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Environmentally Sustainable and Energy-Efficient Nanobubble Engineering: Applications in the Oil and Fuels Sector

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Abstract

In bulk liquid or on solid surfaces, nanobubbles (NBs) are gaseous domains at the nanoscale. They stand out due to their extended (meta)stability and great potential for use in practical settings. However, due to the high energy cost of bubble generation, maintenance issues, membrane bio-fouling, and the small actual population of NBs, significant advancements in nanobubble engineering through traditional mechanical generation approaches have been impeded thus far. With the introduction of the electric field approach to NB creation, which is based on electrostrictive NB generation from an incoming population of "electro-fragmented" meso-to micro bubbles (i.e., with bubble size broken down by the applied electric field), when properly engineered with a convective-flow turbulence profile, there have been noticeable improvements in solid-state operation and energy efficiency, even allowing for solar-powered deployment. Here, these innovative methods were applied to a selection of upstream and downstream activities in the oil–water–fuels nexus: advancing core flood tests, oil–water separation, boosting the performance of produced-water treatment, and improving the thermodynamic cycle efficiency and carbon footprint of internal combustion engines. It was found that the application of electric field NBs results in a superior performance in these disparate operations from a variety of perspectives; for instance, ~20 and 7% drops in surface tension for CO_2- and air-NBs, respectively, a ~45% increase in core-flood yield for CO_2-NBs and 55% for oil–water separation efficiency for air-NBs, a rough doubling of magnesium- and calcium-carbonate formation in produced-water treatment via CO_2-NB addition, and air-NBs boosting diesel combustion efficiency by ~16%. This augurs well for NBs being a potent agent for sustainability in the oil and fuels sector (whether up-, mid-, or downstream), not least in terms of energy efficiency and environmental sustainability.

Keywords: nanobubbles; fuel enhancement; diesel; petroleum; enhanced oil recovery; surface tension; well stimulation

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1. Introduction

Nanobubbles (NBs) are gaseous domains at the nanoscale, existing on solid surfaces or in bulk liquid, which are noted for their long-term (meta)stability and high potential for real-world applications [1–3], e.g., nanoscopic cleaning [4], boundary-slip control in microfluidics [5], wastewater treatment [6], hetero-coagulation [7], and medical applications [8]. While NBs on surfaces have been observed, NBs in the bulk have been less-studied. It is speculated that NBs' longevity arises from negative-charge build-up at the bubble–liquid interface, with the surface having strong electron affinity [9]. Generated properly, nanobubbles offer a chance, promisingly, to overcome fundamental gas-in-liquid solubility "bottlenecks" and—owing to their Stokes' Law "defying" longevity—have enhanced mass-transfer properties [1–3].

NBs have special characteristics that set them apart from regular bubbles, including a large specific surface area, a slow rate of rise, a high mass transfer efficiency, and charged surfaces [10], all of which are important for the oil and fuel industries. They have important potential applications in the context of nanostructured fluids to improve oil recovery. For instance, pressure change [11], a decreased injected fluid mobility ratio and declining interfacial tension [12], altered wettability [13], and the prevention of asphaltene precipitation [14] have all been found to be prominent amongst certain nanofluids' mechanisms to improve oil recovery. Nevertheless, despite traditional nanofluids' often-positive effects on oil recovery, the presence of nanoparticles has sometimes led to a significant potential for reservoir damage owing to solid-phase nanoparticles' retention in the reservoir. Tiny bubbles with sizes between micro- and nanometers are referred to as nanobubbles. In this sense, NBs offer a particularly attractive option for improving mass transfer rates at the gas–liquid interface to design more effective nanofluids for the oil industry in terms of promoting physical adsorption and chemical reactions. Furthermore, the solubility of CO_2 in the liquid phase is greatly enhanced by the nanobubbles' small curvature radius and high internal pressure [15]. These bubbles can stay stable in the liquid phase for long periods of time without the need for chemical additives and are simple to create using a variety of techniques [16,17]. In terms of NBs enhancing core phenomena, the generation of NBs in cores and their dissolution profile therein has been studied [18]. Zhenhao et al. examined oil recovery experiments involving gas flooding, water flooding, and dispersed water–gas systems, making use of micro-etching and high-speed cameras [19], and concluded that mechanical alterations in the fluid, which serve to lessen interfacial tension and facilitate CO_2 penetration into tiny pores, are the fundamental "driving forces" of ultrafine-bubble-driven oil recovery. They suggested, insightfully, that the smaller the bubble, the more marked these twin drivers are for displacement. In addition, Telmadarrreie et al. showed that CO_2 ultrafine-bubble technology improves injected fluid sweep efficiency [20]. In general, a number of experimental techniques have confirmed the viability of CO_2 finebubble-driven oil recovery [19–21]. However, these studies have mostly examined micron-sized bubbles, with there being less investigation into the mechanisms underlying the oil recovery of genuinely nanoscale bubbles due to limitations in experimental methods.

