Commonly Used Nanofluids in Oil Recovery Technology

Subjects: Nanoscience & Nanotechnology
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Nanofluid-enhanced oil recovery (EOR) technology is an innovative approach to enhancing oil production in oilfields. It entails the dispersion of nanoparticles within a fluid, strategically utilizing the distinctive properties of these nanoparticles (NPs) to engage with reservoir rocks or crude oil, resulting in a significant enhancement of the oil recovery rate.

nanofluid enhanced oil recovery oilfield applications

1. Introduction

Nanofluids were initially proposed by Choi and Eastman in 1995 [1]. With the continuous advancement of research and the rapid growth of various industries, nanofluids have found widespread applications in fields such as medicine and pharmaceuticals [2], electronics and mechanical engineering [3][4], agriculture and pesticides [5], as well as petrochemicals [6][7]. Notably, within the realm of the oil industry, nanofluids have demonstrated versatility, proving applicable not only in oil and gas extraction but also in hydraulic fracturing, downhole casing monitoring, drilling fluids, well completion fluids, and oilfield wastewater treatment [8]. In the early stages of oil and gas production, the use of binary and ternary EOR systems often led to the development of preferential flow channels within the reservoir. Conventional oil displacement agents were rendered ineffective along these preferential pathways, hampering their effectiveness. The emergence of nanofluids has significantly ameliorated these issues, driving advancements in EOR technology. In present-day China, there is a growing prominence of low-permeability reservoirs, tight oil formations, heavy oil deposits, and high-water-cut oil and gas resources [9][10]. These oilfields face the daunting challenge of injection without production. Nanofluid EOR technology, with its unique capabilities tailored to address the complexities of such reservoirs, has ushered in innovative breakthroughs in EOR techniques, greatly advancing the rejuvenation and development of aging oilfields.

Nanofluid EOR technology is a technique that utilizes a system formed by mixing nanoparticles with a solution to enhance the recovery of crude oil from reservoirs [11]. Nanofluids have the ability to alter the interaction forces between crude oil and water, reducing the oil–water IFT between them. Additionally, due to their small particle size, nanofluids possess a larger specific surface area and surface energy [12], allowing them to penetrate tiny reservoir pores, operate within these pores, and improve oil–water separation performance as well as the mobility ratio [13]. Furthermore, nanoparticles can modify the surface charge properties of reservoir rocks, thereby altering surface wettability, enhancing pore-throat permeability, and facilitating smoother crude oil flow, ultimately increasing crude oil recovery. Against the backdrop of increasingly challenging oil and gas exploration and production, the continuous innovation and deepening application of nanofluid EOR technology can infuse new vitality into aging oilfields [14].

2. Inorganic Nanofluids

Due to the superior heat and weather resistance of inorganic materials, inorganic nanofluids have a wider range of applications.

Due to the magnetic properties of Fe_3O_4 particles, the prepared nanofluid is typically utilized in magnetic nanofluid applications. During the oil recovery process, controlling the fluid with a magnetic field enhances its controllability. Esmaeilnezhad et al. [15] through core flooding experiments, compared the effectiveness of nanosized Fe_3O_4 particles in improving oil recovery under the presence and absence of a magnetic field. The results revealed that in the presence of a magnetic field, the petroleum recovery rate increased by nearly 14%. This effect is attributed to the magnetic field's ability to control the specific placement of nanosized Fe_3O_4 particles within pore channels, creating a plugging effect in the direction of the magnetic field, from this, it can be concluded that the essential principle of improving oil recovery of magnetic nanofluids under magnetic field control is to increase the swept volume of the fluid.

TiO_2 is typically applied in the field of photosensitive materials. However, recent research by Hosseini et al. [16] has shown that nanofluids prepared using TiO_2 can alter the wettability of rocks. In this study, surface-modified TiO_2 NPs were prepared using coupling agents, and nanofluids prepared with these NPs were used to treat the rock surfaces. This treatment transformed the originally oil-wet rock surfaces into water-wet conditions. Furthermore, the research revealed that the higher the concentration of NPs, the more effective they were in altering the wettability of the rocks. Keykhosravi et al. [17] conducted a comparative study on the influence of TiO_2 NPs on the viscosity of xanthan gum. Their findings revealed that the addition of TiO_2 NPs to xanthan gum suspensions resulted in a smaller decrease in viscosity with increasing shear force, and increased underwater contact angle (CA) of oil droplets. Moreover, when compared to suspensions without TiO_2 and polymer solutions, TiO_2-induced xanthan gum polymer flooding enhanced the oil recovery rate by at least 6 percentage points.

