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RESEARCH PROGRESS ON THE EFFECT OF NANOPARTICLES ON FOAM STABILITY

Abstract

As a fluid with a certain viscosity, foam is widely used to control gas channeling and reduce gas mobility in oil fields due to its simple process, low cost and stability in water, and has achieved good results. Through literature research and the research results of our team in recent years, the research status of CO_2 foam is expounded from the direction of foam structure and foam decay. On this basis, the research progress of the effects of nanoparticles and external conditions on foam stability is introduced. Finally, the mechanism of nanoparticle stabilized foam was discussed by introducing the maximum desorption energy theory, the maximum capillary pressure theory and the interaction theory between particles. With the continuous development of foam flooding technology, the diversity and functionality of foam will continue to show, the development cost will be further reduced, and its application prospects in oil fields will become more and more broad.

Key words: foam, fluid mobility, gas channeling, nanoparticles.

Introduction

Researchers consider foam flooding a crucial technology for enhancing oil recovery due to its straightforward process, cost-effectiveness, and ability to control gas channeling. Foam demonstrates good stability in formation water within reservoir channels, allowing it to effectively block high permeability layers, adjust reservoir heterogeneity, and increase sweep efficiency. Additionally, using foam as a displacement fluid offers advantages such as low density, minimal formation leakage, and limited formation damage, making it a widely employed method. China began the experiment of foam flooding in Yumen oilfield in 1965. Since then, a large number of foam flooding research and field tests have been carried out in Daqing, Liaohe and Shengli [1]. Currently, gases like flue gas, N_2, and CO_2 are predominantly used in foam flooding. However, as global focus on reducing CO_2

emissions has grown, carbon capture, utilization, and storage technologies have gained significant attention from major energy companies worldwide. CO_2 foam flooding is an important technology for enhancing oil recovery in oilfields. It not only overcomes issues of CO_2 gas channeling seen in conventional CO_2 flooding but also enhances swept volume and oil displacement efficiency while utilizing and sealing CO_2 gas. Despite these benefits, challenges like poor foam stability during application persist, and existing methods using polymers as foam stabilizers have not adequately addressed this issue. As a result, researchers have suggested using hydrophobic inorganic nanoparticles to stabilize CO_2 foam [2]. The addition of nanoparticles can enhance foam's mechanical strength by adsorbing onto the gas-liquid interface, reducing foam's elastic deformation from gas collision, preventing coarsening and coalescence, and thus improving foam stability [3]. However, the use of inorganic nanoparticles can cause irreversible damage to low permeability layers after foam rupture, limiting its application in oilfields.

In view of the above problems, this work focuses on the research status and application of nanoparticles in the direction of foam, and analyzes and summarizes the stability of foam under different conditions. The effects of nanoparticles, external conditions and other factors on foam stability were described in detail. Combined with the theory of foam stability factors, the mechanism of nanoparticle stabilized foam was systematically introduced. It lays a theoretical foundation for the popularization and application of foam in the direction of oil and gas field development.

Research status of CO_2 foam

During the 1950s, the United States, with its abundant CO_2 gas resources, laid the groundwork for CO_2 foam flooding and was the pioneering country in researching this technology. In China, research on CO_2 foam systems started relatively late. However, both domestic and international research results have demonstrated the efficacy of foam plugging in controlling channeling. The crux of CO_2 foam flooding technology lies in the foaming effect and stability of the foam system. The primary cause of foam instability is the decay of the foam structure itself.

The structure of foam

Foam can be described as a dispersion system of 'bubble polymer,' where gas is separated by a liquid film. There are various foam shapes, with spherical foam containing more liquid and thicker liquid film between bubbles. As foam loses liquid and the liquid film between bubbles thins, it transitions from spherical to polyhedral, forming polyhedral foam.