Reflecting further on the drivers affecting NB performance with respect to oil recovery, a number of intricate variables emerge, such as the liquid film's characteristics, the pore geometry, and the injection conditions; naturally, all of these affect foam mobility in porous media. These variables mainly impact bubble size, which modifies the mobility of the foam, which is fundamental to the (projected) oil recovery performance [21–24]. In any event, despite the admitted challenges in the direct observation of bubble transport processes within pores because of the present limitations in experimental techniques, the phase changes of CO_2 nanobubbles must be assessed before, during, and after oil recovery from various perspectives; this includes the quantity of nanobubbles and gauging putative CO_2 gas production upon the bubbles expiring. Clarifying the mechanisms underlying CO_2 nanobubble-driven oil recovery in reservoirs requires such (however preliminary) assessments as a starting point.

Having considered the potential promise of nanobubbles as an agent for improving oil recovery (as well as the associated challenges and complications), we can consider other similar prospects and challenges more broadly, i.e., beyond the "upstream oil arena". Aside from NB prospects in EOR [21–24], midstream work is also important (e.g., produced-water demineralization/treatment [25] and oil–water separations [26]), as well as downstream operations (e.g., gas absorption [27] the and promotion of thermodynamic cycle efficiency for more efficient and cleaner engine burning [28]).

However, there are many reasons as to why NBs have not yet made a deep impact on the oil and fuel sectors—and typically, these overlap heavily with rather universal factors impeding the "nano-gasification" of all liquids (most typically, water, wastewater, and aqueous solutions) [16]. In essence, these refer, *inter alia*, to the high energy cost and maintenance challenges of biofouling involved in traditional, mechanical-based NB-generation approaches, with the latter problem often resulting in industrially unaffordable intolerable unpredictable and unscheduled downtime in commercial unit operations [16], regardless of the particular application. This is discussed at some greater length in [16].

Given that NBs have much to offer a whole suite of unit operations in the oil and fuel sectors, the present report applies the discovery and patented invention of electric field-imparted nanobubble and nanodroplet generation and stabilization via the application of external electric fields to gas–liquid systems (at arbitrary gas pressures) [16]. This leads to the dramatic result of massively increased gas uptake in the liquid in dense-NB form [16]. In the present article, we apply this method to investigate disparate operations in the oil and fuel sector.

Considering NB effects on enhanced oil recovery (EOR), there are two main "levers" (or, in essence, agents of influence) imparted by NB infusion in wellhead injection water—i.e., thermodynamic and kinetic. The thermodynamic lever asserts that the greater level of gas solubility—beyond Henry's Law (super)saturation—allows the added gas (e.g., CO_2) to shift the phase-diagram boundary in favor of removing great levels of rock-intercalated hydrocarbon. The kinetic lever (or influence) is "two-pronged" in that the NBs (acting as gas "reservoirs" or "batteries") allow for the Fick's Law-driven replenishment of the Henry's Law state-dissolved gas levels, whilst the surface tension of the "mother liquid" itself is also somewhat reduced by the NBs [21], allowing for more facile and rapid penetration into the rock–sediment matrix and reaching, more completely and quickly, the pore-intercalated hydrocarbon therein for kinetic dislodgement. It may also be hypothesized that the greater electrostatic charge and dipole–quadrupole interactions of electric field-generated CO_2-NBs with the surrounding water (also quite possibly containing acid and emulsifying agents) serves to lead to a greater degree of adsorption of surfactants thereto, thereby reducing the amount of surfactant needed.

