Review Article

Lipei Fu, Qianli Ma, Kaili Liao*, Junnan An, Jinmei Bai, and Yanfeng He*

Application of Pickering emulsion in oil drilling and production

https://doi.org/10.1515/ntrev-2022-0003 received September 12, 2021; accepted October 10, 2021

Abstract: When surfactant is used as emulsifier, the stability of emulsion is often greatly reduced with the influence of reservoir conditions (temperature, pressure, salinity, etc.), which shortens the validity period of emulsion. Pickering emulsion has a wide range of applications in the oil and gas field due to its advantages of good stability and easy regulation. In this article, the formation, stabilization mechanism, and influencing factors of Pickering emulsions were introduced, and the application status and prospects of Pickering emulsions in oil and gas field were summarized. It was pointed out that Pickering emulsion has many advantages and important research value when applied in deep strata and complicated reservoirs. It is expected that this article can effectively reflect the application value of Pickering emulsion in oil and gas field and promote the application of Pickering emulsion in petroleum industry.

Keywords: Pickering emulsion, influencing factors, petroleum industry application, emulsifier

1 Introduction

Emulsion is a dispersion system in which one liquid is dispersed in the form of liquid beads in another immiscible liquid. Pickering emulsion is a special one, which uses ultrafine solid particles as an emulsifier [1]. Pickering first found in 1907 that solid particles could be adsorbed

Lipei Fu, Qianli Ma, Junnan An, Jinmei Bai: School of Petroleum Engineering, Changzhou University, Changzhou 213164, China on the surface of oil droplets to form a stable emulsion [1]. Later, people called this emulsion system as Pickering emulsion, and the solid particles which can emulsify and stabilize were called Pickering particles. The biggest difference between Pickering emulsion and common emulsion is that emulsifier is solid particles. In addition, compared with common emulsion, Pickering emulsion has the advantages of better stability, less emulsifier, recyclability, and environmental friendliness [2-5]. Therefore, Pickering emulsion has been widely studied and applied in the fields of food, fine chemical synthesis, medicine, cosmetics, and so on [6–10]. Pickering emulsion has also attracted more and more attention in petroleum industry, such as drilling, enhanced oil recovery (EOR), sand control, and petroleum wastewater treatment [11-16]. In this article, the formation, stability mechanism, influencing factors, and application progress of Pickering emulsion in oil and gas field will be introduced.

2 Pickering emulsion and its stability

2.1 Formation of Pickering emulsion

Pickering emulsion is prepared by homogenizing or ultrasonic emulsification of aqueous phase (some containing electrolytes), oil phase (strong polarity, medium polarity, weak polarity, or non-polarity), and solid emulsifiers. The droplet size of Pickering emulsion is generally in micron order, and the smaller the size, the better the emulsification ability [17–19]. Solid particles can be divided into flakes and granular. Flake solid particles mainly include kaolin, clay, synthetic lithium saponite, montmorillonite, graphene oxide (GO), and so on [20–22,46]. Granular solid particles include silicon dioxide, zinc oxide, iron oxide, titanium silicate, metal sulfate, polystyrene, Janus microspheres, starch nanocrystals, and so on [23–30].

Pickering emulsion can be classified into oil-in-water (O/W) and water-in-oil (W/O) types as well as surfactant

^{*} Corresponding author: Kaili Liao, School of Petroleum Engineering, Changzhou University, Changzhou 213164, China, e-mail: liaokaili@cczu.edu.cn

^{*} Corresponding author: Yanfeng He, School of Petroleum Engineering, Changzhou University, Changzhou 213164, China; Jiangsu Key Laboratory of Oil & Gas Storage and Transportation Technology, Changzhou University, Changzhou 213164, China, e-mail: heyanfeng@cczu.edu.cn

stabilized emulsion. Schematic diagram of classical (surfactant based) emulsion and Pickering emulsion are shown in Figure 1.

Surfactants generally have hydrophilic groups and hydrophobic groups, belonging to amphiphilic molecules. They are directionally arranged at the oil-water interface to form common emulsion, and the main performance evaluation parameter is hydrophilic-lipophilic balance value. Pickering emulsion is mainly formed by the adsorption of solid particles with certain wettability to the oil-water interface, which would form a single-layer or multi-layer film of solid particles. The three-phase contact angle is the main parameter for evaluating the performance of solid particles. When the three-phase contact angle θ is less than 90°, the solid particles are hydrophilic. The wettability of solid particles is lipophilic when the three-phase contact angle θ is more than 90° [32]. Relationship between wettability of particles and emulsion type is shown in Figure 2.

2.2 Stability mechanisms and influencing factors of Pickering emulsion

2.2.1 Stability mechanisms

The stability mechanisms of Pickering emulsion mainly include the following viewpoints: mechanical barrier mechanism and three-dimensional viscoelastic particle network mechanism [32]. Among them, the mechanism of barrier mechanism has been widely recognized [33–35].

(1) Mechanical barrier mechanism [36]: The compact arrangement of solid emulsifiers on the surface of the emulsion hinders the collision and agglomeration between droplets in space. At the same time, the particle emulsifier adsorbed on the surface of the droplet increases the

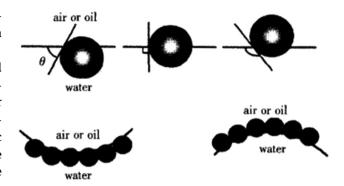


Figure 2: Relationship between wettability of particles and emulsion type [36].

repulsive force between the droplets. These two effects improve the stability of emulsion, as shown in Figure 3(a).

(2) Three-dimensional viscoelastic particle network mechanism [37]: This theory was proposed by Lagaly *et al.* in 1999. As shown in Figure 3(b), the interaction between particles and particles and between particles forms a stable three-dimensional network structure, which increases the viscosity of the continuous phase, prevents the aggregation of the droplets, and inhibits the delamination of the emulsion. The ability of resisting deformation has also been enhanced.

The evaluation methods of emulsion stability mainly include microscope analysis, particle size analysis, zeta potential analysis, high-speed centrifugation method, conductivity method, turbidity method, and rheological analysis. The microscopic analysis has its own shortcomings, for example improper operation in the process of sample preparation will destroy the structure of the sample to a certain extent. The optical particle size analyzer is only suitable for emulsion with relatively smaller volume fraction. Zeta potential analysis, high-speed centrifugation method, and conductivity and turbidity method have requirements on the volume fraction and viscosity of

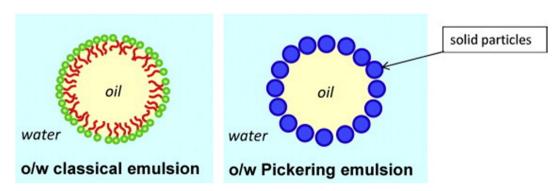


Figure 1: Schematic diagram of classical (surfactant based) emulsion and Pickering emulsion [31].

28 — Lipei Fu et al. DE GRUYTER

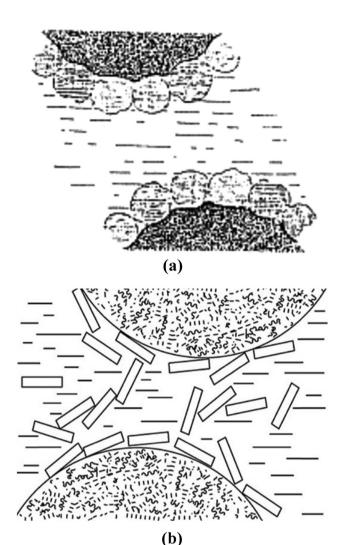


Figure 3: Stability mechanism of Pickering emulsion [38]. (a) Mechanical barrier mechanism and (b) three-dimensional viscoelastic particle network mechanism.

emulsion, but they cannot accurately analyze emulsion with higher volume fraction and viscosity. For rheological analysis, the influence of other variables on emulsion stability should be ignored [39].

2.2.2 Influencing factors

2.2.2.1 Wettability of solid particles

The wettability of solid particles plays a decisive role in the type of emulsion, because it greatly affects the performance of the emulsion, and it is one of the most important factors affecting the properties of the emulsion. Binks *et al.* [36] found that most of the surfaces of hydrophilic particles were adsorbed in polar water rather than in non-polar phase, and most of the surfaces of hydrophobic particles

were adsorbed in non-polar air or oil. When the particles are hydrophobic, W/O Pickering emulsion was formed, and when the particles are hydrophilic, O/W Pickering emulsion was formed. Emir *et al.* [40] studied the influence of ordinary glass beads (contact angle $48 \pm 4^{\circ}$) and modified glass beads (contact angle $93 \pm 3^{\circ}$) on Pickering emulsion, and they found that the droplets' size and distribution width of emulsion stabilized by modified glass beads were smaller than those stabilized by ordinary glass beads.

