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Characterization and Influence of Sustainable Hybrid Silica Nanoparticles on Enhanced Oil Recovery and Carbon Geosequestration

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ABSTRACT

The growing demand for energy, coupled with the continued dominance of fossil fuels as the primary energy source, necessitates eco-friendly technologies that simultaneously enhance oil recovery (EOR) and reduce the impact of their emissions. Only one task, which is the CO_2-EOR project, can combine these two sustainable development goals. Further, employing green nanotechnology, including nanoparticles and nanofluids, ensures a sustainable approach to controlling and enhancing rock wettability, thereby enhancing hydrocarbon production and carbon storage. However, the performance of nanofluids in subsurface formations is limited by the stability of these nano-dispersions at the harsh conditions of reservoirs. This work thus synthesizes silica nanoparticles from waste bentonite as a green source and modifies the surface properties with a silane group to formulate a stable nanofluid for subsurface applications. The produced nanoparticles were characterized via Fourier Transform Infrared (FTIR) spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), zetasizer, and dynamic light scattering (DLS). Moreover, the efficiency of nanoparticles as wettability-modifying agents was studied using contact angle and spontaneous imbibition tests. FTIR measurements confirmed the presence of silane on the surface of hybrid silica nanoparticles, as indicated within the Wavenumber 2950 cm-1. Moreover, XRD measurements revealed that hybrid nanoparticles showed lower noise than pure ones. Results also showed that silane-treated nanoparticles (hybrid) are more tolerant to high salinity ($\geq$ 0.5wt% brine), and green-synthesized nanoparticles have a drastic ability to invert the wettability of oil-wet surfaces ($\theta \geq 123°$) to water-wet ($\theta \leq 28°$) at ambient conditions and also reduce the contact angle from 175° to 68°) at CO_2-EOR conditions. The study concludes that these green nanofluids are highly efficient for EOR and carbon geosequestration projects when properly formulated.

1. Introduction

Subsurface industries, such as enhanced oil recovery (EOR) and carbon geosequestration, cannot be divorced from rapidly growing sustainable technologies such as nanotechnology. With the development of nano-sized materials and the subsequent formulation of engineered

nanofluids, the geological industry has witnessed significant potential for controlling subsurface interfacial properties, which is key to efficient CO_2-EOR projects [1]. Such a possible manipulation of both the rocks' wettability and multiphase flow in hydrocarbon reservoirs can take the CO_2-EOR industry and the global efforts to mitigate greenhouse gas emissions to the next level [2-6]. In these projects, injecting the CO_2 into depleted oil reservoirs can extract additional hydrocarbons while simultaneously storing anthropogenic gas geologically [7]. However, hydrocarbon reservoirs are located thousands of meters deep in the geological formation under very severe thermodynamic parameters along with extensive heterogeneity, and salinity [8, 9], which limit the stability, efficiency, and consistency of the nanofluid's effect on the CO_2-EOR process [10]. Thus, a highly tolerant nanofluid composed of engineered nanoparticles (NPs) dispersion in the base fluid should be designed and formulated to adapt to the CO_2-EOR under harsh conditions.

Oil reserves in the Middle East region, which mainly includes Saudi Arabia, Iraq, Iran, and Kuwait, store up to 50% of the confirmed discovered hydrocarbon globally, and around 70% of these reserves are located in carbonate formations [11, 12]. However, oil production from carbonate reservoirs is one of the crucial challenges in the oil industry due to the heterogeneity, fracturing, oil-wet and mixed-wet nature of carbonate rocks [13], which retain around 70-90% of the original oil in place after the primary and secondary recovery stages [8]. The key mechanism to produce more oil after these two stages is to adjust the wetting property of the carbonate porous media to water-wet [14]. In line with this, rendering the wettability of oil-wet rock matrix water-wet is of great benefit to carbon capture and storage (CCS) projects, as it leads to higher carbon storage capacity and minimum leak risks [15]. Mechanistically, switching the wettability from oil-wet and mixed-wet to water-wet facilitates the displacement of oil from the rock's matrix and increases the structural and residual trapping of carbon [16-20].