In the case of NB influence on produced-water demineralization, this may also be achieved by CO_2-NBs, which allow for more facile carbonation reactions, e.g., to calcium- and/or magnesium-carbonate. In this case, more rapid "crash" precipitation of a larger quantity of the respective carbonates may be affected, leading to a greater degree of demineralization.

For NB-enhanced oily water, for oil–water separations in midstream oil-production, or in environmental remediation efforts after oil spills, the use of air-NBs in dissolved air flotation (DAF) operations becomes important (hinging on an exquisite surface-area to volume ratio), especially with judicious choice of phase-segregation surfactants. It may quite reasonably be hypothesized that the greater "electrostatic personality" of NBs generated by electric field effects (i.e., a shift in electrostatic potential surrounding the nanobubbles [2,3]) allows for the potent adsorption of surfactants (needing less thereof per unit volume of liquid), with the NBs then serving as the center of "colonies" that rapidly become micro- and meso-scale via electrostatic adsorption thereon, alongside the more facile DAF-induced oil–water phase segregation.

It has also been shown in a previous work that electric field-generated air-NBs in petroleum serve to boost thermodynamic cycle efficiency in internal combustion engines [28]; hence, the current study considers diesel engines and associated exhaust emissions.

Given this "backdrop" of the dual kinetic–thermodynamic role of NBs in influencing the surface tension and overall *de facto* gas solubility of nanofluids, as well as the paucity of such studies in the oil–water fuels sectors, as outlined above, the purpose—and the novelty—of the current study lies in its applying dense, electric field-generated nanobubbles to improve and enhance a variety of important unit operations in these sectors. In this sense, we exploit both the kinetic and thermodynamic "levers" of these unique and dense electric field NBs to bring about tangible improvements to core flood phenomena, flotation, oil–water separation, produced-water treatment, fuel combustion efficiency, and exhaust-emissions profiles—essentially rendering the oil–water fuels sector a more sustainable undertaking.

2. Materials and Methods

In the present study, with ref. [16] having compared, in detail, the electric field approach for generating large quantities of long-lived NBs in an energy- and operationally efficient manner compared with traditional mechanical generation approaches, we have opted to use the electric field approach given its clear superiority from various perspectives. In brief, ref. [16] found substantially elevated and longer-lived NB populations via the electric field innovation, together with the generation of much higher levels of reactive species, in tandem with a much lower energy requirement compared to traditional mechanical generation approaches.

To assess and investigate the CO_2-NB injection water effect, *inter alia*, on EOR, core flood testing was performed to determine the rate of recovery, the law of change arising from differential repulsion, and, of course, the gas–oil ratio for production. Here, a long-core oil-repulsion run was carried out indoors, with a timed schedule of aqueous CO_2 nano-fluid flush injection. A double-tube parallel mandrel drive was used in conjunction with a 6-bar regulator output CO_2 cylinder (BOC Gases), a double-acting hydraulic cylinder-pump from White House Products, Ltd. (for isothermal–isobaric operation), an isothermal box, and surfactant solution (incorporating a 99%-pure cationic surfactant cetyltrimethylammonium bromide (CTAB)). Further, the core flood set-up comprised a view window, a Bronkhorst mass-flow controller flow, a pressure and temperature controller, and a gripper for the sandstone core (0.0223 μm^2 permeability, 98% water flooding to 98% water content, and CO_2-NBs to 1500 m^3/t gas–oil ratio). The viscosity of the synthetic oil was set to be formulated to 3.2 mPa·s, whilst the mineralization of the synthetic in situ water (fashioned from ion addition to deionized (DI) water from CarPlan Motor Factors) was 1875 mg/L (548 Na^+, 10 K^+, 20 Ca^{2+}, 7 Mg^{2+}, 860 HCO_3^-, 430 Cl^- mg/L).