2.2.2.2 Solid particle concentration

The concentration of solid particles influences the droplet size and stability of Pickering emulsion. Under certain emulsification conditions, when the concentration of solid particles increases, the size of the emulsion droplets decreases, and the stability of the concentrated emulsion improves. However, when the concentration of solid particles reaches the critical micelle concentration, the size of the emulsion droplets will remain unchanged. Aveyard et al. [41] took monodisperse spherical silica particles with a diameter of 25 nm as the research object and found that the viscosity of the emulsion increased with the increase in the particle concentration, the concentration of solid particles increased by ten times, and the droplet size of the emulsion decreased by about eight times. However, when the particle concentration reached 3%, the solid particle concentration reached the critical micelle concentration, the polarity of the particle concentration increased, and the droplet size of the emulsion was basically unchanged. When studying the influence of silica concentration on the stability of emulsions, Justyna et al. [42] also reached a similar conclusion. As the silica concentration increased, the droplet size of the emulsion decreased gradually until it reached the critical micelle concentration, and the droplet size remained stable. By observing the stability of the emulsion, it was found that no demulsification occurred in 2 years. He et al. [46] used only GO as stabilizer to prepare Pickering emulsion, and the effect of GO concentration on emulsion stability was investigated. It was found that with the increase in GO concentration, the average droplet size of emulsion decreased gradually and the stability improved.

2.2.2.3 Oil-water ratio

The oil-water ratio is an important factor affecting the stability of the Pickering emulsion. The change in oil-water ratio may lead to the reverse of emulsion.

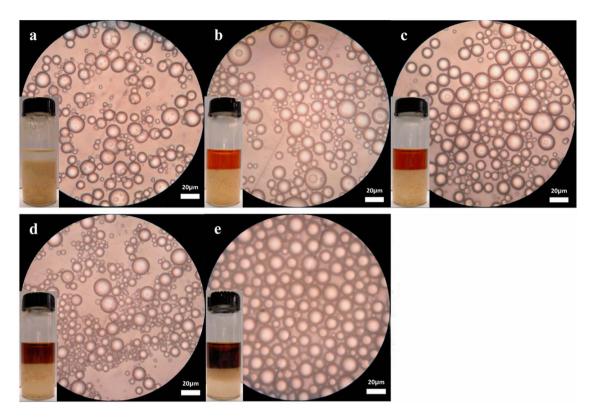


Figure 4: Pickering emulsions stabilized by GO at different pH values: (a) pH = 1, (b) pH = 3, (c) pH = 6, (d) pH = 9, and (e) pH = 11 [46].

White *et al.* [43] prepared the emulsion with a mixture of modified silica particle, water, and 2,6-lutidine. They found that slight changes in hydration on the surface of the particle could lead to the change in emulsion structure. Reducing particle hydration would transform the emulsion from lutidine-in-water (L/W) to water-inlutidine (W/L). Stilier *et al.* [44] studied the influence of different surface-modified titanium dioxides on the type and stability of the emulsion. They found that the type of emulsion will change from water/oil to oil/water with the increase in water volume. With the increase in the particle hydrophobicity, the long-term stability of O/W emulsion decreased, while that of W/O emulsion increased.

2.2.2.4 Aqueous phase pH value

The change in pH value of aqueous phase will affect the wettability or electrical properties of the particles, thereby affecting the adsorption behavior of the particles at the oil–water interface, and finally affecting the properties of the Pickering emulsion. Yang *et al.* [45] used positively charged lamellar double hydroxide (LDH) particles as emulsifier and liquid paraffin as oil phase to

prepare emulsion. Their research pointed out that with the increase in pH value, the zeta potential of LDH particles decreased, the contact angle increased (only changed little), and the structural strength of LDHs dispersion increased, and the stability of emulsion improved. By adjusting the pH value of LDHs dispersion, the adsorption capacity of particles on oil-water surface could be regulated. This study proved that by changing the pH value of the LDHs dispersion, the adsorption of LDHs particles at the oil-water interface could be controlled, which in turn affected the stability of the Pickering emulsion. Tang et al. [3] studied the influence of pH change on the stability of the Pickering emulsion by using the self-assembly structure of the Pickering emulsion. They pointed out that the change in pH value would affect the aggregation and dispersion behavior of Janus particles. When pH <7, the surface of Janus particles was acidic and easily protonated, which made the particles more easily wetted by oil phase, thus achieving the stability of W/O Pickering emulsion; When pH >7, acrylic acid would deprotonate to stabilize the Pickering emulsion. Tang et al. believed that this phenomenon was caused by the strong electrostatic charge repulsion between the Janus particles under alkaline conditions. He et al. [46] studied the factors affecting the stability of GO Pickering emulsion. They found that with the increase in pH value (Figure 4), the hydrophilicity of GO increased, the Zeta potential decreased, the surface charge density increased, and electrostatic repulsion between GOs increased. This would destroy the accumulation of GO at the oil–water interface, affect the formation and strength of the interface film, and be detrimental to the stability of the emulsion.

2.2.2.5 Salinity

The salinity of the aqueous phase may directly change the potential of the particle surface, and may also cause flocculation and sedimentation of the particles, which may affect the stability of the Pickering emulsion to a certain extent. Sharma *et al.* [47] found that adding appropriate concentration of NaCl to the flocculated micron-sized silica (SiO₂) could achieve long-term stability and make the nanoparticles (NPs) aggregate, thus enhancing the coagulation stability of the emulsion droplets. Yu *et al.* [48] pointed out that when the salinity of the oil-in-water Pickering emulsion stabilized by Na-montmorillonite was too low or too high, it was not conducive to maintain the viscosity of the Pickering emulsion. The mechanism is shown in Figure 5.

2.2.2.6 Oil phase

The selection of oil phase also has a great influence on the Pickering emulsion, and the main influencing parameters are viscosity and polarity of the oil phase. Binks and Lumsdon [49] used more than a dozen different polar oil phases and hydrophobic particles to prepare emulsions. They found that for some polar oils (such as esters and alcohols), W/O emulsions were formed. But for non-polar oils such as hydrocarbons, even though the particles are more hydrophobic, O/W emulsions are still formed. The reason is mainly related to the influence of adsorption

between oil phase and water phase on the contact angle. The selection of oil phase also has a great influence on the Pickering emulsion, mainly the viscosity and polarity of the oil phase affects the Pickering emulsion. Tsabet and Fradette [40] found that when the oil phase viscosity was lower than 485.5 mPa s, the droplet diameter of emulsion remains unchanged with the change in viscosity, and when the oil phase viscosity is higher than this value, the droplet diameter increases obviously. Chesters [50] gave the following explanation for this. When the viscosity of oil phase is very high, the high viscosity of oil reduces the fluidity of the droplet interface, prevents the formation of liquid film and the adsorption of particles on it, and slows down the adsorption speed, resulting in poor emulsion stability and large droplets.

There are many factors that affect the Pickering emulsion, such as particle type, particle shape and size, dispersion mode, dispersion time, temperature, pressure, *etc.* [46,51–53]. When preparing or using the Pickering emulsion, a more detailed experiment should be carried out to find the best formula.

3 Application of Pickering emulsion in oil and gas field

3.1 Drilling

The main function of drilling fluid are to clean the bottom hole, absorb cuttings, cool and lubricate the drill bit and drill string, form mud cake, and seal the well wall. [54–57]. Drilling fluid is a typical colloidal dispersion system, which can be divided into water-based drilling fluid, oil-based drilling fluid, and gas drilling fluid according to the dispersion medium. Water-based drilling fluid is suitable for reservoirs with low temperature and low pressure, while oil-based drilling fluid is suitable for reservoirs

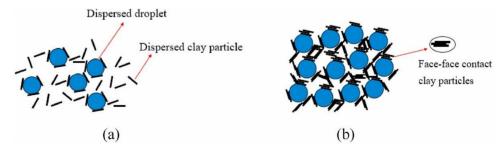


Figure 5: Pickering emulsion stabilized by clay at very low (a) and very high (b) salinities [48].

with high temperature and high pressure [58-64]. Oilbased drilling fluid is a complicated W/O Pickering emulsion system, which is stabilized by surfactant and NPs. Adding solid particles to the drilling fluid can improve the rheological properties of the fluid, reduce filtration loss and friction coefficient, and improve heat transfer rate. With the deep development of exploration and development of oil and gas resources, reservoirs are becoming more and more complex, and the requirements of oilbased drilling fluid are getting higher and higher. In the application of oil-based drilling fluid, the stability of the drilling fluid emulsion is of great importance. The excellent stability of Pickering emulsion just provides a solution to improve the stability of oil-based drilling fluid.