Al_2O_3 also exhibits a significant impact on enhancing oil recovery. Samba et al. [18] conducted spontaneous imbibition tests on core samples of oil-saturated sandstone using nanosized Al_2O_3 particles. The results demonstrated that as the concentration and temperature of nano-Al_2O_3 increased, the oil recovery rate also increased. When the nanoparticle concentration reached 2%, it led to a 3.1% increase in oil recovery. This phenomenon can be attributed to the intensified Brownian motion of nano-Al_2O_3 particles within the sandstone cores at higher temperatures. Additionally, nano-Al_2O_3 particles possess good thermal conductivity, which reduces viscosity and enhances oil flow, effectively boosting oil recovery. However, nano-Al_2O_3 particles are highly sensitive to ion concentrations, which can lead to particle aggregation and deposition [19].

Conventional metal NPs are mostly spherical [20] and cannot achieve the maximum efficacy of nanofluids in geological environments. The synergistic effect is limited, and the preparation process is complex and difficult to control [21]. Zaid et al. [22] altered the morphology of Al_2O_3 NPs to a sheet-like structure through hydrothermal treatment with varying NaOH concentrations. The research revealed that the sheet-like Al_2O_3 NPs exhibited better dispersibility in the fluid. Furthermore, they reduced the oil–water IFT compared to spherical particles, resulting in a 10% increase in oil recovery in simulated oil displacement experiments. Changing particle morphology enhances particle dispersion in the fluid. Additionally, studies have shown that parameters such as pH, temperature, concentration, and ion strength can also affect particle dispersion [23].

Compared to Al_2O_3 nanosheets, Raj [24] inspected synergistic effect of foam produced by α- sodium olefin sulfonate (AOS) and MoS_2 nanosheet (**Figure 1**) on foaming and oil recovery performance. It is found that the half-life of the foam is enhanced due to the formation of a protective layer around the foam sheet by the nanosheet. The ability to improve oil recovery was verified through sand loading experiments. The obtained results show that the foam stabilized by MoS_2 nanosheet has an increasing oil recovery rate.

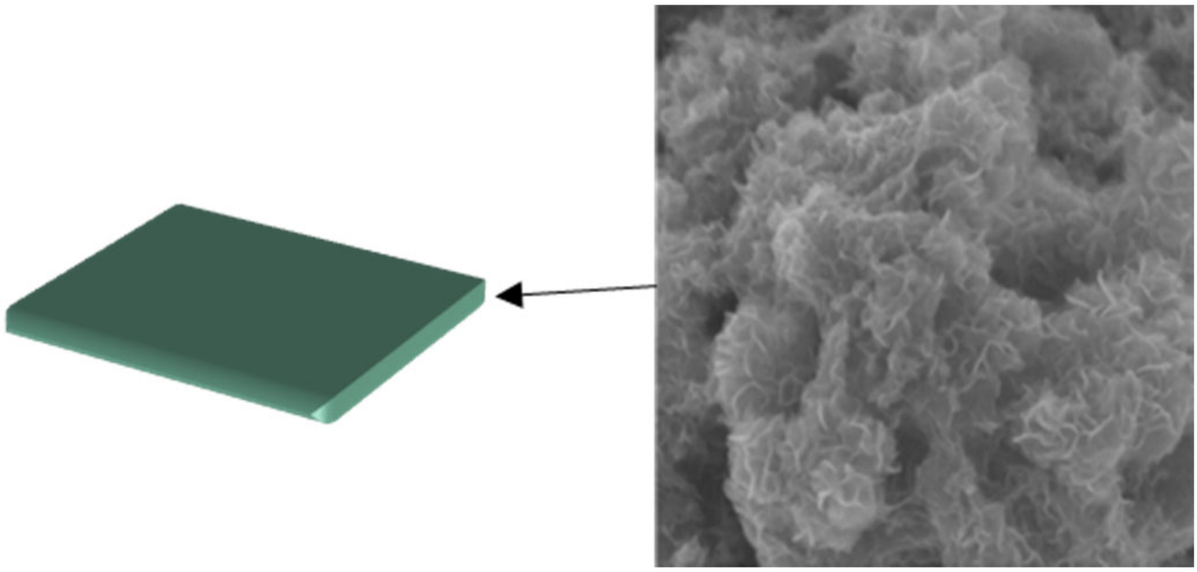

Figure 1. TEM of MoS_2 nanosheet [24].