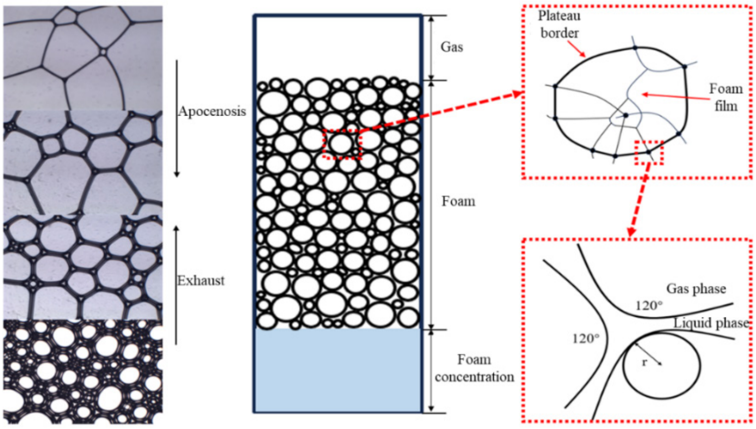

Figure 1 – Composition and structure of foam

Foam is a dynamic system that naturally decays over time. Its basic elements include the liquid film, node, and Plateau channel, as illustrated in Figure 1. The fundamental framework of foam, known as the Plateau channel, is created by the meeting of liquid films from three adjacent bubbles. Four adjacent frameworks join to form a node, which acts as the connecting point of the framework [4].

During the defoaming process, the structure of foam in layers of varying heights differs. Due to gravity, the foam system expels liquid from top to bottom, while gas is released from bottom to top. Consequently, the lower layers of the system have a higher liquid content in the liquid film, resulting in smaller, more spherical bubbles with lower gas content. As the height of the foam layer increases, the liquid content in the system's liquid film decreases, leading to thinner liquid films and larger bubble sizes. Excessive spherical foam transitions to polygonal foam, which is more stable than spherical foam [5].

The decay of foam

Foam is a thermodynamically unstable dispersion system where the gas phase is dispersed in the liquid phase. With numerous gas-liquid interfaces, the foam naturally tends to transform into its lowest energy form according to the principle of minimum energy. As the interface area decreases, the system's energy lowers, leading to foam collapse [6]. The collapse of foam primarily occurs due to the drainage of the liquid film and the coalescence and enlargement of bubbles.

Film Drainage: Liquid film drainage consists of two main processes. Initially, when the foam contains a high liquid content, gravity causes the liquid to drain mainly through the Plateau channel. As the liquid film thins, drainage shifts from gravity-driven to thermodynamic. Thermodynamic drainage includes capillary pressure and surface tension-induced separation pressure at the gas-liquid interface [7].

Bubble Coalescence: When adjacent bubbles collide during defoaming, two outcomes can result: elastic collision or bubble coalescence. Elastic collision occurs when the liquid film's elastic deformation offsets the collision force, maintaining the number and size of bubbles. Bubble coalescence happens when the liquid film cannot withstand the collision force, leading to film rupture and the merging of bubbles into larger ones [8]. In relatively stable dynamic environments, bubble collisions are primarily driven by coalescence due to the weak motion intensity between bubbles, making coalescence the main cause of bubble instability.

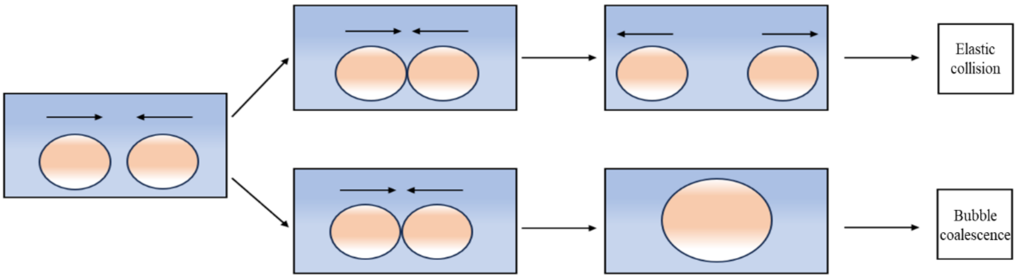

Figure 2 – Collision process of adjacent bubbles

Research progress on the effect of nanoparticles on foam stability

To address the stability of CO_2 foam, foam stabilizers are commonly added, with polyacrylamide, sodium carboxymethyl cellulose, xanthan gum, and other polymer stabilizers being widely used. These stabilizers work by increasing the viscosity of the liquid phase. Higher viscosity slows down liquid film drainage and gas exchange between bubbles, but this can also reduce foaming ability due to increased viscous resistance.