Liu et al. [65] developed a Pickering emulsion stabilized by high-temperature-resistant organoclay and moderately hydrophobic nano-SiO2 to solve the problems of poor thermal stability and unsatisfactory application of the Pickering emulsion in high temperature formation environment. They pointed out that the Pickering emulsion was easy to prepare and friendly to the environment, and kept good rheological properties after hot rolling tests at 220°C, which showed great application potential in high-temperature-resistant drilling fluids. The research by Ai et al. [66] also got similar results. NP-stabilized W/O emulsion could increase the viscosity and shear resistance of the drilling fluid, and greatly improve the stability of the drilling fluid. The drilling fluid developed by Ai et al. could be used in shale reservoirs. There are also many patents related to the preparation of drilling fluid by the Pickering emulsion [67-69]. Dargahi-Zaboli et al. [70] formed a stable W/O invert emulsion with hydrophobic nano-SiO₂ NPs for drilling, and pointed out that the properties and content of NPs could be adjusted to improve the performance of drilling fluid, so that the emulsion still had good thermal stability at 120°C. Sharma and Sangwai [71] prepared Pickering emulsion with SiO₂, clay, sodium dodecyl sulfate (SDS), polyacrylamide, and sodium chloride. They pointed out that the emulsion had good viscoelasticity under high pressure and high temperature conditions, and was suitable for drilling fluid at high temperature and high pressure. Aiming at the damage of oil-based drilling fluid in oil well completion, Huo et al. [72] prepared bentonite solid particles with different surface wettability through the in situ activation technology by changing the concentration of the surfactant cetyltrimethylammonium bromide (CTAB), and studied the phase transition mechanism of CTAB inducing bentonite emulsion rotation. The experimental results showed that the wettability of bentonite particles can be changed by changing CTAB concentration, and then the bentonite emulsion can be induced to undergo twophase inversion behaviors. The research on application performance indicated that the reversible emulsion oil-based drilling fluid system has good thermal stability with small filtration, so as to avoid the damage of traditional oilbased drilling fluid in oil well completion. Halliburton Energy Services has developed a Pickering foam drilling fluid, which can be pumped through a drill string, and extend the wellbore through the subterranean formation [73]. Cui et al. prepared Pickering emulsion with nano-Al₂O₃ and diesel oil. This emulsion had strong stability and could be stored for more than 1 year at room temperature. The emulsion could be demulsified by adding a small amount of cationic surfactant, which had potential applications in diesel oil transportation and drilling fluid preparation [74].

Pickering emulsion can also be used to cool the drill bit. As the specific surface area of drilling fluid molecules increases, the heat exchange rate increases. The NPs have a very high specific surface area just to improve the ability of the drill bit to transfer heat. Farshad et al. [75] used nano titanium dioxide and carbon nanotubes to change the thermal properties of the drilling fluids. They pointed out that the ratio of convection heat transfer and conduction heat transfer of the drilling fluid containing carbon nanotubes was about 30% higher than that of the drilling fluid containing titanium dioxide NPs. The convective heat transfer coefficient increased from 2,950 W/m².°C to 3,360 W/m².°C by decreasing the average size of the carbon nanotubes from 76 to 54 nm. Their research showed that Pickering emulsion could improve the thermal efficiency of the liquid as the transport fluid.

3.2 Enhanced oil recovery

3.2.1 Oil displacing agent

Traditional emulsion flooding is to inject the emulsion formed by emulsifier (surfactant or polymer with surface activity) and crude oil under high-speed stirring into the formation to displace the residual oil after water flooding. Indoor and on-site practice have shown that emulsion flooding can effectively reduce the amount of residual oil in the formation [76-78]. However, the traditional emulsion cannot be widely used in oil displacement because of its poor long-distance migration performance and not good enough thermal stability. Pickering emulsion formed by NPs as emulsifier can overcome the above difficulties and be used as oil displacement agent. Because nano-SiO₂ and nano-clay are relatively easy to prepare and cheap, there were many reports about the use of nano-SiO₂ and nano-clay as emulsifiers when studying the use of Picketing emulsion in oil fields.

Pickering emulsion with solid particles as emulsifier provides more options for emulsion to enhance oil recovery. The NP-stabilized solvent-based emulsion studied by Kumar et al. [79] can easily pass through the pore throat size of the reservoir, which is helpful to improve the recovery of heavy oil. Jia et al. [80] studied multiple O/W/O Pickering emulsions stabilized by amphiphilic Janus-SiO2 NPs (Janus-C12), which showed excellent EOR performance in core displacement experiments, which can improve oil recovery by 27.2%. Mo et al. [81] modified kaolinite with dimethyl sulfoxide (DMSO) and 3-aminopropyltrimethoxysilane (APTMS) and used it as emulsifier to prepare Pickering emulsion, which can maintain stability for at least 60 days and has great potential application in oil recovery in the field. Wang et al. [82] pointed out that Pickering emulsion stabilized by cellulose nanocrystals (CNCs) has good stability at 100°C. They believed that this emulsion could reduce costs and facilitate field applications of emulsion flooding in heavy oil recovery. Li et al. [83] studied Pickering emulsion with clay particles (sodium montmorillonite) as emulsifier, which can be used for development of high salinity reservoirs. The experimental results show that after Pickering emulsion flooding, the recovery ratio increased from 67% (water flooding) to more than 80%. Radnia et al. [84] prepared a stable Pickering emulsion with GO, and studied the effects of GO concentration, salinity of aqueous phase, asphaltene concentration of organic phase on emulsion stability, and the interfacial tension between the organic phase and the aqueous phase, and explored its potential application in enhancing oil recovery. The results showed that the concentration of GO and asphaltene were inversely proportional to the interfacial tension. And compared with the O/W emulsion, the O/W emulsion was more suitable for enhanced oil recovery (EOR). W/O emulsion was stabilized when the asphaltene concentration was 1.5% or higher. And an increase in the water/oil ratio caused the inversion in the emulsion type yielding an O/W emulsion. When the salinity was greater than 1 wt%, some droplets would change into W/O/W type multiple emulsion. When the concentration of GO was 1 mg/mL and the concentration of asphaltene was 0.05 wt%, the droplet size of the emulsion was the smallest. Chen et al. [85] modified the prepared high crystalline α-zirconium phosphate (α-ZrP) nanometers with octadecyltrichlorosilane (OTS) to obtain hydrophobic nanosheets, and prepared Pickering emulsion using this material as an emulsifier. The droplet diameter of the Pickering emulsion was inversely proportional to the concentration of NPs. When the concentration

was greater than 100 mg/L, the change in nanosheets' concentration had almost no effect on the droplet diameter; after the core wettability changed, the viscosity of the Pickering emulsion increased, which reduced the fluidity ratio and improved the sweep efficiency, so as to improve the recovery.

Many scholars have studied the stability of the Pickering emulsion by using solid particles and surfactants. The research shows that the emulsion formed by solid particles and surfactant shows excellent stability, which is not available by using solid particles or surfactant alone [86.87]. When solid particles and surfactant are used as emulsifiers at the same time, the surfactant can change the surface properties of the NPs through electrostatic adsorption or repulsion, resulting in synergy, thus improving the stability of the emulsion. In recent years, Pickering emulsion, which is co-stabilized by particles and surfactants, has been actively studied in the field of EOR. Akshit et al. [88] compared the emulsion stabilized by hydrophilic silica NPs with emulsion that was stabilized by surfactant at 80°C. They found that the nanofluid containing only NPs is easier to form emulsion than the surfactant aqueous solution and nanoparticle/surfactant nanofluid, and the required concentration of NPs is lower than that of the surfactant. Kim et al. [89] studied emulsions stabilized by different types of surfactants and nano-SiO₂ particles. They found that the emulsion stabilized by cationic surfactant and nano-SiO₂ has the best stability, and have a good mobility control effect on water flooding reservoirs. Pei et al. [90,91] applied the emulsion stabilized by nano-SiO₂ and cetyl trimethyl ammonium bromide to develop heavy oil with viscosity of 325 mPas (50°C), which can improve oil recovery by more than 30%. Their research showed that the emulsion has a good potential to improve the recovery of heavy oil by water flooding.

