

Supplementary file

CO₂ injection for enhanced oil recovery: A review of existing methods, challenges and promising solutions

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Appendix A

Nanoparticles

In general, interfacial tension (IFT) increases with rising temperature and salinity, and decreases under elevated pressure. The addition of SiO₂ nanoparticles mitigates the effects of temperature and salinity by reducing the IFT (Al-Anssari et al., 2018). The authors also noted that at low concentrations (> 0.25 wt%), nanoparticles had a more pronounced impact on IFT compared to higher concentrations. Particle size had a minor effect, which was attributed to the tendency of nanoparticles to agglomerate into larger aggregates upon contact with water. Furthermore, the introduction of SiO₂ exhibited a synergistic effect when combined with moderate pressure increases.

In the study (Espinosa et al., 2010), SiO₂ nanoparticles were employed to enhance the stability of surfactant-generated foams under high-temperature reservoir conditions. The results demonstrated that incorporating nanoparticles into the aqueous phase provided 2-18 times greater flow resistance compared to the same fluids without nanoparticles. However, foam stability decreased with increasing temperature. The concentration of SiO₂ required for foam generation was 0.05 wt%; however, higher salinity conditions demanded a greater concentration of nanoparticles. One of the advantages of using nanoparticles in combination with surfactants, or as a substitute for surfactants in gas-based EOR processes, is their resistance to harsh reservoir conditions, such as high pressure, elevated temperature and significant formation water salinity. Unlike conventional surfactants, nanoparticles exhibit greater stability under such extreme conditions (Shafiei et al., 2024).

In a study on wettability alteration from oil-wet to gas-wet conditions using Fe₃O₄-based nanoparticles (in the forms of Fe₃O₄-PVA and Fe₃O₄-HAp), it was found that both formulations effectively rendered carbonate rocks gas-wet, reducing water penetration by 50%-75% and condensate penetration by 74%-80% (Safaei et al., 2020). Fe₃O₄-HAp nanostructures exhibited higher efficiency, particularly at elevated temperatures (20-90 °C), although their performance decreased with increasing salinity. These results confirm the potential of such nanomodifiers for improving gas recovery under real reservoir conditions.

In addition to previously discussed SiO₂-, Fe₃O₄-, and graphene oxide-based systems, study (Hosseini et al., 2022) investigated the effect of surface-modified TiO₂ nanoparticles on

nanofluid stability and wettability alteration of carbonate rocks. The authors synthesized TiO₂ nanoparticles functionalized with aminopropylsilane (AEAPTMS) and demonstrated that such surface treatment significantly enhances dispersion stability at temperatures up to 90 °C and salinities up to 30 wt%, conditions typical of oil reservoirs. Under these conditions, the particle size remained below 100 nm, and at an optimal modifier dosage (5 ml AEAPTMS per 10 ml TTIP precursor), the zeta potential reached values below -30 mV, indicating good colloidal stability.

Contact angle measurements on carbonate plates before and after nanofluid treatment revealed a significant wettability shift: the initially strongly oil-wet surface (contact angles of 165.1°/166.2° for advancing/receding) became water-wet after treatment with a 3 wt% TiO₂ suspension (37.6°/48.2°, respectively). The effect of nanoparticle concentration was pronounced: increasing the content from 0.1 to 3 wt% led to a monotonic decrease in contact angle, with no signs of aggregation or loss of stability, even at 90 °C. For comparison, unmodified TiO₂ under the same conditions exhibited poorer performance in terms of both colloidal stability and wettability alteration efficiency.

The results showed that Al₂O₃-SiO₂-based nanofluids exerted a stronger effect than TiO₂-SiO₂ and TiO₂-Al₂O₃ nanofluids in promoting wettability alteration toward a water-wet state and reducing IFT, under optimal water-to-gas ratio conditions (1:1) (Sun et al., 2024).

In addition to the previously discussed approaches, study (Amraeiniya et al., 2023) demonstrated that the addition of 0.06 wt% γ -Al₂O₃ nanoparticles effectively inhibits asphaltene precipitation during CO₂ injection. Measurements of IFT and Bond number at 60 °C indicated that the nanoparticles reduce the intensity of asphaltene aggregation and shift the onset of precipitation (~6.8 MPa). This effect was particularly pronounced for crude oils containing more condensed, aromatic asphaltene molecules with a high content of heteroatoms, such as nitrogen. These findings highlight the potential of γ -Al₂O₃ as a selective inhibitor of asphaltene deposition under CO₂-EOR conditions.