In addition to polymers, nanoparticles exhibit excellent foam stabilization due to their high desorption energy, allowing them to adsorb effectively at the gas-liquid interface. This inhibits foam disproportionation and enhances liquid film strength. In a three-phase foam system, nanoparticles enhance foam stability by increasing the mechanical strength of the liquid film and preventing liquid film drainage [9].

Effect of nanoparticles on foam stability

(1) Effect of Particle Size on Foam Stability: The particle size of nanoparticles influences their long-term adsorption at the foam liquid film boundary and their arrangement on the film, crucial factors in foam stability. Studies have shown that smaller nanoparticles generally enhance foam stability compared to larger ones. For example, Tang et al. [10] studied nano-SiO_2 particles (20-500 nm) in sodium dodecyl benzene sulfonate (SDBS) foam, finding that smaller particles led to better foam stability. Similarly, Aktas et al. [11] observed that smaller particle sizes significantly improved foam stability. He et al. developed hydrophobic nanoparticles and discovered that smaller particle sizes correlated with stronger foam stability. However, there can be an optimal particle size range for stability. Liu et al. investigated the effect of PTFE particle size on foam stability, noting that stability initially increased and then decreased with particle size. They concluded that extremely small or large particle sizes were detrimental to foam stability, as they couldn't stably adsorb at the foam's liquid film boundary.

(2) Effect of Surface Hydrophobicity on Foam Stability: The hydrophobicity of spherical nanoparticle surfaces is often characterized by the three-phase contact angle. When the contact angle between the nanoparticles and the liquid film is less than 90°, the nanoparticle area in the liquid phase exceeds that in the gas or oil phase. Conversely, when the contact angle is greater than 90°, the nanoparticle area in the gas or oil phase surpasses that in the liquid phase. This principle also applies to curved interfaces [12].

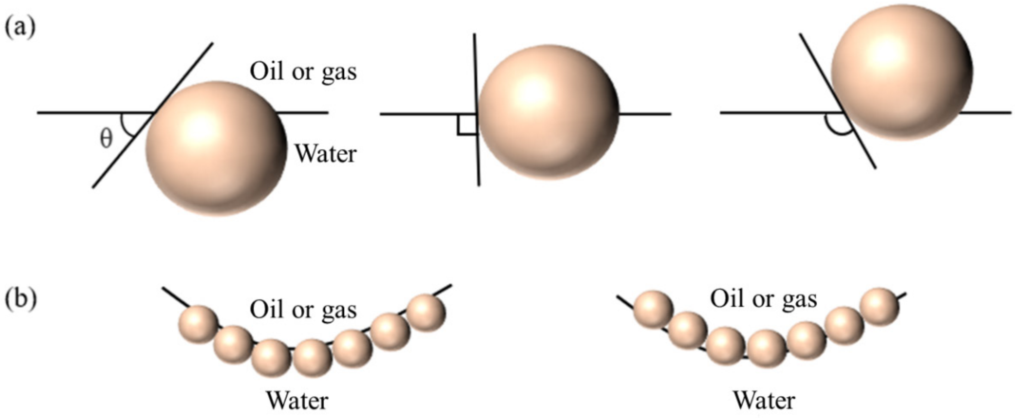

Figure 3 – The adsorption state of spherical particles at the interface (a) plane (b) curved interface