Some researchers have also studied the application potential of Pickering emulsion stabilized by particles, surfactants, and/or polymers in improving oil recovery. Sharma et al. [11] prepared stable emulsion with nano-SiO₂, SDS, polyacrylamide, and lubricating oil. Using this emulsion, Berea core flooding was carried out for heavy oil with viscosity of 161 mPas, and the results showed that the recovery efficiency was increased by more than 23%. Khalil et al. [92] functionalized superparamagnetic nanoparticles (SPN) with oleic acid and polyacrylamide (PAM), and compared the effects of the particles before and after surface functionalization on improving the secondary or tertiary recovery capacity of the sand layer. The results showed that the concentration of NPs and the types and structure of surface modifiers had significant effects on the viscosity and mobility of the Pickering emulsion. The hydrophilicity of NPs depends on the type and structure of surface modification. If the suspended SPN-PAM can be used as a fluidity control and wettability modifier, it can promote the formation and separation pressure of Pickering emulsion, and thus increase the oil recovery. Kumar *et al.* [13] prepared stable O/W surfactant-polymer nanoparticles (surfactant-polymer-nanoparticles (SPN)) Pickering emulsion by using light mineral oil, carboxy methyl cellulose (CMC) and SiO₂ NPs, and anionic surfactant. The emulsion had good thermal stability and its viscosity was relatively stable in the range of 30–100°C. After conventional water flooding, additional recovery of more than 24% was observed by Pickering emulsion.

Some studies have applied stimuliresponsive Pickering emulsion to oil production. Liang *et al.* [93] used Fe₃O₄ NP and poly[2-(dimethylamino)ethyl methacrylate] as raw materials, and synthesized Pickering emulsion which was responsive to pH and magnetism by ultrasonic-assisted *in situ* precipitation. Pickering emulsion could be rapidly emulsified/demulsified for more than six cycles, which had great application prospects in intelligent oil recovery. A summary on Pickering emulsion for enhanced oil recovery is given in Table 1.

To sum up, Pickering emulsion is an effective method for developing high temperature, high salinity, and heavy oil reservoirs.

3.2.2 Profile modification agent

The problem of production of associated water from the oil wells is common in the oilfield development. It is

necessary to implement water plugging in production wells and adjust the water injection profile of water injection wells. It is more difficult to profile control and water shutoff after the oilfield enters the period of high water cut or ultra-high water cut stage. Pickering emulsion based on nanomaterials shows good application prospects.

Xu et al. [95] reported that injecting O/W emulsions stabilized with NPs or surfactants is a promising option for (EOR) in harsh-condition reservoirs. They used microfluidic experiments to confirm that interaction between droplets caused by NPs in the thin liquid film between neighboring oil/water interfaces is enhanced, so the flow of emulsions stabilized by a NP/surfactant mixture shows droplet accumulation in high permeability regions, which was denser than the region stabilized by surfactant alone. Li et al. [83] prepared Pickering emulsion with clay particles as emulsifier, and tested its performance for water flooding under high salinity conditions. The results showed that clay particles were good emulsifiers, and stable emulsions could be formed at low concentrations. After water flooding in sandpack with higher permeability, the injection of Pickering emulsion mobilized more than 10% residual oil. The oil recovery ratio could be increased from 67% (water flooding) to over 80% by using Pickering emulsion for oil displacement. The emulsified gel system (Pickering emulsion) studied by Saikia et al. [96] could be effectively used in high temperature reservoir. The Pickering emulsion could maintain good stability at 105°C and provide required water flow resistance, and allow easy production of diesel oil in the core flooding experiment. The above research indicates that Pickering emulsion can be applied to harsh reservoirs such as high temperature and high salt to adjust water-sucked section.

Table 1: Pickering emulsion as oil displacement agent for EOR

| Materials | Particles | References |
|--------------------------|---|------------|
| Particles | SiO ₂ | [78] |
| | Amphiphilic Janus-SiO ₂ NPs | [79] |
| | Modified kaolinite with dimethyl sulfoxide (DMSO) and 3-aminopropyltrimethoxysilane (APTMS) | [80] |
| | Cellulose nanocrystals (CNCs) | [81] |
| | Sodium montmorillonite | [82] |
| | Graphene oxide | [83] |
| | High crystalline α -ZrP nanometers with OTS | [84] |
| Particles + surfactant | SiO ₂ and anionic surfactant | [87] |
| | SiO ₂ , AlOOH, and TX-100 | [86] |
| | SiO ₂ and cethyltrimethylammonium bromide | [90,91] |
| Particles + polymer | Fe ₃ O ₄ NP and poly[2-(dimethylamino)ethyl methacrylate] | [93] |
| | Functionalized SPN with OA and PAM | [92] |
| Particles + surfactant + | Light mineral oil, CMC, SiO ₂ NPs, and anionic surfactant | [13] |
| polymer | SiO ₂ , clay, SDS, and PAM | [94] |

3.2.3 Fracturing fluid

Emulsion fracturing fluid is a kind of fracturing fluid system developed in the 1970s which can be divided into W/O fracturing fluid and O/W fracturing fluid [97–99]. Among them, the water-in-oil emulsion fracturing fluid is suitable for the fracturing with water sensitive, low pressure, and low-permeability reservoirs [100–104]. Because of its high viscosity, strong sand suspension ability, low filtration loss, less residual sand, and low cost, it has developed rapidly in recent decades [103]. Compared with W/O emulsion fracturing fluid, Pickering emulsion has better temperature resistance and better stability when injected. In addition, if fracturing is performed in unconventional reservoir, the solid particles carried by Pickering emulsion can be adsorbed in the formation, which may achieve the effect of proppant [104].

Roberts et al. [105] studied the fracturing conditions and three different two-phase flow models of Pickering emulsion stabilized by surface-modified nanomaterials in Pickering emulsion fracturing, and conducted fracturing experiments in Boise block, and achieved certain results. Yang et al. [106] used Pickering emulsion stabilized by SiO₂ nanomaterials for fracturing construction. It was found that proppant can be better suspended and the conductivity after fracturing is also more stable. Acid fracturing treatment is usually more successful and effective than hydraulic fracturing [107]. Pickering emulsion can also be used as an emulsified acid for acid fracturing. Emulsified acids have been used to improve the recovery of oil and gas in carbonate reservoirs through acid fracturing. Huang et al. [108] pointed out that very small particles, such as colloidal clay particles and/or NPs, can increase the stability of the emulsified acids over an elevated temperature range.

3.3 Sand control

Sand production in the reservoir has been acknowledged as a critical problem related to oil and gas fields' exploitation for many years because it causes many serious problems in oil and gas production [109]. Sand production not only easily leads to production reduction and shutdown of oil wells, but also aggravates the wear of ground and downhole equipment, and even causes casing damage and oil well scrapping in severe cases. In order to ensure stable and high production in oil fields, some effective measures must be taken to solve the sand production of oil wells. Resin sand control technology is

one of the common technical means for chemical sand control [110,111]. Although the commonly used sandfixing resin of resin sand control has high consolidation strength, compared with Pickering emulsion resin, it has higher density, higher cost, poor permeability of the solidified body, and cannot meet the demand of the heterogeneous reservoir. Wang [112] selected nano-SiO₂ as emulsifier, amino resin solution as aqueous phase, and kerosene as oil phase, and preferred a Pickering emulsion resin system. This emulsion sand consolidation system is especially suitable for silt fine sand reservoirs at 60°C. After being solidified at 60°C for 12 h, the strength of the consolidated core could reach 4.61-5.82 MPa, and the permeability could reach $3.12-5.34 \,\mu\text{m}^2$. This Pickering emulsion resin system had excellent water resistance, oil resistance, alkali resistance, and salt resistance. Ikem et al. [113] added nonionic surfactant and dispersant to premade Pickering emulsions that were stabilized by OA-modified SIO₂ particles. They believed that this emulsion as an alternative to gravel packing can prepare void-free and mechanically sound permeable barriers in subterranean formations. Wang et al. prepared the low-temperature-emulsified sand consolidating agent with SIO₂ NPs as emulsion stabilizer, cementing agent (melamine formaldehyde resin solution), curing agent (ammonium chloride), and coupling agent (silane coupling agent KH-550) as water phase and kerosene as oil phase. The sand consolidation agent could not only meet the sand control requirements of low-temperature formations, but also had the characteristics of high temperature resistance. It had a wide range of applications in sand control [114].