Experimental data on the use of a graphene oxide (GO)-based nanofluid, namely GO-Su-HMDS, demonstrated that at a concentration of 500 ppm, the contact angle was reduced from 161° to 35°, and the IFT decreased from 18.45 to 8.8 mN/m, confirming its high efficiency in altering rock wettability (Jafarbeigi et al., 2022). The dependence of oil recovery on

nanoparticle concentration showed an increasing trend: additional recovery reached 20% at 400 ppm and 19% at 500 ppm, indicating optimal performance within this range. Thus, modified GO nanosheets significantly enhance oil displacement by lowering IFT and promoting surface hydrophilization of the reservoir rock.

A recent study explored the potential for improving heavy oil recovery through the combined use of nanoparticle-based fluids and alternating injection of CO₂ microbubbles (Koca et al., 2018). CO₂ microbubbles exhibit greater dissolution and more efficient utilization of pore space compared to conventional CO₂ gas. In this context, microbubbles can enhance mobility control by minimizing gravitational effects, delaying CO₂ breakthrough, and achieving higher displacement efficiency (Akai et al., 2015; Jiang et al., 2019). Key findings from relevant experimental and simulation studies on various types of nanoparticles are summarized in Table S1.

Table S1. Results of experimental and simulation studies on nanoparticles.

NPs	Conditions	Conclusions	Reference
Silicon dioxide (SiO ₂)	0.1 - 20 MPa 23 - 70 °C 0 - 20 wt% NaCl Porous spherical 5 - 25 nm 0.01 - 0.05 wt% SiO ₂ 0.4 cm ³ /min	<ul style="list-style-type: none"> • Effective at low concentrations (>0.25 wt%) • Mitigate the effects of temperature and salinity on IFT • Particle size has minor influence on IFT due to agglomeration tendencies • Exhibit a synergistic effect with increased pressure in reducing IFT 	(Al-Anssari et al., 2018)
	9.3 - 9.65 MPa 21.1 - 95 °C 0 - 4 wt% NaCl Porous spherical 5 nm 0.025 - 10 wt% SiO ₂ 6 cm ³ /min	<ul style="list-style-type: none"> • Effective in stabilizing foams under high-temperature reservoir conditions • Nanoparticle concentration has limited impact on IFT and viscosity • Foam stability decreases with increasing temperature • Provides 2-18 times higher flow resistance compared to nanoparticle-free fluids • Low nanoparticle concentrations sufficient for foam generation 	(Espinosa et al., 2010)
Copper(II) oxide (CuO)	15 - 25 MPa 76.85 - 136.85 °C 0 - 4 wt% NaCl Porous spherical 1 - 8.56 nm 1 wt% CuO	<ul style="list-style-type: none"> • Increases CO₂ viscosity by 30-150% • Repulsive forces between particles must dominate to ensure nanofluid stability • Combination of DFT and molecular dynamics confirmed the effectiveness of the proposed approach for nanofluid property modeling and optimization 	(Khaledialidusti et al., 2018)