The surface tension of the "nanofluids", as well as that of the "control" liquids (in the absence of NBs), was measured by the pendant-drop method after 1 h of aging time [29]. The sensitivity was 0.01 mN/m, and the arithmetic mean and standard deviations were found for all measured properties.

For the CO_2-NB-induced "crash carbonate precipitation" of produced water, the above in situ water was used. In the case of air-NBs in DAF for oil–water separation, the solution for synthetically produced water was made by mixing 3 liters of the above-described in situ water with 2.5 g of synthetic oil per liter for subsequent mixer emulsification over 25 min at 22,000 r.p.m., leaving it to stand for 3 h in a plastic column, leading to a stable emulsion. For subsequent pH-shifting to help induce flocculation, 0.1 M NaOH solutions were prepared; ferric chloride was added at 15 mg/L, whilst a polyacrylamide flocculation polymer was deployed.

In the case of fuel enhancement by air-NBs, following the independent verification of the results of petroleum enhancement by air-NBs in [28], i.e., *ceteris paribus*, a *circa* 14% improvement in running times for internal combustion engines [30], we applied, in the present study, air NB generation in retail diesel (ISO-4406 [31]) using a tubular-flow NB generator for subsequent use in a Hyundai 5.2 kW diesel generator for running time enhancement.

In all of these cases in the present study, an AquaB tubular-flow pipe-type NB generator was employed for NB generation in either aqueous solutions or diesel, whether from air or CO_2, as described further in [16,28]. This NB generator routine delivers NB populations in the order of 10^7 NBs per ml for flows in the order of 30–120 liters per minute [16]. Here, in brief, the 1 m long electrostriction section saw the generation of NBs after upstream macro-, meso- and micro-bubble generation from Venturi-created air or compressor-created CO_2 bubbles on a single-pass basis. These "nanofluids" were then passed on to the process in question (e.g., the core flood test, produced-water "crash" precipitation, the diesel generator running-time test, or oil–water separation), and each was measured three times. Three "control" runs were also carried out under the same conditions with identical aqueous solution process waters (or oil/water emulsions), or diesel, without the addition of NBs. The amounts (i.e., the concentrations) of CTAB and the flocculation polymer were recorded for the respective core flood and oil–water-separation operations, whether enhanced by NBs or in the "control" mode, to gauge if a reduction in such levels could be realized using NB generation for these respective operations.

3. Results

3.1. Surface Tension

Of relevance to both core flood experiments and oil–water separation is the surface tension. In the case of DI water at 20 deg C, this was 72.6 mN/m, in contrast to circa 69.2 and 68.7 for DI water containing air- and CO_2-NBs, respectively, in such water—a greater level of reduction than in [21,29], most likely due to the greater level of mass density of the electric field-generated NBs in contrast to those generated by mechanical generation approaches [16], as well as their high populations in the present work. With CTAB and the flocculation polymer at 0.2 wt % in DI water, this was reduced to circa 39.4 and 64.2 mN/m for CO_2- and air-NBs, respectively. In the respective presence of CO_2- and air-NBs, these were reduced to 31.7 (a ~20% drop) and 59.7 mN/m (a ~7% drop) for the same 0.2 wt % concentration. Interestingly, however, with using half of that concentration (i.e., 0.1 wt %) in the respective "nano-bubbly" water solutions, these corresponding values were similar at 32.6 and 60.4 mN/m. This offers the attractive prospect of adding perhaps a fraction of the initial charge in (often somewhat expensive) surfactants and polymers in conjunction with NBs to achieve a similar reduction in surface tension. This is attributable to enhanced levels of the electrostatic adsorption of such molecules to NB surfaces, which themselves are electrostatically active (and especially so in the case of electric field-generated NBs [16]). This same phenomenon has been characterized and studied in more depth in the case of agricultural fertilizer molecules vis-à-vis plant-growth levels [32]. The results of the percentage change imparted by the introduction of nanobubbles are summarized in Table 1.

Table 1. Summary of the effect of introduction of air- and CO_2-NBs.