Furthermore, MgO [25], ZnO [26], CuO [27], and other nanofluids have also shown favorable effects on enhancing oil recovery. However, a common drawback of metal compound NPs, which limits their widespread application in oilfields, is their high cost and certain toxicity to reservoir formations [28]. Currently, they remain in the laboratory research stage, and for practical application, further optimization of preparation processes and cost reduction are required to meet real-world demands. In contrast, nano-SiO_2 fluids are more environmentally friendly and cost-effective, making them a material with broader prospects for EOR applications. Commonly used nano-SiO_2 particles have an average particle size ranging from 10 to 50 nm. Tangestani et al. [29] added SiO_2 NPs (**Figure 2**) to KCl solution to prepare nanofluids, and simulation experiments indicated that 0.05 wt% SiO_2 NPs improved the original oil in place (OOIP) by approximately 4% compared to low-salinity-water flooding. Additionally, it was demonstrated that changes in salinity had no significant impact on the performance of SiO_2 nanofluids.

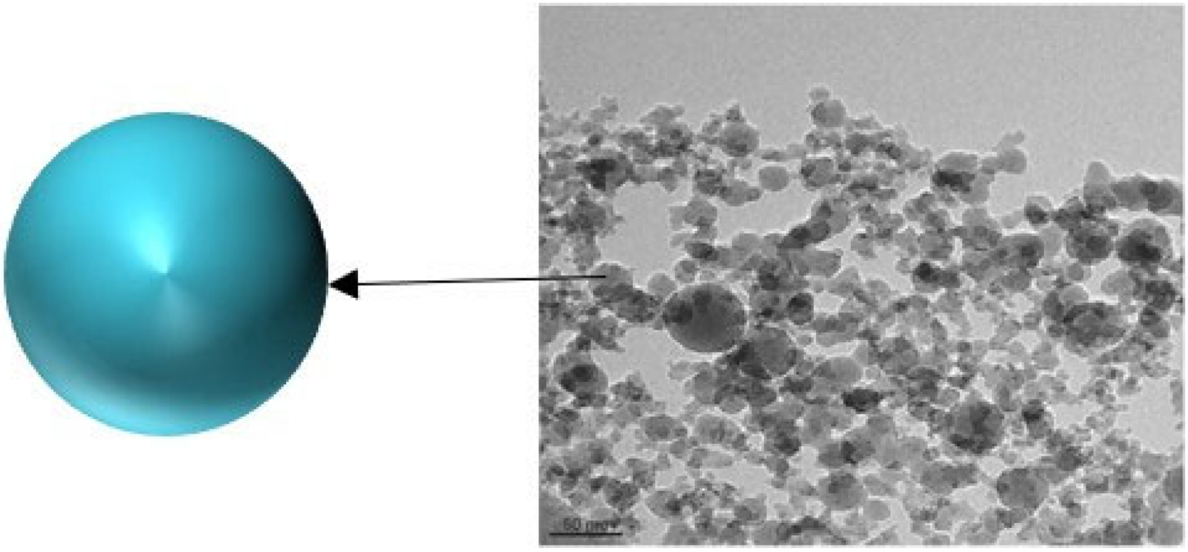

Figure 2. TEM of SiO_2 NPs [29].

Inorganic nanofluids typically require the use of stabilizers to create stable formulations. While inorganic nanomaterials exhibit notable effects in reducing the oil–water IFT and altering rock surface wettability, they are often susceptible to aggregation and precipitation under unmodified conditions, particularly influenced by reservoir conditions. Moreover, many inorganic nanoparticles exhibit poor economic viability, rendering them less suitable for large-scale field applications. Therefore, it is imperative to employ modifications or combine them with organic materials to enhance their weather resistance, reduce aggregation tendencies, and lower production costs, thereby enabling their broader application.