The contact angle between nanoparticles' surfaces and water (surface wettability) is another crucial factor in stabilizing foam. If the contact angle is too large or too small, it can hinder foam stabilization. Liang et al. [13] found that when the contact angle between nanoparticles and the liquid film was around 80°, it had the best stabilizing effect on foam. Nanoparticles with strong hydrophilicity had almost no effect on foam stabilization. Johansson et al. [14] observed that excessively hydrophobic particle surfaces were unable to stabilize foam. Wang et al. developed a high-performance three-phase foam system using α-olefin sulfonate (AOS) as a foaming agent and fly ash as a foam stabilizer. They discovered that at low AOS concentrations, the particles' surface became hydrophobic, enhancing their adsorption and dispersion at the foam interface, thus improving foam stability. However, at high AOS concentrations, excessive AOS molecules on the particle surface changed its wettability from hydrophobic to hydrophilic, reducing its ability to adsorb at the foam interface and thus decreasing foam stability. Zhang et al. used Fe3O4 nanoparticles as a foam stabilizer in a foam flooding system, modifying their surface to be hydrophobic. They found that nanoparticles with a water contact angle of 68° had the best foam stabilization effect. Stephanie et al.

[15] stabilized supercritical CO_2 foams with both hydrophilic and hydrophobic SiO_2 nanoparticles. They found that nanoparticles with extreme hydrophilicity or hydrophobicity were not adsorbed on the liquid film and were more likely to remain in the liquid or gas phase, lacking the ability to stabilize foam.

(3) Effect of Concentration on Foam Stability: Nanoparticle concentration influences their adsorption and arrangement on the foam membrane. Guignot et al. [16] observed that increasing particle concentration inhibited liquid film drainage and stabilized foam by reducing particle agglomeration. Sheng et al. studied SiO_2 particles' enhancement mechanism on firefighting CO_2 foam stability, noting a slight decrease in foam volume with increasing nanoparticle concentration but a significant increase in foam stability. Carn et al. [17] found that exceeding a 1% nanoparticle concentration led to most particles being adsorbed on the liquid film, significantly reducing foam liquid drainage in the Plateau channel. Foam stability generally increases with nanoparticle concentration up to a critical value, beyond which stability decreases due to particle coalescence. Hunter et al. [18] observed that high nanoparticle concentrations formed a shell on the liquid film surface, enveloping the gas-liquid interface and reducing liquid film drainage, thus improving foam stability. However, exceeding the maximum load the liquid film can withstand causes nanoparticle coalescence, negatively impacting foam stability.

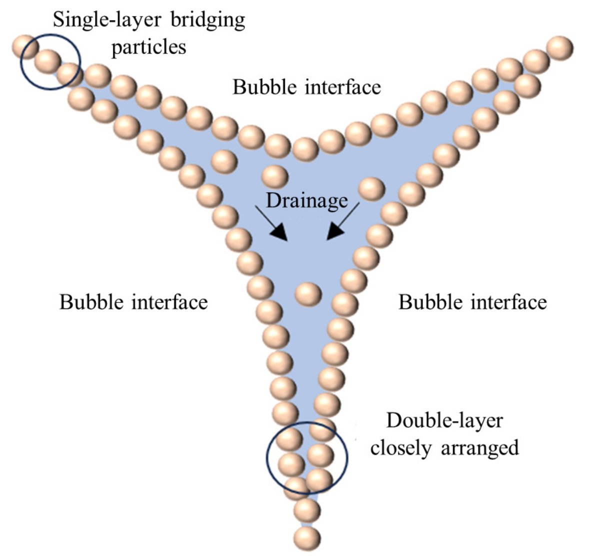

Figure 4 – Particles adsorbed at the boundary of foam liquid film

Effect of external conditions on foam stability

(1) Oil saturation

After the foam agent encounters water, it will produce a large amount of foam after the formation encounters water, blocking the high permeability channel, to achieve the purpose of expanding the spread range. The foam system will quickly defoam after contacting a small amount of residual oil on the rock wall, resulting in a decrease in plugging effect. The addition of nanoparticles can form a protective layer between crude oil and foam to prevent direct contact between crude oil and foam liquid, reduce the damage of crude oil to foam structure, thus improve the oil resistance of foam [19]. Yang et al. [20] found that the foam system with nanoparticles (AIOOH) as a foam stabilizer had better oil resistance than the foam system with a single surfactant. This is because nanoparticles (AIOOH) can be adsorbed at the gas-liquid interface of the foam to form a spatial network structure, and the hydrophobic groups on the surface can effectively adsorb crude oil, slowing down the contact between crude oil and the liquid film and the diffusion on the liquid film.