3.4 Petroleum wastewater treatment

Petroleum wastewater or oilfield wastewater refers to the water produced from oil wells with crude oil, including oilfield-produced water, sewage generated during drilling, and other forms of oily sewage. Oilfield-produced water is produced in the process of water flooding, which contains a large number of refractory organic pollutants and high concentration ions. If it fails to meet the standards of reinjection and direct discharge, it needs to be treated until it reaches the discharge standard [115,116]. The produced water of sulfur-containing oil fields contains hydrogen sulfide, which has corrosive effects. If the produced water of sulfur-containing oil fields is directly connected to the produced water treatment unit of oil field, it will cause corrosion of pipelines and equipment,

and cause hidden dangers to safety production [117]. Meanwhile, the volatilization and precipitation of hydrogen sulfide will seriously affect personal safety. Therefore, it is necessary to remove sulfur from the produced water of sulfur-containing oil fields before treatment to ensure safe production. Dou and Wang [118] prepared an amphiphilic catalyst for oxidative desulfurization by loading the phosphotungstic active component $(PW_{12}O_{40}^{3-})$ on the bi-component carbon-organosilica Janus particles, and investigated its desulfurization ratio. The results showed that the final desulfurization ratio of the stable Pickering emulsion in the *n*-octane/acetonitrile system was 99.86%. This emulsion exhibited the best desulfurization performance, and compared with the conventional bi-phase system using H₃PW₁₂O₄₀ as catalyst the desulfurization ratio increased sharply.

Pickering emulsion can also be used for oily sewage treatment. Some studies have pointed out that the switching Pickering emulsion has super stability, which can achieve rapid demulsification, recovery of internal phase, and the recycling of oil phase by triggering mechanism [119]. He et al. [120] prepared magnetically responsive Janus NPs by using hydrophobic ethyl cellulose, hydrophilic CMC, and Fe₃O₄ NPs as raw materials. This material could effectively separate emulsified water from water-in-crude oil emulsions and the oil from oily wastewater under an external magnetic field, and can be reused for five times. Shang et al. [121] prepared a cationic emulsion water clarifier by emulsion polymerization method using diallyl dimethyl ammonium chloride as cationic monomer, styrene and butyl acrylate as hydrophobic monomers, hexadecyl trimethyl ammonium bromide and polyoxyethylene octyl phenol ether as emulsifiers, and ammonium persulfate as initiator. The prepared O20 emulsion water clarifier had good oil removal effect. When the concentration was 30 mg/L, the oilfield wastewater could be reduced from 295 mg/L to 13 mg/L. Zhang et al. [122] prepared the dual-responsive Pickering emulsion by using negatively charged Fe₃O₄ NPs in combination with 1-dodecyl-1H-imidazole (C₁₂mim) as stabilizers. This Pickering emulsion was CO₂/N₂ and magnetic responsive, and could be used for oily sewage treatment.

4 Conclusion

In the petroleum industry, Pickering emulsion has many advantages and has great research value in the application of harsh reservoirs. Pickering emulsion has been effectively used in drilling, oil displacement, profile control and water shutoff, fracturing, sand control, petroleum wastewater treatment, etc. However, Pickering emulsion is still a relatively new field for the petroleum industry, which has not been widely used and still has great development potential. With the development of nanomaterial technology and in-depth study of Pickering emulsion, the application scope of Pickering emulsion in the petroleum industry will be expanded.

Pickering emulsion has good stability, which is not conducive to demulsification. In order to make it fully and widely used in the petroleum field, the demulsification technology of Pickering emulsion will be an important research direction. For example, the environmentally responsive Pickering emulsion will better promote the application of Pickering emulsion in the oil field.

In addition, developing a cheap and efficient Pickering emulsifier, which can better control the rheological property of the emulsion, will be the key to the wide application of Pickering emulsion in the oil and gas field. When Pickering emulsion is used in petroleum industry, the cost control is an important consideration. From laboratory research results to final field application, researchers need to make joint efforts.

Funding information: National Natural Science Foundation of China (No. 51804045), the Science & Technology Program of Changzhou (No. CJ20200066), and Jiangsu Key Laboratory of Oil-gas Storage and Transportation Technology (No. CDYQCY202001).

Author contributions: All authors have accepted responsibility for the entire content of this article and approved its submission.

Conflict of interest: The authors state no conflict of interest.

References

- [1] Spencer P. CXCVI.-Emulsions. J Chem Soc. 1907;91:2001-21.
- [2] Yang F, Wang J, Lan Q, Sun DJ, Li CX. Research progress on pickering emulsions. Prog Chem. 2009;21(Z2):1418-26.
- [3] Tang JT, Quinlan PJ, Tam KC. Stimuli-responsive pickering emulsions: recent advances and potential applications. Soft Matter. 2015;11(18):3512-29.
- [4] Wu J, Ma GH. Recent studies of pickering emulsions: particles make the difference. Small. 2016;12(34):4633-48.
- Danae GO, Celine P, Julien C, Mikhael B, Philippe M. [5] Pickering the development trend of emulsion-particle morphology and its application. Engineering-Prc. 2020;6(04):468-99.
- [6] Zhang JF, Zhang J, Wang S, Yi T. Development of an oral compound pickering emulsion composed of nanocrystals of

- poorly soluble ingredient and volatile oils from traditional Chinese medicine. Pharmaceutics. 2018;10(4):170.
- [7] Han J, Chen FL, Gao CC, Zhang Y, Tang XZ. Environmental stability and curcumin release properties of Pickering emulsion stabilized by chitosan/gum arabic nanoparticles. Int J Biol Macromol. 2020;157:202-11.
- Yan HQ, Chen XQ, Song HW, Li JH, Feng YH. Synthesis of bacterial cellulose and bacterial cellulose nanocrystals for their applications in the stabilization of olive oil Pickering emulsion. Food Hydrocolloid. 2017;72:127-35.
- Wei YS, Niu ZC, Wang FQ, Feng K, Zong MH, Wu H. A novel pickering emulsion system as the carrier of tocopheryl acetate for its application in cosmetics. Mater Sci Eng C. 2020:109:110503.
- Liu DW, Xue N, Wei LJ, Zhang Y, Qin ZF, Li XK, et al. Surfactant [10] assembly within pickering emulsion droplets for fabrication of interior-structured mesoporous carbon microspheres. Angew Chem. 2018;130(34):11065-70.
- Sharma T, Velmurugan N, Patel P, Chon BH, Sangwai JS. Use of oil-in-water pickering emulsion stabilized by nanoparticles in combination with polymer flood for enhanced oil recovery. Petrol Sci Technol. 2015;33(17-18):1595-1604.
- [12] AfzaliTabar M, Alaei M, Khojasteh RR, Motiee F, Rashidi AM. Preference of multi-walled carbon nanotube (MWCNT) to single-walled carbon nanotube (SWCNT) and activated carbon for preparing silica nanohybrid pickering emulsion for chemical enhanced oil recovery (C-EOR). J Solid State Chem. 2017;245:164-73.
- [13] Kumar N, Gaur T, Mandal A. Characterization of SPN Pickering emulsions for application in enhanced oil recovery. J Ind Eng Chem. 2017;54:304-15.
- Pal N, Mandal A. Oil recovery mechanisms of pickering nanoemulsions stabilized by surfactant-polymer-nanoparticle assemblies: a versatile surface energies' approach. Fuel. 2020;276:118138.
- [15] Wang Z, Babadagli T, Maeda N. Preliminary screening and formulation of new generation nanoparticles for stable pickering emulsion in cold and hot heavy-oil recovery. SPE Res Eval Eng. 2021;24(01):66-79.
- Ahmed A, Sharifi Haddad A, Rafati R, Bashair A, AlSabagh AM, Aboulrous AA. Developing a thermally stable ester-based drilling fluid for offshore drilling operations by using aluminum oxide nanorods. Sustainability-Basel. 2021;13(6):3399.
- Wang XL, Zhou WZ, Cao J, Liu WC, Zhu SQ. Preparation of core-shell CaCO₃ capsules via Pickering emulsion templates. J Colloid Interface Sci Sustain-Basel. 2012;372(1):24-31.
- [18] Xiao J, Li Y, Huang Q. Recent advances on food-grade particles stabilized Pickering emulsions: Fabrication, characterization and research trends. Trends Food Sci Tech. 2016;55:48-60.
- Song XY, Zheng F, Ma FL, Kang HX, Ren HT. The physical and [19] oxidative stabilities of pickering emulsion stabilized by starch particle and small molecular surfactant. Food Chem. 2020;303:125391.
- Brunier B, Sheibat-Othman N, Chniguir M, Chevalier Y, Bourgeat-Lami E. Investigation of four different laponite clays as stabilizers in pickering emulsion polymerization. Langmuir. 2016;32(24):6046-57.