3. Organic Nanofluids

Organic nanofluids offer a higher degree of controllability compared to inorganic nanofluids. It can achieve precise control over the morphology, size, and surface properties of added NPs by adjusting reaction conditions and the ratios of reactants. Organic nanofluids are commonly applied in reservoir protection and enhanced oil recovery techniques [30]. Typically, the surfaces of organic NPs feature both hydrophilic and hydrophobic functional groups, allowing them to stably exist at the oil–water IFT phases and effectively reduce IFT. Common types of organic nanofluids include polymer nanofluids, cellulose nanofluids, and oxidized graphene nanofluids, among others.

Polymer nanospheres can serve as carriers for surfactants, facilitating the release of surfactants deep into the reservoir. This reduces surfactant adsorption on the rock walls during the injection process, thereby promoting enhanced oil recovery [31]. Polymer nanospheres also adsorb and deform along interfaces, and they can expand within the reservoir to block larger channels, thereby increasing the affected volume. Consequently, polymer nanofluids can be employed as profile control agents. For instance, Esfahlan et al. [32] employed a reverse-phase microemulsion polymerization method to produce nanogel microspheres. The swelling behavior and rheological properties of these microspheres were tested. The experiments revealed that even under high-temperature and high-salinity conditions, the nanogel particles exhibited good water absorption and had a lower elastic modulus compared to regular hydrogels. This characteristic enables these nanogel particles to remain effective for plugging and profile modification in harsh reservoir conditions characterized by high temperature and salinity.

Research has demonstrated the effectiveness of needle-shaped cellulose nanocrystals (CNCs) and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-oxidized cellulose nanofibrils (T-CNFs) (**Figure 3**) in enhancing oil recovery. Aadland et al. [33] through microfluidic control oil displacement experiment, confirmed that both types of nanofluids can increase recovery rates by at least 5.8% (CNCs) (**Figure 3**a) and 8.6% (T-CNFs) (**Figure 3**b) compared to low-salinity-water (LSW) flooding. To explore the oil displacement mechanism of nanofluids, measurements of CA and IFT were conducted. The results provided evidence that CNCs effectively reduce the oil–water IFT, T-CNFs can lead to a change in the wettability of the rock surface.