Approach	% Change (Air-NBs)	% Change (CO_2-NBs)
Surface tension (0.1 wt % CTAB/polymer)	−6.0	−17.2
Surface tension (0.2 wt % CTAB/polymer)	−7.1	−20.3
Core flood yield	-	45
Core flood breakthrough curve PV shift	-	−37
Core flood pressure stabilization shift (gauge)	-	−78
Oil–water separation efficiency (0.1 wt %)	54.8	-
Oil–water separation efficiency (0.2 wt %)	58.9	-
Produced-water magnesium-carbonate yield	-	~90

Table 1. *Cont.*

Approach	% Change (Air-NBs)	% Change (CO_2-NBs)
Produced-water calcium-carbonate yield	-	~160
Diesel combustion efficiency	16	-
Diesel exhaust gas CO_2 concentration	−9	-
Diesel exhaust gas CO concentration	−11	-

3.2. Core-Flood Testing

The core flood results are summarized as follows. It was seen that the presence of CO_2-NBs with CTAB at 0.1 and 0.2 wt % improved the ultimate oil recovery from about 49% (in the "control" case of water flooding and CO_2 gas flooding) to 71 and 72%, respectively (a roughly 45% improvement for water flooding and the CO_2-NB solution with the two different levels of CTAB), with the recovery plateau at 2–2.5 pore volumes. The breakthrough curve in the gas–oil ratio occurred at circa 1.7 versus 2.7 pore volumes (PVs) for the "control" case versus the NB cases (similar for both CTAB concentrations). Pressure stabilization was circa 8.2 bar g versus 37.3 and 38.2 bar g for the "NB-flooding"-approach 0.1 and 0.2 wt % CTAB cases after almost two PVs. The results of the percentage change imparted by the introduction of nanobubbles are summarized in Table 1. These results show that NBs offer a good deal of promise. In fact, the positive operational implications of these core flood tests suggest that larger-scale EOR operations employing CO_2-NBs will be impactful.

3.3. Oil–Water Separation

The oil removal efficiency was boosted in the case of air-NB-enhanced DAF in conjunction with the application of the flocculation polymer versus the "control" of regular air sparging and the use of 0.2 wt % polymer in conjunction with the pH-shift procedure (leading to oil removal of 62% in the case of a saturation pressure of 4 bar). In contrast, in the case of air-NB usage, both 0.1 and 0.2 wt % polymer levels were used, with slightly better oil removal results for the 0.2 wt % level: 96 and 98.5%, respectively (roughly 55% better), which is clearly superior to the case of using a regular-air hose (with coarse macrobubbles of air in the ~0.5–2 mm size range). Since air macrobubbles escape readily and quickly from the water according to Stokes' Law (within less than tens of seconds), the presence of air-NBs serves to enhance the surface-area-to-volume ratio in flotation operations (given that this ratio for bubbles is related to d^2/d^3, i.e., $1/d$, and therefore enhanced by smaller bubble diameters, d). This enhances flocculation operations, owing to their electrostatic attraction with respect to the flocculation polymer; the use of less polymer to achieve similar oil removal levels is important for operational and cost reasons, as well as for improving the environmental/sustainability profile of oil removal operations. In terms of oil removal kinetics, it was found that the ultimate (higher) removal level of NB-enhanced flotation flocculation occurred at a rate of about 20% faster compared to the control case (of regular air sparging with macrobubbles). The results of the percentage change imparted by the introduction of nanobubbles are summarized in Table 1.

3.4. Produced-Water Treatment

Compared to the regular CO_2-macrobubble sparging of the synthetically produced water (with a similar bubble-size distribution as for the regular air sparging in the case of oil–water separation in Section 3.3), it was found that the use of CO_2-NBs generated in such synthetically produced water led to a boost in the "crash-precipitation" yield of magnesium- and calcium-carbonate of ~1.9 and 2.6-fold in a similar time as for the control case using CO_2 macrobubbling. The greater level of mineralization is enhanced by the boost in the mass-transfer kinetics efficiency afforded by the far more favorable surface-area-to-volume ratio, as well as the quadrupole–dipole interactions of CO_2-NBs and the surrounding hydration-layer water molecules leading to electrostatic effects on the attraction of ions present in the produced water, allowing for such carbonation reactions to happen more readily in their locale. This enhances the local supersaturation of such carbonates to the point that precipitation occurs more readily. The results of the percentage change imparted by the introduction of nanobubbles are summarized in Table 1.