- Voorn DJ, Ming W, Van HAM. Polymer-clay nanocomposite latex particles by inverse pickering emulsion polymerization stabilized with hydrophobic montmorillonite platelets. Macromolecules. 2006;39(6):2137-43.
- [22] Gudarzi MM, Sharif F. Self-assembly of graphene oxide at the liquid-liquid interface: a new route to the fabrication of graphene based composites. Soft Matter. 2011;7(7):3432-40.
- [23] Zhang Y, Lu HS, Wang BG, Wang N, Liu DF. pH-responsive non-pickering emulsion stabilized by dynamic covalent bond surfactants and nano-SiO₂ particles. Langmuir. 2020;36(50):15230-9.
- [24] Zhou YY, Shen F, Zhang SD, Zhao QQ, Xu Z, Chen HL. Synthesis of methyl-capped TiO2-SiO2 Janus pickering emulsifiers for selective photodegradation of water-soluble dyes. ACS Appl Mater Inter. 2020;12(26):29876-82.
- [25] Yang YQ, Fang ZW, Chen X, Zhang WW, Xie YM, Chen YH, et al. An overview of Pickering emulsions: solid-particle materials, classification, morphology, and applications. Front Pharmacol. 2017;8:287.
- [26] Tian XW, Ge XH, Guo MY, Ma JX, Meng ZQ, Lu P. An antimicrobial bio-based polymer foam from ZnO-stabilised pickering emulsion templated polymerisation. J Mater Sci. 2021;56(2):1643-57.
- Sofla MJD, Norouzi-Apourvari S, Schaffie M. The effect of [27] magnetic field on stability of conventional and pickering water-in-crude oil emulsions stabilized with fumed silica and iron oxide nanoparticles. J Mol Liq. 2020;314:113629.
- [28] Xu J, Yang B. Nanostructured phase-changeable heat transfer fluids. Nanotechnol Rev. 2013;2(3):289-306.
- [29] Zhu P, Wang F, Ding YF, Zhang SM, Gao C, Liu P, et al. Double phase inversion of pickering emulsion induced by magnesium hydroxide nanosheets adsorbed with sodium dodecyl sulfate. Langmuir. 2021;37(14):4082-90.
- [30] Kim YJ, Liu YD, Seo Y, Choi HJ. Pickering-emulsion-polymerized polystyrene/Fe₂O₃ composite particles and their magnetoresponsive characteristics. Langmuir. 2013;29(16):4959-65.
- Chevalier Y, Bolzinger MA. Emulsions stabilized with solid [31] nanoparticles: pickering emulsions. Colloid Surface A. 2013:12:23-34.
- Bergström L. Colloidal particles at liquid interfaces. In: [32] Binks BP, Horozov TS, editors.. Structure and Formation of Particle Monolayers at Liquid Interfaces. Massachusetts: Cambridge University Press; 2006. p. 186-224
- [33] Meirelles AAD, Costa ALR, Cunha RL. Cellulose nanocrystals from ultrasound process stabilizing O/W Pickering emulsion. Int J Biol Macromol. 2020;158:75-84.
- [34] Su JQ, Guo Q, Chen YL, Dong WX, Mao LK, Gao YX, et al. Characterization and formation mechanism of lutein pickering emulsion gels stabilized by β-lactoglobulin-gum arabic composite colloidal nanoparticles. Food Hydrocolloid. 2020;98:105276.
- Mao XH, Yang DL, Xie L, Li Q, Tang T, Zhang H, et al. Probing [35] the interactions between pickering emulsion droplets stabilized with pH-responsive nanoparticles. J Phys Chem B. 2021;125(26):7320-31.
- [36] Bink BP. Particles as surfactants: similarities and differences. Curr Opin Colloid In. 2020;7(1):21-41.
- Lagaly G, Reese M, Abend S. Smectites as colloidal stabili-[37] zers of emulsion: I. preparation and properties of emulsions

- with smectites and nonionic surfactants. Appl Clay Sci. 1999;14(1):83-103.
- Lagaly G, Reese M, Abend S. Smectites as colloidal stabili-[38] zers of emulsion: II. rheological properties of smectite-laden emulsion. Appl Clay Sci. 1999;14(5):279-98.
- Gan L, Zhang C, Zhang L, Niu YL, Zhang ZW. Prediction and rapid evaluation of long-term physical stability of emulsions. China Surfactant Deterg & Cosmetics. 2015;45(8):452-6.
- [40] Tsabet E, Fradette L. Effect of the properties of oil, particles, and water on the production of pickering emulsions. Chem Eng Res Des. 2015;97:9-17.
- Aveyard R, Binks BP, Clint JH. Emulsions stabilised solely by colloidal particles. Adv Colloid Interface Sci. 2003;100-102:503-46.
- [42] Frelichowska J, Bolzinger MA, Chevalier Y. Effects of solid particle content on properties of o/w pickering emulsions. J Colloid Interf Sci. 2010;351(2):348-56.
- White KA, Schofield AB, Wormald P, Joseph WT, Bernard PB, Paul SC. Inversion of particle-stabilized emulsions of partially miscible liquids by mild drying of modified silica particles. J Colloid Interface. 2011;359(1):126-35.
- Stiller S, Gers-Barlag H, Lergenmueller M, Pflücker F, Schulz J, Wittern KP, et al. Investigation of the stability in emulsions stabilized with different surface-modified titanium dioxides. Colloid Surface A. 2004;232(2-3):261-7.
- [45] Yang F, Quan N, Qiang L, Sun DJ. Effect of dispersion pH on the formation and stability of Pickering emulsions stabilized by layered double hydroxides particles. J Colloid Interf Sci. 2007;306(2):285-95.
- [46] He YQ, Wu F, Sun XY, Li RQ, Guo YQ, Li CB, et al. Factors that affect pickering emulsions stabilized by graphene oxide. ACS Appl Mater Inter. 2013;5(11):4843-55.
- Sharma T, Kumar GS, Chon BH, Sangwei JS. Thermal stability of oil-in-water pickering emulsion in the presence of nanoparticle, surfactant and polymer. J Ind Eng Chem. 2015;22:324-34.
- Yu L, Li S, Stubbs LP, Lau HC. Rheological investigation of clay-stabilized oil-in-water Pickering emulsions for potential reservoir applications. J Petrol Sci Eng. 2021;204(21):108722.
- Binks BP, Lumsdon SO. Effects of oil type and aqueous phase composition on oil-water mixtures containing particles of intermediate hydrophobicity. Chem Phys. 2000;2(13):2959-67.
- Chesters AK. The modelling of coalescence processes in fluid-liquid dispersions: a review of current understanding. Chem Eng Res Des. 1991;69(4):259-70.
- [51] Tang MY, Wu T, Xu XY, Zhang L, Wu F. Factors that affect the stability, type and morphology of Pickering emulsion stabilized by silver nanoparticles/graphene oxide nanocomposites. Mater Res Bull. 2014;60:118-29.
- [52] Giakoumatos EC, Aloi A, Voets IK. Illuminating the impact of submicron particle size and surface chemistry on interfacial position and pickering emulsion type. Nano Lett. 2020;20(7):4837-41.
- Wang Z, Wang Y. Tuning amphiphilicity of particles for controllable pickering emulsion. Materials. 2016;9(11):903.
- Skalle P. Drilling fluid engineering. In: Skalle P, editor. Drilling fluid engineering 8 introduction 1. Internet Archive; 2018. p. 11-26