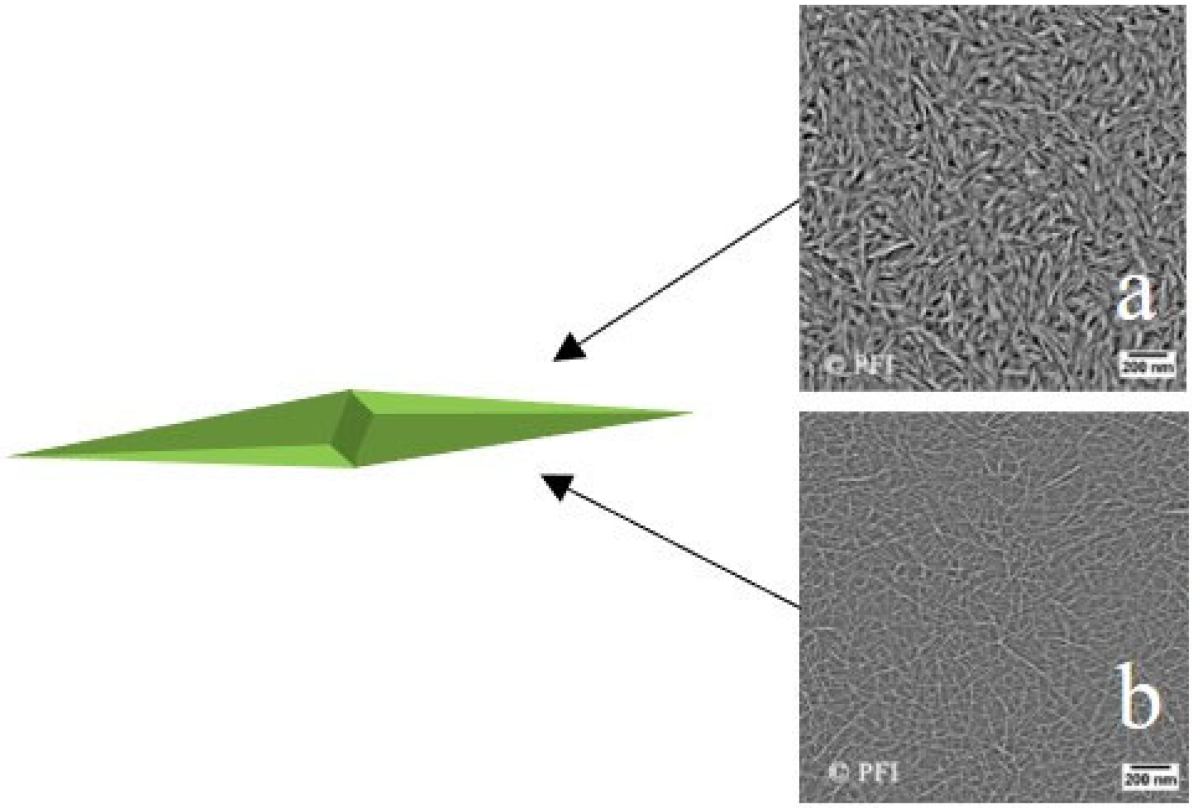

Figure 3. (**a**) CNCs atomic force microscopy (AFM) image. (**b**) T-CNFs AFM image [33].

Sheet-like graphene materials have gained significant favor among researchers in enhanced oil recovery techniques due to their smaller size and thickness, larger specific surface area, and excellent amphiphilic stability [34]. Jafarbeigi et al. [35] synthesized graphene oxide nanosheets (GONs) using the Hummer's method and subsequently modified their surfaces with hexamethyldisilazane (HMDS) and diazonium sulfonate (DS) to create GO-Su-HMDS nanosheets. By formulating modified nanosheets into GO-Su-HMDS nanofluids, the rock surface treated with this fluid underwent a wettability alteration from oil-wet to water-wet conditions, achieving wetting reversal. Simultaneously, the oil–water IFT was reduced from 18.45 mN/m to 8.8 mN/m. Simulation-based oil displacement experiments demonstrated that GO-Su-HMDS nanofluids could increase oil recovery rates by up to 20%.

The polymer NPs in organic nanofluids have a wider range of action during the profile control process, because polymer NPs are deformable particles that can enter deeper formations through deformation at the pore channels. Another type is carbon based NPs, including carbon nanotubes and graphene flakes, whose mechanism of action is mostly to reduce the oil–water IFT, thereby achieving the goal of improving oil recovery.

4. Organic–Inorganic Composite Nanofluid

Organic–inorganic composite nanofluids are materials composed of both organic and inorganic NPs, forming a unique nanofluid with a combination of organic flexibility and inorganic nanoparticle strength. In the realm of oilfield oil recovery, these composite nanofluids play a pivotal role by altering rock surface properties, reducing oil–water IFT, and enhancing oil recovery. Furthermore, the synergistic interaction between the organic and inorganic phases within these composite nanofluids results in a more stable dispersion system. This comprehensive material holds great promise for a wide range of applications in the oilfield.

In aqueous solutions, SiO_2 particles are rich in hydroxyl groups, making them easily modifiable [36][37]. However, this also renders SiO_2 particles susceptible to hydrogen bond interactions with each other, leading to aggregation in the fluid. The introduction of various organic functional groups through surface chemical modifications can enhance the stability of these particles in the solution. Afifi et al. [38] and colleagues achieved long-term stability of modified nanoscale SiO_2 in a medium through their modification efforts. In the field of enhanced oil recovery, Janus NPs, particularly those based on nanoscale SiO_2, are quite common. The surface of nanoscale SiO_2 particles is readily modifiable, facilitating the successful preparation of Janus NPs. Jia et al. [39] using the Pickering emulsion method, successfully synthesized amphiphilic nanoscale SiO_2 particles (Janus-C_{12}). Precise control over the degree of modification allows for adjustments in the phase transition of emulsions, ranging from O/W to multiple W/O/W to W/O emulsions. Furthermore, Janus-C_{12} stabilized multiple O/W/O nanofluids have demonstrated excellent performance in enhancing oil recovery in core flooding experiments.

