hybridization of inorganic nanoparticles with organic polymers endows composite plugging agents with multiple synergistic effects: specifically, the polymer shell layer regulates surface charge density, functional group types, and chemical reactivity, thereby not only enhancing the dimensional stability and dispersion uniformity of the colloidal core but also significantly increasing the polymer’s thermal decomposition temperature and mechanical strength, ultimately forming a core–shell synergistic sealing layer. In view of their substantially superior comprehensive performance compared to single-component materials, such composite plugging agents have attracted widespread attention from both academic and industrial communities for their potential applications within drilling-fluid systems [8].

Emulsion-type plugging agents

In order to suppress the accelerated hydration swelling of mud shale under high-temperature and ultra-high-temperature conditions, cationic inhibitors are commonly employed to inhibit hydration, seal pore throats or micro-fractures to reduce the likelihood of free water entering these features, and form hydrophobic adsorption films to prevent water from contacting the wellbore wall. Nano-emulsions possess three key characteristics: strong blocking ability, strong film-forming capability, and strong inhibition capacity. Consequently, they can serve as multifunctional water-based drilling-fluid plugging agents to address wellbore-instability issues encountered during drilling through mudstone and shale formations. Additionally, in comparison with nano-particles, nano-emulsions offer the following advantages: (1) Their particle size is smaller and more uniformly distributed, enabling them to remain stable under high-temperature (197 °C) and high-salinity conditions, thereby avoiding the agglomeration and failure phenomena commonly associated with traditional nanoparticles. (2) They can significantly reduce fluid loss at low concentrations (e.g., 1 %–2 %) while exerting minimal impact on drilling-fluid rheology (viscosity change <5 %), thus circumventing the high-viscosity issues that arise from high concentrations of traditional nanoparticles. (3) The sealant layer formed by the emulsion sealant is readily removable at later stages, reducing formation damage and facilitating subsequent production operations. Currently, nano-emulsion sealants are primarily synthesized using surfactants, coupling agents, and polymers.

Yang et al.[9] employed non-ionic surfactants possessing both water-soluble and oil-soluble properties as raw materials to prepare an emulsion (OSE) via emulsification, which was subsequently blended with lithium silicate to obtain a lithium silicate/emulsion composite plugging agent (LOSE). This plugging agent exhibits favorable rheological properties and sealing performance; however, when the dosage reaches 4 %, the filtrate loss is reduced by only 29.1 %. Wang [10] prepared microemulsion plugging agents using surfactants, co-surfactants, oil phase, and brine. These agents maintain their micro-nano structure even in high-salt environments, exhibit excellent salt resistance, and can effectively seal micro-nano-sized pores, significantly inhibiting filtrate intrusion, thereby achieving a balance between strong inhibition and strong sealing prepared micro-emulsion plugging agents using surfactants, co-surfactants, oil phase, and brine. These agents maintain their micro-/nano-structure even in high-salt environments, exhibit excellent salt resistance, and can effectively seal micro- to nano-sized pores, thereby significantly inhibiting filtrate intrusion and achieving a balance between strong inhibition and robust sealing. Zhong et al.[11] blended the oil phase, brine, primary and secondary surfactants, and co-surfactants to obtain micro-emulsion plugging agents endowed with both strong inhibition and strong sealing functionalities.

Wang et al.[12] developed a multifunctional emulsion plugging agent exhibiting exceptional elastic deformation capability, strong sealing ability, film-forming properties, and robust inhibition and salt resistance, employing nano-hard core monomers, silane coupling agents, emulsifiers, hydrophobic monomers, hydrophilic monomers, initiators, and water as raw materials. Chen et al. [13] obtained modified graphene by grafting zwitterionic compounds onto graphene that had been pre-treated with silane coupling agents, mixed bentonite and asphalt-treated materials to form composite particles, and prepared an aqueous dispersion of chitosan nanogel, which subsequently formed a nano-emulsion plugging agent within the oil phase. Graphene and bentonite serve as rigid framework materials, conferring superior sealing performance upon the drilling fluid. The grafting of zwitterionic polymer chains enhances the flexibility of graphene, while the introduction of quaternised chitosan enables the polymer chains to intercalate between bentonite layers, thereby forming a stable composite structure. Chitosan nano-microgels further seal micro-pores, with their abundant cations neutralizing the negative charges present on clay surfaces and firmly adsorbing thereto, whereas sulfonic acid groups enhance the salt resistance of the overall system. Xie et al.[14] synthesized a nano-emulsion as a nano-plugging agent using styrene, acrylic ester compounds, and acrylamide compounds as raw materials. The resultant particle-size distribution ranges from 25 to 60 nm, effectively sealing nano-scale pores within mudstone wellbores, stabilizing the wellbore, and preventing collapse. Halliburton Baroid Company has developed the BaraFLC Nano-1 wellbore plugging agent, which enhances the sealing capability of water-based drilling fluids, inhibits pore-pressure transmission, and prevents shale instability. This agent contains polymer-coated particles with an average particle size of approximately 150 nm, which synergistically interact with traditional loss-control additives and solid particles to rapidly seal shale micro-fractures and pores, thereby blocking pressure transmission through the wellbore wall. While high concentrations of traditional loss-control additives can achieve comparable fluid-loss control, most starch and synthetic-polymer blends result in excessively high fluid viscosity; in contrast, BaraFLC Nano-1 not only delivers excellent loss-control performance but also exerts virtually no impact on fluid rheology.

Development Prospects

In summary, after decades of intensive research and field application, plugging agents have achieved a series of significant accomplishments and are now generally capable of meeting the plugging requirements of conventional reservoirs. However, with the continuous development of oilfields within China and the progressive shift of focus toward unconventional oil and gas resources such as shale oil and gas, traditional nano-particle and nano-emulsion plugging agents have revealed numerous shortcomings, including the pronounced tendency of nano-particles to agglomerate, their poor dispersibility, and inadequate size matching, all of which ultimately limit plugging efficiency. Research concerning the capacity of nano-emulsions to repair wellbores and to enhance wellbore stability remains in its infancy within China. In the future, by systematically elucidating the influence of sealing-material structure upon sealing behavior and by quantitatively expressing the relationship between the microscopic structural composition of materials and their macroscopic sealing performance, substantial theoretical value and practical significance will be realized for the large-scale, environmentally responsible development of shale oil and gas under complex geological conditions.

Future plugging agents should possess characteristics such as multifunctionality, high efficiency, low cost, and environmental safety. Consequently, the future development trajectory of plugging agents can be contemplated from the following perspectives: (1) modification of nanoparticles via surfactants, coupling agents, and high-molecular-weight polymers to address issues such as agglomeration and poor dispersion; (2) blending of nanoparticle plugging agents with nano-emulsion plugging agents in precisely defined ratios to formulate high-performance composite plugging agents that simultaneously exhibit strong inhibitory and film-forming capabilities; (3) utilization of Pickering emulsions, which replace traditional emulsifiers with solid particles, thereby reducing or eliminating the need for organic surfactants, lowering overall costs, and diminishing environmental impact, while concurrently exhibiting robust stability that remains unaffected by factors such as pH, salinity, temperature, and oil-phase composition [15, 16], indicating that Pickering-emulsion sealants may represent a future trend; (4) introduction of salt-responsive and temperature-responsive polymers to modify nanoparticles, thereby enhancing the temperature resistance and salt tolerance of plugging agents; and (5) continued development of cost-effective and environmentally friendly plugging agents conducive to sustainable economic development.

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