3.5. Diesel Combustion Enhancement

In a similar way to [28], and independently confirmed in [30], air-NBs were incorporated into diesel in the present work, as opposed to petroleum in the earlier study. Using the diesel generator to measure running time tests for the equivalent volume of "control" diesel and its nano-aerated variant (i.e., the time taken for the generator to stop running on the equivalent mass of diesel), it was found that there was a ~16% enhancement in the case of NB-containing diesel. This is a slight improvement over petroleum (14%, as discussed in [28]). In addition, usage of a Bosch diesel exhaust gas analyzer showed a decline of ~9% for CO_2 and 11% for CO, since more complete combustion occurs owing to the entrained NBs inside the fuel micro-droplets (i.e., simultaneous combustion of the micro-droplets from the inside of the droplets from the entrained air oxygen in NBs and from the outside [28,30]). The results of the percentage change imparted by the introduction of nanobubbles are summarized in Table 1.

4. Discussion

It is clear that a variety of operations in the oil and fuel sector, from up- to downstream, can be enhanced by the generation of air or CO_2-NBs. The enhanced electrostatic potential of NBs leads to a boost in the adsorption of agents such as surfactants or polymers (as is the case with fertilizer molecules in agriculture [32]), meaning that there is "delivery agency" or a "carrier effect", leading to a greater chance of these molecules being yet more thermodynamically and kinetically effective for a given concentration in the solution; not only do coulombic attraction and interactions lead to a greater accumulation of charged, dipolar, and quadrupolar species (e.g., ions, surfactants, polymers, etc.) in the local hydration-layer milieux of NBs, their proximity to the gas molecules themselves, entrained therein, allows for greatly accelerated mass-transfer kinetics (by Ficks' Law) into the main solvent phase (and for faster carbonation reaction kinetics in the case of produced-water demineralization in the current work).

It would appear that for the displacement of oil in reservoirs, especially those characterized by tight shale rock-geology, injected CO_2 nanobubbles convert to regularly dissolved CO_2 via Fick's Law-driven molecular CO_2 transport; this over-saturation of CO_2 in the regularly dissolved state (i.e., the Henry's Law state of standard molecular dissolution—a single solute molecule surrounded locally in its coordination shell milieu by solvent molecules) can lead to concomitant phase segregation of CO_2 gas. This two-phase, *de facto* "composite" oil–gas then undergoes displacement. With CO_2 molecules themselves being over-saturated in the regularly dissolved state, as a result of (even sluggish) CO_2-nanobubble decomposition, even temporarily, this facilitates CO_2 penetration into smaller rock pore sizes more easily, and this is readily apparent in the shorter-term surface-tension measurements reported in the present study. Naturally, in terms of the realization of progressively smaller CO_2-NBs and the over-saturation of smaller species still in the regularly dissolved state, this is all the more effective in crude oil recovery (as the present study's results also indicate)—and especially so in reservoirs characterized by tight-shale rock formations.

From the present core flood tests, it would appear that CO_2 nanobubbles may exhibit both some thermal expansion and pressure-induced compression effects in the higher-temperature and higher-pressure reservoir milieu, although they can retain their dimensions at the nanoscale range with a comparative degree of metastability, according to dynamic light scattering analysis [16]. Indeed, it must be borne in mind that extrapolation to high-temperature and high-pressure experimental approaches that stimulate any dimensional changes in CO_2 nanobubbles, especially of the ultra-dense variety generated by the presently deployed electric field methods featuring strong quadrupolar–dipolar interactions at the nanoscale CO_2–water interface, will lead to changes in the properties of the "nano-bubbly" core liquids, especially after being displaced from high-temperature and high-pressure reservoir environments to ambient conditions via NB-enhanced EOR processes. In any event, the present study's experiments, using various field-measurable metrics as de facto "proxies", tend to reflect the fundamental trends in nanobubble-size changes from surface injection into the core of the reservoir itself. However, as this study has hinted via surface-tension measurements, beyond core flood testing, during the change in the oil flow profile from static conditions in a reservoir to essentially near-ambient conditions, any P/T changes tend to maximize variations induced by thermally caused expansion and pressure-driven densification.