Ojo et al. [40] loaded surfactants into halloysite nanotubes and subsequently coated them with a layer of wax to prevent premature surfactant release. Permeation experiments with the nanofluid showed a 40% increase in oil recovery, whereas using surfactants alone resulted in only a 16% improvement. This innovative approach of incorporating surfactants into inorganic materials offers a novel strategy for surfactant injection.

Asl et al. [41] prepared ZnO@PAM nanocomposite materials using polyacrylamide (PAM) and ZnO NPs and blended them with surfactants at various concentrations to create nanofluids. Experimental results demonstrated a synergistic effect between the surfactant and composite NPs, reducing the oil–water IFT from 29.16 mN/m to 0.176 mN/m. Additionally, it altered the wettability of the rock surface from oil-wet to water-wet, significantly enhancing oil recovery in core flooding experiments.

Mahdavinezhad et al. [42] created a novel nanocomplex (f-MWCNT-CTAB) by modifying functionalized multi-walled carbon nanotubes (f-MWCNTs) with cetyltrimethylammonium bromide (CTAB) (**Figure 4**) and tested in low-salinity-seawater (LSSW). The results indicate that the nanocomplex significantly reduces IFT between crude oil and brine, with a low critical micelle concentration (CMC) of 20 ppm and minimal IFT (0.33 mN/m). Furthermore, it alters the wettability of dolomite rock from oil-wet to water-wet. Tertiary flooding experiments resulted in a 21% increase in oil recovery following secondary water injection, attributed to the combined effects of the nanocomplex and low-salinity-brine.

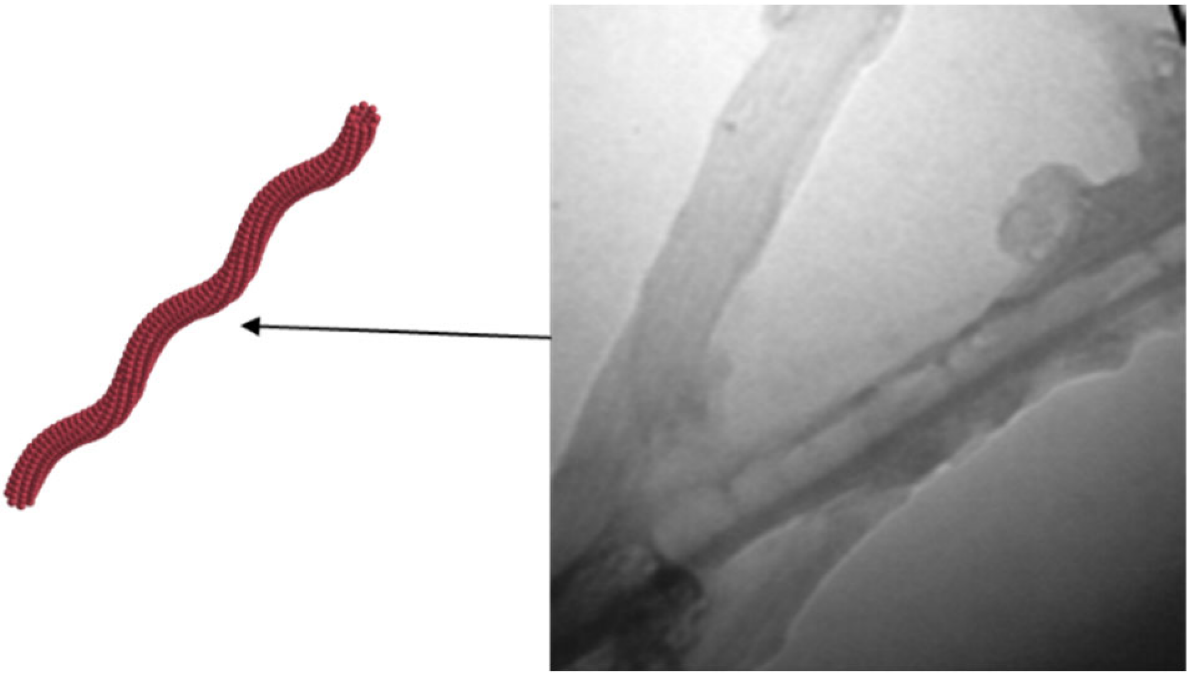

Figure 4. TEM images of the f-MWCNT-CTAB [42].