(2) Salinity

The inorganic salt ions in the formation will affect the stability of the foam. Generally, the stability of the foam increases with the increase of the concentration of inorganic salt ions. This is because inorganic salt ions can be adsorbed on the liquid film of the foam, to increase the stability of the foam. However, with the increase of salinity, the concentration of inorganic salt ions in the solution increases, the diffusion electric double layer is compressed, the electric repulsion is weakened, the thickness of the liquid film becomes smaller, the drainage speed of the liquid film increases, and the stability of the foam decreases. Dickinson et al. [21] found that different concentrations of sodium chloride (0-4 mol·L^{-1}) had a certain effect on the stability of the foam. With the increase of sodium chloride concentration, the Zeta potential of the particles decreased and agglomerated, which had an adverse effect on the stability of the foam.

Study on foam stabilization mechanism of nanoparticles

The foam system is inherently thermodynamically unstable, leading to various factors contributing to foam collapse, such as liquid film drainage, bubble coalescence, and bubble coarsening [22]. In recent years, there has been increasing research on the mechanism of nanoparticle-stabilized foam. Currently, the maximum capillary pressure theory, desorption energy theory, and particle interaction theory are used to explain the mechanism of nanoparticle-stabilized foam.

(1) Maximum Desorption Energy Theory: Desorption energy refers to the energy required for nanoparticles adsorbed at the gas-liquid interface of the foam liquid film to detach. Studies have shown that nanoparticles can be stably adsorbed at the gas-liquid interface, enhancing foam's mechanical strength and stability. Horozov et al. [23] observed that nanoparticle adsorption on the gas-liquid interface effectively reduces liquid loss from the liquid film, decreases the gas-liquid interface's surface area, and increases gas diffusion resistance between different foams, thereby inhibiting foam coarsening to some extent.

The desorption energy of particles at the gas-liquid interface of foam is much greater than that of surfactants. A higher desorption energy indicates stronger particle adsorption capacity at the gas-liquid interface, making it more challenging for particles to desorb and thus stabilizing the liquid film [24]. The desorption energy ΔG_remove of spherical particles is expressed in Equation (1), with a schematic diagram shown in Figure 5.

$$\Delta G_{remove} = \pi a^{2}\gamma(1-\left|\cos\theta\right|^{2} \qquad (1)$$

Where a is the particle radius, m. γ is the surface tension of the gas-liquid interface, mN·m^{-1}. θ is the contact angle between particles and liquid phase, °.