Over the last decade, nanofluids, which are solid nanosized materials dispersed in an aqueous solution, have been extensively investigated for their potential as wettability modifier agents. Due to their small size (1-100nm), nanoparticles (NPs) can penetrate and enter the smallest pores in porous media, allowing water to displace oil with the aid of NP's structural disjoining pressure [2, 21-24]. Such a mechanism can significantly influence the interfacial properties of porous media, providing better economic and environmental potentials for subsurface projects, including EOR and CCS, particularly if such NPs are eco-friendly and produced from sustainable sources. Previous studies mainly used metal oxides or semiconductor NPs dispersed in brine or DI water to manipulate the wettability of carbonate surfaces [25]. Roustaei and Bagherzadeh [26] reported that aging oil-wet calcite in 4 g/L silica nanofluid can alter its wettability to strongly water-wet under ambient circumstances. Additionally, the results showed that aging an oil-saturated limestone plug in the nanofluid, followed by water flooding, can produce a significant amount of oil. Nwidee, et al. [27] revealed that treating strongly oil-wet calcite surfaces with zirconia nanofluids for 24 hours can render the wetness status water-wet through reducing the water contact angle from 152° to 44°, and a consistent effect on coreflooding was reported. The iconic study by Al-Anssari, et al. [28] marked the beginning of an investigation of the impact of silica nanofluid on the wettability of strongly oil-wet calcite at carbon storage conditions (e.g., 80°C and 25 MPa). Their results starkly declare that oil-wet rocks are simultaneously CO_2-wet, and treating such rocks by silica nanofluids under carbon storage harsh conditions may efficiently render the wetting status of CO_2-wet rocks water-wet, thereby increasing the carbon tapping capacity and reducing leakage risks. Rostami, et al. [29] studied the performance of silicon dioxide (SiO2) NPs as a wettability modifier in a saline environment and reported that the increase of salinity strength can intensify the rendering of an oil-wet surface water-wet owing to the higher penetration rate of silica NPs into the rock's matrix. However, such a high adsorption rate refers to a dramatic instability of the nanofluid. This was confirmed by Arain, et al. [30], who demonstrated that bare (hydrophilic) silica NPs may rapidly aggregate once they come into contact with the liquid phase, and such aggregation processes increase with salinity. Moreover, they treated the bare silica NPs with silane to produce stable NPs when dispersed in brine, and they referred to these silane-grafted-silica NPs as

hybrid NPs. Using a glass-model porous medium, Mahdi, et al. [3] confirmed the results of the core-plug nanofluid flooding conducted by Al-Anssari, et al. [23], which reported that silica will be retained at the early stage of the core due to instability and rapid aggregation in a saline environment. Recently, studies have been focusing on producing surface-modified silica NPs via treating with silane groups to formulate salt-resistant or stable silica nanofluids [31-33]. The extent of surface modification depends on the type of silane and the method of the silanization process [34]. Further, the traditional synthesis of silica NPs mainly depends on costly methods and precursors [35]. The green synthesis of silica NPs from sustainable raw materials is a crucial approach for feasible applications, as it is inexpensive, non-toxic, and environmentally friendly [36]. Local sand or bentonite, which is primarily a phyllosilicate mineral rich in silica, is a sustainable and ecologically friendly source for the synthesis of silica NPs [37], particularly when this bentonite is a waste of the drilling process. Note that the reservoir drilling process stereotypically generates a substantial amount of bentonite as waste, which requires a considerable amount of storage space and poses environmental challenges for disposal. Thus, this waste-bentonite is typically a sustainable source for producing silica NPs. It is essential to characterize and examine the efficiency of these green-surface-modified NPs as wettability modifier agents under EOR and carbon storage conditions.

This study presents a systematic investigation of a hybrid nanofluid for CO_2-EOR processes in harsh reservoir conditions. The hybrid nanofluids are liquid dispersions of salt-tolerant silica NPs that are sustainably synthesized from bentonite and treated with silane groups. The hybrid NPs were characterized using Fourier Transform Infrared (FTIR) spectroscopy and X-ray diffraction (XRD) to examine their chemical composition and crystalline structure, respectively. Energy-dispersive spectroscopy (EDS) and scanning electron microscopy (SEM) were utilized to confirm the achieved measurements. The stability of the formulated nanofluids was examined via the zeta sizer (zeta potential) and dynamic light scattering (particle size) measurements. Contact angle measurements at CO_2-EOR conditions were conducted to evaluate the effect of hybrid NPs on the wettability of oil-wet carbonate rocks. To the best of our knowledge, this is the first insight for using surface-modified, sustainably synthesized NPs for EOR and CCS applications, which combines the use of sustainable materials in ecologically friendly processes.