5. Conclusions

It has been shown that a wide variety of fuel and oil sector unit operations have been rendered a good deal more efficient, environmentally sustainable, and operationally facile. Large-scale EOR was found to be readily possible via the core flood testing of CO_2-NBs via electric field methods (although, naturally, potential future challenges are discussed further in the "EOR outlook" below, especially in the guise of foam mobility in tighter-shale geologies). The boost in ultimate oil recovery from 49 to 71–72% (depending on CTAB concentration), with the attendant breakthrough curve shift from ~1.7 to 2.7 PVs, is highly encouraging, as is the pressure stabilization moving from ~8 to 37–38 bar. This ~45% increase in oil recovery from the *status quo* (i.e., 71–72% versus 49%) shows the dual thermodynamic–kinetic mechanism of persistent solubility over-saturation and surface-tension reduction afforded by the CO_2-NBs.

In a similar vein, the substantial boost in oil removal efficiency for oil–water separation, moving from 62% to ~96–98% with NBs (an increase of circa 55% relative to the *status quo*), is highly encouraging for larger-operation scale-up efforts, even with some loss of efficiency being envisaged at the industrial scale vis-à-vis the prototype scale. The essential doubling of carbonate precipitation yield in produced-water treatment was also a substantial improvement, as was the ~16%-improved diesel combustion rate in terms of CO emissions, about 10% lower than the *status quo*.

Summarizing, there were ~20 and 7% drops in surface tension for CO_2- and air-NBs, respectively; a ~45% increase in core-flood yield for CO_2-NBs; a 55% increase in oil–water separation efficiency for air-NBs; a rough doubling of magnesium- and calcium-carbonate formation in produced-water treatment through the addition of CO_2-NBs; and air-NBs boosted diesel-combustion efficiency by ~16%.

Clearly, in addition to the presently studied operations, the nanobubble-enhanced carbonation-driven mineralization reactions witnessed in produced-water treatment (and the demineralization of the water itself to sustain such complete and rapid mineralization) opens up new vistas in in situ carbon sequestration in the geological milieu (e.g., saline aquifers, disused coal-mine shafts, etc.). The combination of the higher level of CO_2 in NB form—substantially above Henry's-Law solubility—with lower liquid surface tension and more facile fluid penetration into capillaries and pores in the rock–sediment matrix allows for very positive potential ramifications for geological-setting mineralization. Of course, similar remarks apply to manufactured cement and artificial limestone, with potential positive effects on mechanical strength and durability, as well as the sequestration of carbon therein.

Aside from the importance of enhanced carbonation *per se*, the manipulation of foam-like properties in oil recovery efforts enhanced by nanobubbles warrants further attention following the encouraging preliminary results highlighted in the present study (e.g., in terms of "proxy" variables for nanobubble presence, such as surface tension). In this sense, a future "nanobubbles-for-EOR" research agenda could focus on studying the manipulation of the mobility of NB-foams in porous rock media. More specifically, the mobility of foams depends on various variables, often in a complicated manner, such as the pore geometry, the injection dynamics, surface tension, viscosity, and ionic strength, which do affect NB stability and also influence foaming properties (such as mobility influenced by the surface-area-to-volume ratio). Indeed, these foaming properties, which can be adjusted judiciously in favorable ways via the presence of NBs, both to maximize crude oil production and produced-water treatment yield, also need to be gauged carefully in recognition of the electrostatic "carrier" effect in terms of the role of surfactants in electrostatic binding to NBs, and of how NBs may be used to minimize the needs for various additives and surfactants in oil–water unit operations.

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