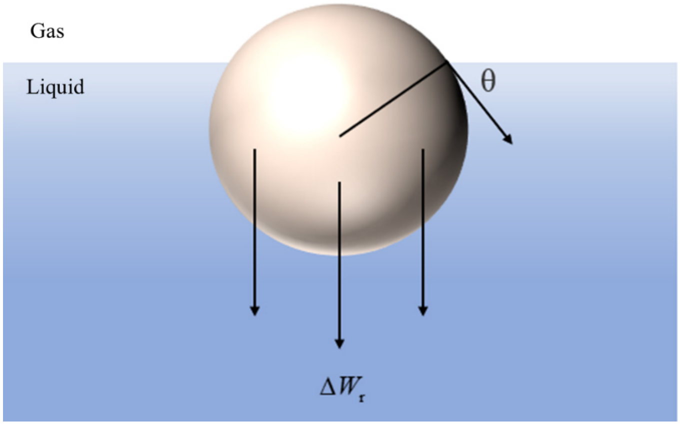

Figure 5 – The desorption energy of particles at the gas-liquid interface

(2) Maximum Capillary Pressure Theory: According to Equation (1), foam is most stable when the contact angle between nanoparticles and the liquid film boundary is around 90°. However, defining the optimal contact angle for nanoparticle-stabilized foam solely based on the maximum desorption energy theory is insufficient. As illustrated in Figure 6, there exists a force between two adjacent particles that prevents adjacent bubbles from merging, known as the maximum capillary pressure. This pressure represents the dispersing effect of nanoparticles on the foam liquid film. A higher maximum capillary pressure indicates better nanoparticle dispersion between bubbles and greater foam stability. The formula for maximum capillary pressure Pc is shown in Equation (2). Combining this theory with the maximum desorption energy theory, the most stable state for a three-phase foam system occurs when the contact angle between nanoparticles and the gas-liquid interface is in the range of 50°–70°.

$$P_c = \pm \beta \frac{2\gamma}{a} \cos\theta \qquad (2)$$

Where β is the theoretical packing constant. a is the particle radius, m. γ is the surface tension of gas-liquid interface, $mN \cdot m^{-1}$. θ is the contact angle between particles and liquid phase, °.

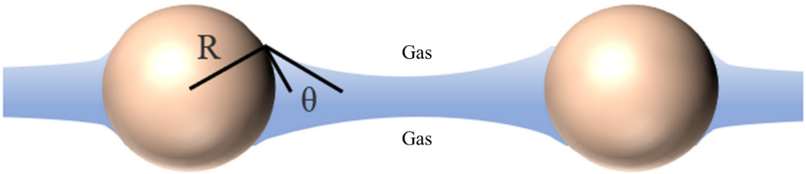

Figure 6 – Maximum capillary pressure between particles

(3) Interaction theory between particles

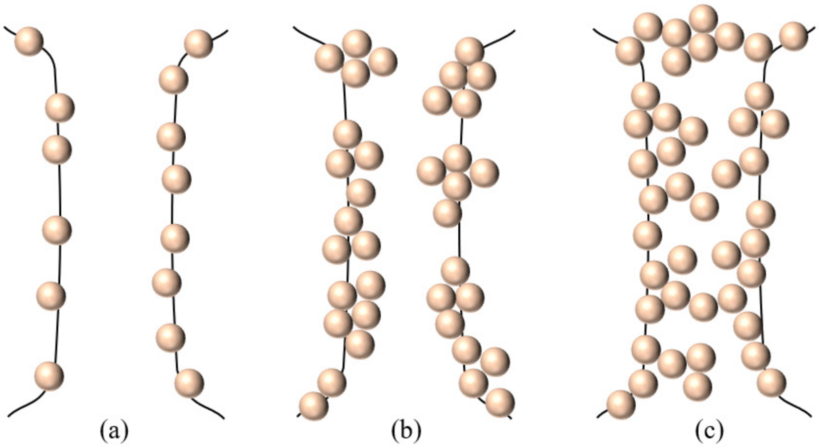
(a) (b) (c)

Figure 7 – The arrangement of particles on the liquid film

The arrangement of particles on the liquid film surface can be categorized into (a) single-layer arrangement, (b) double-layer compact arrangement, and (c) spatial network arrangement, as depicted in Figure 7. Lian et al. discovered that interactions between particles at the interface can alter the interfacial tension of the liquid film. When gravitational forces dominate, particles tend to decrease interfacial tension. Conversely, when repulsive forces are at play, particles increase interfacial tension. This interaction theory suggests that nanoparticles can form a 'mesh protective film' at the foam surface, reducing contact between adjacent liquid films, enhancing foam's resilience, and preventing bubble merging, thereby stabilizing the foam.

In summary, according to the maximum capillary pressure theory, desorption energy theory, and particle interaction theory, only nanoparticles can stably adsorb at the gas-liquid boundary of the foam liquid film to stabilize the foam. Nanoparticle size, concentration, and surface wettability affect their adsorption at this boundary.