- [55] Saboori R, Sabbaghi S, Mowla D, Soltani A. Decreasing of water loss and mud cake thickness by CMC nanoparticles in mud drilling. Int J Nano Dimen. 2012;3(2):101-4.
- [56] Elkatatny S. Real-time prediction of rheological parameters of KCL water-based drilling fluid using artificial neural networks. Arab J Sci Eng. 2017;42(4):1655-65.
- [57] Elkatatny S. Mitigation of barite sagging during the drilling of high-pressure high-temperature wells using an invert emulsion drilling fluid. Powder Technol. 2019;352:325-30.
- [58] Marinescu P, Young S, Iskander GR. New generation ultrahigh temperature synthetic-based drilling fluid; development and best practices for extreme conditions and ecd management. The Abu Dhabi International Petroleum Exhibition and Conference, 2014 Nov 10-13; Abu Dhabi, UAE: SPE Res Eval & Eng; 2014.
- Srungavarapu M, Patidar KK, Pathak AK, Mandal A. [59] Performance studies of water-based drilling fluid for drilling through hydrate bearing sediments. Appl Clay Sci. 2018;152:211-20.
- [60] He Y, Long Z, Lu JS, Shi LL, Yan W, Liang DQ. Investigation on methane hydrate formation in water-based drilling fluid. Energ Fuel. 2021;35(6):5264-70.
- [61] Nikolaev NI, Tianle L, Zhen W, Jiang GS, Sun JX, Zheng MM, et al. The experimental study on a new type low temperature water-based composite alcohol drilling fluid. Procedia Eng. 2014;73:276-82.
- Taugbol K, Gunnar F, Prebensen OI, Kaare S, Omland TH, [62] Svela PE, et al. Development and field testing of a unique high temperature and high pressure (HTHP) oil based drilling fluid with minimum rheology and maximum sag stability. The SPE Offshore Europe Oil and Gas Exhibition and Conference, 2005 Sep 6-9; Aberdeen, United Kingdom: SPE Res Eval & Eng; 2005.
- [63] Zhao SY, Yan JN, Shu Y, Zhang HX. Rheological properties of oil-based drilling fluids at high temperature and high pressure. J Cent South Univ T. 2008;15(1):457-61.
- Xu ZM, Song XZ, Li GS, Zhu ZP, Zhu B. Gas kick simulation in oil-based drilling fluids with the gas solubility effect during high-temperature and high-pressure well drilling. Appl Therm Eng. 2019;149:1080-97.
- [65] Liu R, Pu XL, Tao HZ, Chen K, Guo WJ, Luo D, et al. Pickering emulsion stabilized by organoclay and intermediately hydrophobic nanosilica for high-temperature conditions. Colloid Surface A. 2020;610:125694.
- [66] Ai JW, Pang M, Chen F, Luo TT, Tao HZ. Effect of DSW-S nanoparticle on the stability of oil-based drilling fluid. Oilfield Chem. 2016;33(1):5-8.
- [67] Cui ZG, Lin Q, Xu MD, Pei XM, Jiang JZ, Song BL. Ultra-stable pickering diesel emulsion and preparation method thereof. CN Pat. CN109929635B: June 2020.
- [68] Tatyana VK, Jody MB, Alwattari A, Pickering foam drilling fluids, US Pat. US11053425B2: 2017.
- Jones TA, Clark DE, Quintero L, Ewen BR. Method of removing [69] an invert emulsion filter cake after the drilling process using a single phase microemulsion. US Pat. US7134496B2: 2004.
- [70] Dargahi-Zaboli M, Sahraei E, Pourabbas B. Hydrophobic silica nanoparticle-stabilized invert emulsion as drilling fluid for deep drilling. Petrol Sci. 2017;14(01):105-15.

- [71] Sharma T, Sangwai JS. Effects of electrolytes on the stability and dynamic rheological properties of an oil-in-water pickering emulsion stabilized by a nanoparticle-surfactantpolymer system. Ind Eng Chem Res. 2015;54(21):5842-52.
- Huo JH, Zhang R, Yang L. Phase transition mechanism of CTAB inducing bentonite emulsion and its application in reversible emulsification oil-based drilling fluids. Acta Petrol Sin. 2018:39(001):122-8.
- Alwattari A, Burks JM, Khamatnurova TV, Pickering foam drilling fluids, US Pat. US2020270504A1: August 2020.
- Cui ZG, Lin Q, Xu MD, Pei XM, Jiang JZ, Song BL, Ultra-stable pickering diesel oil emulsion and its preparation, CN Pat. CN109929635B: June 2020.
- [75] Farshad F. Experimental investigation of thermo-physical properties of drilling fluid integrated with nanoparticles: Improvement of drilling operation performance. Powder Technol. 2021;384:125-31.
- Feng HS, Kang WL, Zhang LM, Chen J, Li Z. Experimental study on a fine emulsion flooding system to enhance oil recovery for low permeability reservoirs. J Petrol Sci Eng. 2018;171:974-81.
- Zhou YZ, Yin DY, Cao R, Zhang CL. The mechanism for pore-[77] throat scale emulsion displacing residual oil after water flooding. J Petrol Sci Eng. 2018;163:519-25.
- [78] Kar T, Hascakir B. Effect of solvent type on emulsion formation in steam and solvent-steam flooding processes for heavy oil recovery. Colloid Surface A. 2021;611:125783.
- [79] Kumar G, Kakati A, Mani E, Sangwai JS. Nanoparticle-stabilized solvent-based emulsion for enhanced heavy oil recovery. The SPE Canada Heavy Oil Technical Conference, 2018 Mar 13-14; Calgary, Alberta, Canada: SPE Res Eval &
- [08] Jia H, Dai JJ, Miao LC, Wei X, Tang HT, Huang P, et al. Potential application of novel amphiphilic Janus-SiO2 nanoparticles stabilized O/W/O emulsion for enhanced oil recovery. Colloid Surface A. 2021;622(5):126658.
- Mo SP, Pan T, Wu F, Zeng MX, Huang DL, Zhang LC, et al. Facile one-step microwave-assisted modification of kaolinite and performance evaluation of pickering emulsion stabilization for oil recovery application. J Environ Manage. 2019;238(15):257-62.
- Wang ZJ, Babadagli T, Maeda N. Preliminary screening and formulation of new generation nanoparticles for stable pickering emulsion in cold and hot heavy-oil recovery. SPE Res Eval & Eng. 2021;24(01):66-79.
- [83] Li SD, Yu L, Lau HC, Stubbs LP. Experimental study of mobility control by clay-stabilized pickering emulsions in high-salinity reservoirs. The SPE Annual Technical Conference and Exhibition, 2020 Oct 26-29. Dubai, UAE: Virtual, SPE; 2020.
- [84] Radnia H, Solaiman Y, Nazar AR, Rashidi A. Effect of asphaltene on the emulsions stabilized by graphene oxide: a potential application of graphene oxide in enhanced oil recovery. J Petrol Sci Eng. 2019;175:868-80.
- Chen H, Song Q, Ye ZB, Han LJ, Wang X, Xu L, et al. [85] Experimental investigation of hydrophobically modified α -ZrP nanosheets for enhancing oil recovery in low-permeability sandstone cores. ACS Omega. 2019;4(26):22178-86.
- [86] Binks BP, Rodrigues JA. Enhanced stabilization of emulsions due to surfactant-induced nanoparticle flocculation. Langmuir. 2007;23:7436-9.