	6 cm ³ /min		
Iron(III) oxide (Fe ₃ O ₄)	6.89 MPa 20 - 90 °C 1 - 76 wt% NaCl, KI, CaCl ₂ , MgSO ₄ 20 - 34 nm 0.1 - 1 wt% Fe ₃ O ₄ - PVA/Fe ₃ O ₄ -HAp 0.05 cm ³ /min	<ul style="list-style-type: none"> • Fe₃O₄ NPs coated with HAp considerably improved the wettability of the carbonate rock samples from oil-wetting to preferentially gas-wetting. • Wettability alteration decreased with increasing nanofluid salinity • Optimal mass concentrations for maximum wettability alteration were 0.5 wt% for Fe₃O₄-PVA and 0.4 wt% for Fe₃O₄-HAp 	(Safaei et al., 2020)
Titanium dioxide (TiO ₂)	25 - 90 °C 5 - 30 wt% NaCl, CaCl ₂ Porous spherical 20 - 80 nm 0.1 - 3 wt% TiO ₂ - AEAPTMS	<ul style="list-style-type: none"> • After treatment with 3 wt% TiO₂ nanoparticles, rock wettability shifted to water-wet, with advancing and receding contact angles of 37.6° and 48.2°, respectively (from initial values of 165.1° and 166.2°) • TiO₂-AEAPTMS nanofluid exhibited high stability under high-salinity and high-temperature conditions 	(Hosseini et al., 2022)
Aluminum oxide (Al ₂ O ₃)	1.3 - 10 MPa 60 °C Porous spherical 50 - 80 nm 0.06 wt% Al ₂ O ₃	<ul style="list-style-type: none"> • At 0.06 wt% Al₂O₃ concentration: asphaltene precipitation rate reduced by ~50% (for nitrogen-rich crude oil) • Onset pressure of asphaltene precipitation: ~6.8 MPa • Higher efficiency observed in oils with more aromatic and nitrogen-containing asphaltene structures 	(Amraeiniya et al., 2023)
Graphene oxide (GO)	35 - 116 nm 0.04 - 0.05 wt% GO-Su- HMDS 0.2 cm ³ /min	<ul style="list-style-type: none"> • With increasing concentration, viscosity increases while IFT and contact angle decrease (from 161° to 35°) • At 0,05 wt% GO-Su-HMDS nanofluid, IFT between oil and aqueous phase decreased from 18.45 to 8.8 mN/m • Increasing nanoparticle concentration from 0.04 to 0.05 wt% led to oil recovery improvements of 20% and 19%, respectively 	(Jafarbeigi et al., 2022)

A comparative analysis of the reviewed studies reveals a consistent influence of several key factors on nanoparticle performance in CO₂-EOR processes; however, discrepancies are observed in some cases due to variations in experimental conditions and the specific chemical nature of the systems.

Nearly all studies confirm that elevated temperatures (> 70 °C) and high salinities (> 10-15 wt%) adversely affect the stability of foams and dispersions in the absence of surface

modification (Worthen et al., 2013; Bayat et al., 2016; Fu et al., 2018; Al Yousef et al., 2020). Nonetheless, modified nanoparticles, such as TiO₂-AEAPTMS (Hosseini et al., 2022) и and SiO₂-caprylamidopropyl betaine (Worthen et al., 2013), exhibit stability even under such harsh conditions, highlighting the critical role of surface chemistry and ζ-potential.

A consistent relationship is observed between particle size and aggregation tendency: nanoparticles with diameters >100 nm in the aqueous phase tend to agglomerate, particularly under conditions of elevated ionic strength, which reduces their effectiveness (Bayat et al., 2016; Amraeiniya et al., 2023).

However, when stabilizers such as surfactants, polymers, or functional coatings are employed, even larger particles (e.g., Ag NPs ~26 nm) can retain dispersibility and exhibit pronounced functional effects. This highlights the interdependence between particle size, surface modification, and the dispersion medium.

The influence of crude oil composition on nanoparticle performance is particularly evident in study (Amraeiniya et al., 2023) here the asphaltene inhibition efficiency of Al₂O₃ nanoparticles was higher in oils with more aromatic structures and elevated nitrogen content. This observation aligns with the mechanism of specific sorptive interactions between asphaltene functional groups and the oxide surface, previously reported for Fe₃O₄-HAp as well (Safaei et al., 2020). Thus, the composition of the organic phase plays a critical role in nanoparticle effectiveness and should be considered when formulating nanofluids.

With respect to nanoparticle concentration, both consistent and contradictory trends have been reported. Most studies identify an optimal concentration range between 0.05 and 0.1 wt%, beyond which performance may decline due to aggregation and pore blocking (Bayat et al., 2016; Rahmatmand et al., 2016; Fu et al., 2018). However, in some cases, such as SPN Pickering emulsions (Pal and Mandal, 2020), an increase in efficiency was observed up to 1-2 wt%, which was attributed to the fundamentally different nature of the system: a quasi-stable three-phase structure with nanoscale droplets. Therefore, the type of target system (emulsion, foam, or solution) must be considered when extrapolating results.

Finally, results obtained for mixed compositions, such as CNT + SiO₂ (Sha et al., 2013) or surfactant + SiO₂ (Al Yousef et al., 2020) confirm the presence of synergistic effects, manifested in enhanced foam stabilization or more pronounced wettability alteration. In

contrast, individual components (e.g., CO₂ alone or surfactants alone) often prove insufficiently effective on their own. These findings align with the concept of a multicomponent approach to interfacial stabilization, which is critically important under conditions of high temperature, pressure, and salinity.

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