Zhang et al. studied the effect of nanoparticles ranging from 22 nm to 200 nm on foam stability and found that stability increased with decreasing nanoparticle size. With an appropriate concentration and surface hydrophobicity, smaller nanoparticles led to better foam stability. Therefore, selecting nanoparticles with smaller sizes and suitable surface hydrophobicity is crucial for foam stabilization.

Conclusion

Foam plays an important role in channeling sealing because of its unique rheology and stability. At present, experts and scholars in the field of oil and gas field development have made some progress in the research of foam structure and foam decay. As a component of stable foam, nanoparticles can increase the mechanical strength of the liquid film by adsorbing on the surface of the foam liquid film and prevent the drainage of the liquid film to improve the stability of the foam. However, the application cost of foam technology and nanoparticle materials in the field of oil and gas field development is high, and a mature development system has not been formed. With the expansion of oil and gas exploration and development to deep, ultra-deep, unconventional and other harsh oil and gas resources, the research and development of foam technology will become the main way to efficiently develop oil fields. In the future, foam technology should comprehensively consider reservoir geology, engineering, materials and other disciplines to carry out research and practice, strengthen the universal applicability of foam technology, and then realize the efficient application of foam in the field of oil and gas field development, and accelerate the process of unconventional oil and gas exploration and development.

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НАНОБӨЛШЕКТЕРДІҢ КӨБІК ТҰРАҚТЫЛЫҒЫНА ӘСЕРІН ЗЕРТТЕУ ЖЕТІСТІКТЕРІ

Андатпа

Белгілі бір тұтқырлыққа ие сұйықтық ретінде көбік арзан баға мен судағы тұрақтылық сияқты қарапайым үрдістің арқасында мұнай кен орындарында газ серпілісін бақылау және газ қозғалғыштығын төмендетуде кеңінен қолданылып, жақсы нәтиже көрсетті. Әдебиеттерді талдау мен тобымыздың соңғы жылдары жүргізген зерттеулерінің нәтижесі арқылы CO_2 көбігінің зерттеу күйі баяндалды. Баяндама негізде нанобөлшектер мен сыртқы жағдайлардың көбік тұрақтылығына әсерін зерттеудегі жетістік ұсынылды. Қорытындыда нанобөлшектермен тұрақтандырылған көбік механизмі ұсынылған максималды десорбциялық энергия теориясы, максималды капиллярлық қысым теориясы және бөлшектер арасындағы өзара әрекеттесу теориялары арқылы талқыланды. Көбікті сутоғыту технологиясының үздіксіз дамуымен көбіктің алуан түрлілігі мен функционалдығының жаңа түрлері пайда бола болады. Көбікті игеру құны одан әрі төмендеп, оны мұнай кен орындарында қолдану перспективасы ұлғая түседі.

Тірек сөздер: көбік, сұйықтықтың қозғалғыштығы, газ серпілісі, нанобөлшектер.

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ДОСТИЖЕНИЯ В ИССЛЕДОВАНИЙ ВЛИЯНИЯ НАНОЧАСТИЦ НА СТАБИЛЬНОСТЬ ПЕНЫ

Аннотация

Пена как жидкость с определенной вязкостью широко используется для контроля прорыва газа и уменьшения подвижности газа в нефтяных месторождениях благодаря простому процессу, низкой стоимости и стабильности в воде и показала хорошие результаты. Через исследование литературы и результаты исследований нашей команды за последние годы освещено состояние исследований пены CO_2. На этой основе представлен прогресс исследований влияния наночастиц и внешних условий на стабильность пены. В заключение обсуждается механизм стабилизации пены наночастицами путем представления теории максимальной энергии десорбции, теории максимального капиллярного давления, а также теории взаимодействия между частицами. С постоянным развитием технологии пенного заводнения разнообразие и функциональность пены будут продолжать проявляться, стоимость разработки будет еще больше снижаться, а перспективы ее применения на нефтяных месторождениях будут все более и более широкими.

Ключевые слова: пена, подвижность жидкости, прорыв газа, наночастицы.