Liang et al. [43] prepared amphiphilic KH-550-MoS_2 nanosheets using a hydrothermal synthesis method. The study found that 50 mg/L of KH-550-MoS_2 nanosheets can reduce the oil–water IFT to 2.6 mN/m, and can reduce the CA of quartz flakes after crude oil treatment from 131.2° to 51.7°. Indoor core oil displacement simulation experiments have shown that this nanosheet can improve the oil displacement efficiency by 14% after water flooding.

The above nanofluids have different mechanisms and effects on oil displacement, as summarized in **Table 1**. Selecting the appropriate nanofluid is crucial for enhancing oil recovery. Currently, nanofluid EOR has become a significant technology applied in various fields, including offshore and onshore oil fields. However, numerous challenges persist in practical applications, such as nanoparticle dispersion, stability, and dosage control. Therefore, a thorough investigation into the mechanisms behind nanofluid EOR is essential when making decisions regarding nanofluid selection.

Table 1. Different nanofluid compositions and oil displacement effects.

Nanofluids	Main Components	Mechanism and Effect	Ref
Fe_3O_4	Fe_3O_4 NPs aqueous solution	Increase oil recovery by 14% under the magnetic field.	[15]

Nanofluids	Main Components	Mechanism and Effect	Ref
TiO_2	TiO_2 NPs aqueous solution	Reduce the forward and backward angles of water from 165.1° and 166.2° to 37.6° and 48.2°.	[16]
	TiO_2 NPs; xanthan gum solution	Increase the CA of oil from 21° to 148°, increase oil recovery by 25%.	[17]
Al_2O_3	Spherical Al_2O_3 NPs aqueous solution	Reduce crude oil viscosity, increase 3.1% oil recovery.	[18]
	Sheet-like Al_2O_3 NPs aqueous solution	Reduce the IFT, increase 10% oil recovery.	[22]
MgO	MgO NPs aqueous solution	Reduce the IFT to 3.7 under high temperature and pressure.	[25]
ZnO	ZnO NPs; Steam	Reduce crude oil viscosity; the efficiency of steam flooding has increased by 35.5%.	[26]
	ZnO@PAM nanocomposites; cationic surfactants solution	Reduced the IFT from 29.16 to 0.176 mN/m; decreased the CA of water from 145.86° to 12.79°; increase 30% oil recovery.	[42]
CuO	CuO NPs; Surfactant solution	Increase the thermal conductivity of rocks to 33%, thereby reducing the viscosity of crude oil.	[27]

Nanofluids	Main Components	Mechanism and Effect	Ref
SiO_2	SiO_2 NPs; KCl solution.	Controlling fines migration and reducing the pressure drop in the porous media.	[29]
	Janus C_{12} aqueous solution	The Janus-C_{12} stabilized multiple O/W/O Pickering emulsions improve the oil recovery by 27.2%.	[39]
MoS_2	MoS_2 nanosheets; AOS solution	The addition of modified nanosheets to the foam generation leads to 12.1% of increased oil recovery.	[24]
	KH-550-MoS_2 aqueous solution	Reduce the IFT to 2.6 mN/m, reduce the CA of water from 131.2° to 51.7°; increase 14% oil recovery.	[43]
Polymer NPs	Nanogel microsphere aqueous solution	High water absorption and expansion performance under high temperature and high-salinity-conditions.	[32]
Cellulose nanocrystals	CNCs; T-CNFs; LSW	CNCs can reduce the IFT; T-CNFs can change the wettability of rocks; produced 5.8% of OOIP more oil than LSW.	[33]
Graphene Oxide	Aqueous solution of GO-Su-HMDS	Reduce the IFT from 18.45 to 8.8, change the wettability of rocks; increase oil recovery by 20%.	[35]
Halloysite nanotubes	Aqueous solution of halloysite nanotubes containing surfactants inside	Improved oil displacement by 16% compared to using surfactants alone.	[40]

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Nanofluids	Main Components	Mechanism and Effect	Ref
Carbon nanotubes	f-MWCNT-CTAB; LSSW	Reduced the IFT to 0.3 mN/m, changing the dolomite slabs wettability from an oil-wet toward a neutral-wet state (128–105°), result in a 21% increase in oil recovery after secondary water injection.	[42]

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