- Jia H, Wang DF, Lv FB, Wang Q, Lv L, Wei X, et al. Investigation on the stability of mixed AlOOH/SiO2 aqueous dispersions and their application to stabilize pickering emulsions in the presence of TX-100 and enhance oil recovery. Colloid Surface A. 2021;630:127595.
- [88] Patel A, Nihalani D, Mankad D, Patel D, Chaudhari R, Dhameliya M, et al. Evaluating feasibility of hydrophilic silica nanoparticles for in-situ emulsion formation in presence of co-surfactant: an experimental study. The SPE Kingdom of Saudi Arabia Annual Technical Symposium and Exhibition; 2017 Apr 24-27; Dammam, Saudi Arabia. SPE Res Eval & Eng; 2017.
- [89] Kim I, Worthen AJ, Lotfollahi M, Johnston KP, DiCarlo DA, Huh C. Nanoparticle-stabilized emulsions for improved mobility control for adverse-mobility water flooding. The SPE Improved Oil Recovery Conference, 2016 Apr 11-13; Tulsa, Oklahoma, USA: SPE Res Eval & Eng; 2016.
- [90] Pei HH, Zhang GC, Ge JJ, Zhang J, Zhang Q. Investigation of synergy between nanoparticle and surfactant in stabilizing oil-in-water emulsions for improved heavy oil recovery. Colloid Surface A. 2015;484:478-84.
- [91] Pei HH, Zhan S, Zhang GC, Ge JJ, Jiang P, Qin Y, et al. Experimental study of nanoparticle and surfactant stabilized emulsion flooding to enhance heavy oil recovery. J Petrol Sci Eng. 2018;163:476-83.
- Khalil M, Aulia G, Budianto E, Mohamed JB, Habib SH, Amir Z, [92] et al. Surface-functionalized superparamagnetic nanoparticles (SPNs) for enhanced oil recovery: effects of surface modifiers and their architectures. ACS Omega. 2019;4(25):21477-86.
- [93] Liang EL, Chien WO, Eng SC, Boon HO, Beng TT. Dual (magnetic and pH) stimuli-reversible pickering emulsions based on poly(2-(dimethylamino)ethyl methacrylate)-bonded Fe₃O₄ nanocomposites for oil recovery application. J Environ Chem Eng. 2020;8(2):103715.
- [94] Sharma T, Kumar GS, Sangwai JS. Comparative effectiveness of production performance of Pickering emulsion stabilized by nanoparticle-surfactant-polymer over surfactant-polymer (SP) flooding for enhanced oil recovery for Brownfield reservoir. J Petrol Sci Eng. 2015;129:221-32.
- [95] Ke X, Zhu PX, Colon T, Chun H, Matthew B. A microfluidic investigation of the synergistic effect of nanoparticles and surfactants in macro-emulsion-based enhanced oil recovery. The SPE Improved Oil Recovery Conference, 2016 Apr 11–13; Tulsa, Oklahoma, USA: SPE Res Eval & Eng; 2016.
- Saikia T, Sultan A, Barri A, Shamsan A. Emulsified polymer [96] gel pickering emulsion for conformance control: emulsion formulation, stability and coreflooding investigation. The SPE International Conference and Exhibition on Formation Damage Control, 2020 Feb 19-21; Lafayette, Louisiana, USA: SPE Res Eval & Eng; 2020.
- [97] Siegele FH. Oil well fracturing method using wax emulsions, US Pat. US3477512A: 1967.
- John WG, Clay G, William MS. Method of fracturing subter-[98] ranean formations using oil-in-water emulsions, US Pat. US3977472A: 1975.
- [99] Cawiezel KE, Hodge R. High internal phase ratio water-in-oil emulsion fracturing fluid, US Pat. US5633220 A: 1997.
- [100] Bu JY, Chen DJ, Wang CW, Shui LL, Peng ZG. The Experimental Study on a Water-in-Oil Emulsion Fracturing Fluid. Chem Eng Oil Gas. 2003;32(6):372-74 + 386.

- [101] Gupta DV, Hlidek BT, Hill ESW, Dinsa HS. Fracturing fluid for low permebility gas reservoirs: emulsion of carbon dioxide with aqueous methanol base fluid: chemistry and applications. The SPE Hydraulic Fracturing Technology Conference, 2007 Jan 29–31; College Station, Texas, USA: SPE Res Eval & Eng; 2007.
- [102] Al-Anazi MS, Al-Khaldi MH, Fuseni A, Al-Marshad KM. Use of nano-emulsion surfactants during hydraulic fracturing treatments. The Abu Dhabi International Petroleum Exhibition and Conference, 2014 Nov 10–13; Abu Dhabi, UAE: SPE Res Eval & Eng; 2014.
- [103] Al-Hameedi AT, Alkinani HH, Dunn-Norman S, Trevino HA, Al-Alwani MA. Conventional and eco-friendly hydraulic fracturing fluid additives: a review. The SPE Hydraulic Fracturing Technology Conference and Exhibition, 2020 Feb 4–6; The Woodlands, Texas, USA: SPE Res Eval & Eng; 2020.
- [104] Liu D, Yan Y, Bai G, Yuan YJ, Zhu TY, Zhang F, et al. Mechanisms for stabilizing and supporting shale fractures with nanoparticles in Pickering emulsion. J Petrol Sci Eng. 2018;164:103-9.
- [105] Roberts MR, Aminzadeh B, DiCarlo DA, Bryant SL, Huh C. Generation of Nanoparticle-Stabilized Emulsions in Fractures. The SPE Improved Oil Recovery Symposium; 2012 Apr 14–18; Tulsa, Oklahoma, USA. SPE Res Eval & Eng; 2012.
- [106] Yang F, Raymond LJ, Mary G, Manouchehr H, Kunakorn P. Experimental and numerical investigation into nano-stabilized foams in low permeability reservoir hydraulic fracturing applications. Fuel. 2018;213:133–43.
- [107] Khaled A, Mahmoud TA, Hisham AN Acid Wormholing in Multistage Acid Fractured Wells Completed in Tight Naturally Fractured Dolomite Formation: Benefits and Impacts on Acid Fracturing Stimulation Design. The SPE International Hydraulic Fracturing Technology Conference and Exhibition, 2018 Oct 16–18; Muscat, Oman: SPE Res Eval & Eng; 2018.
- [108] Huang TP, Crews JB, Willingham JR, Stabilizing emulsified acids for carbonate acidizing, US Patent. US8551926B2: 2010.
- [109] Mishra S, Ojha K. Application of an improvised inorganicorganic chemical mixture to consolidate loose sand formations in oil fields. J Petrol Sci Eng. 2016;137:1–9.
- [110] Zhang FS, Ouyang J, Ma XT, Feng XF. A new phenolic resin for sand control in wells. Chem Tech Fuels Oil+. 2013;49(5):425-9.
- [111] Hassan NA, Yeap WJ, Singh R, Khansani NZN Performance review of chemical sand consolidation and agglomeration for

- maximum potential as downhole sand control: an operator's experience. The SPE Asia Pacific Oil & Gas Conference and Exhibition, 2020 Nov 17–19. Bali, Indonesia: Virtual, SPE Res Eval & Eng; 2020.
- [112] Wang Q. Study on the sand control system of foaming/ emulsified resin and its adaptability (dissertation). Qingdao, Shandong: China University of Petroleum (East China); 2017
- [113] Ikem VOO, Menner A, Bismarck A, Norman LRR. Liquid Screen: a novel method to produce an in-situ gravel pack. SPE J. 2014;19(3):437-42.
- [114] Wang ZB, He HF, Wang Q, Chen AS, Bai YR, Zhao XT, et al. A Low temperature emulsified sand consolidating agent and its preparation and application, CN Pat. CN108659805B: October 2020.
- [115] Zhang Y, Zhu YY, Ma DS, Han D, Han DK, Wang SY. Studies on the electro-catalytic degradation of EOR wastewater by Ce-Ti/TiO₂ electrode. The International Oil and Gas Conference and Exhibition, 2010 Jun 8–10; Beijing, China: SPE Res Eval & Eng; 2010.
- [116] Vasiliu CC, Pierce D, Bertrand K. Challenging wastewater treatment. The international conference on health, safety and environment in oil and gas exploration and production, 2012 Sep 11–13; Perth, Australia: SPE Res Eval & Eng; 2012.
- [117] Andrew HG, Lial FT, William HF. An evaluation of protective concentrations for hydrogen sulfide in produced water discharged in california outer continental shelf ocean waters. The SPE/EPA Exploration and Production Environmental Conference, 1999 Mar 1-3; Austin, Texas: SPE Res Eval & Eng; 1999.
- [118] Dou SY, Wang R. The C-Si Janus nanoparticles with supported phosphotungstic active component for Pickering emulsion desulfurization of fuel oil without stirring. Chem Eng J. 2019;369:64–76.
- [119] Tian SW, Mao GL, Zhang JY, Li N, Jiang YY, Wu W. Switchable pickering emulsion system. Prog Chem. 2020;32(4):434–53.
- [120] He X, Liang C, Liu QX, Xu ZH. Magnetically responsive Janus nanoparticles synthesized using cellulosic materials for enhanced phase separation in oily wastewaters and waterin-crude oil emulsions. Chem Eng J. 2019;378:122045.
- [121] Shang YZ, Qin JL, Zhao QF, Xu H, Wang ML. Preparation of cationic emulsion water clarifier and application in oily wastewater treatment. Environ Prot Chem Ind. 2019;39(3):304–9.
- [122] Zhang M, Ma X, Yang W, Wang FJC, Yu H, Song AX. Dualresponsive pickering emulsions triggered by CO₂ and magnetism. J Mol Liq. 2021;341:116906.