2. Experimental Methodology

2.1 Materials

Bentonite was supplied by the Missan Oil Company and utilized as a green raw material to produce silica NPs. 3-aminopropyl triethoxysilane (Mol wt = 221.37 $g.mol^{-1}$) purchased from Sigma-Aldrich) was used in the treatment of silica NPs via the silanization process to produce hybrid silica NPs. Homemade DI water with a resistivity of 18.25 $m\Omega\, cm^{-1}$ was used to formulate various aqueous phases and for cleaning purposes. Ethanol (CH_3CH_2OH, purity ≥ 99.5%, ACS reagent, from Sigma-Aldrich) was used in the silanization process. Normal decane (99.5%, supplied by Sigma-Aldrich) was used in various preparation processes and served as the model oil for this study. Sodium chloride (NaCl >99.5%) and calcium chloride (CaCl2 ≥93%) were purchased from Alfa Chemistry and used to prepare brine according to the API ratio (80% NaCl, and 20% CaCl2). Nitrogen (N2 gas, 99.9 %) for a contamination-free drying process, and carbon dioxide (CO_2 gas, 99.9 %) to provide conditions for CO_2-EOR and CCS processes were both supplied by BOC. Hydrochloric acid (HCl, 37%, ACS reagent), sodium hydroxide (NaOH, 98%), and nitric acid (HNO3, 95% white fuming nitric acid) from Sigma-Aldrich were used to prepare the predesigned 2.5 M HCl, 2 M NaOH, and 10 M HNO3 solutions, respectively.

Cylindrical core plugs (17 mm in length and 4.8 mm in diameter) drilled from limestone rock (limestone, WARD'S Natural Science) served as carbonate rocks in the spontaneous imbibition experiments [23]. These cores were almost identical in dimensions and physical properties (porosity = 20%, pore volume ≈ 0.0615 cm3, and permeability = 370 mD), since they were drilled from the same rock sample using the same bit. These cores were connected to Swagelok connectors using heat-shrink sleeves protected with epoxy resin

Calcite substrates were used as representatives of the carbonate surface in contact angle measurements, which directly measure the wettability. However, natural calcite is strongly water-wet, while carbonate rocks in hydrocarbon reservoirs are characteristically strongly oil-wet and mixed-wet, mainly due to the thousands of years of oil invasions into such underground formations [38, 39]. Subsequently, to mimic the scenario in limestone formations, natural calcite substrates were modified with long-chain acids, such as stearic acid (CH3(CH2)16COOH >99%, white waxy solid insoluble in water, Sigma-Aldrich), to transition from naturally water-wet conditions to an oily wetness status.

2.2 Synthesis of silica NPs

Bentonite, as a by-product of the drilling process, is primarily a phyllosilicate mineral composite of silica, which makes it a sustainable green source to produce silica NPs. To achieve this, a synthesis process, as highlighted in Figure 1, was conducted.

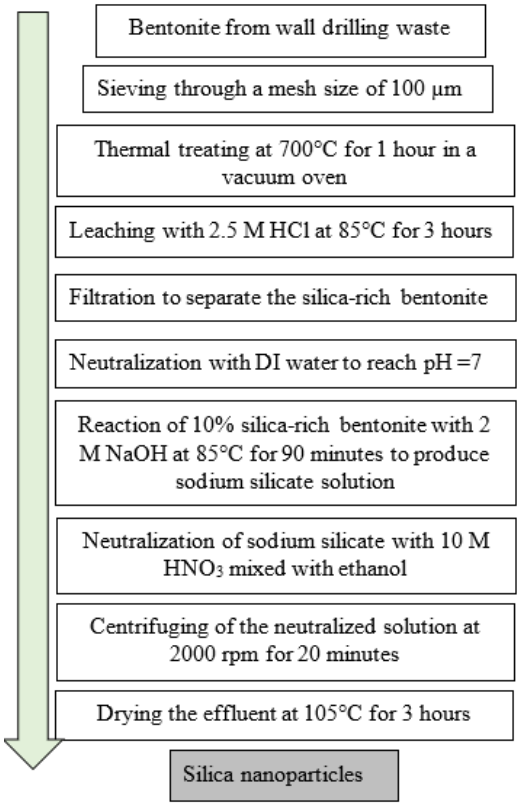

Figure 1. Flow diagram of the green synthesis of silica NPs from waste-bentonite sustainably.

Initially, bentonite was first sieved through a 50 µm mesh size, then dried at 700°C for 60 minutes in a vacuum oven. Subsequently, 50 g of dried bentonite was mixed with 500 ml of 2.5 M HCl solution for three hours at 85°C, and the aqueous phase was then filtered to separate the silica-rich mud. Using DI water, multi-washing and filtration processes were conducted on the bentonite residue until neutralization was reached (pH =7). Then, the neutralized silica-rich bentonite was reacted with an excess amount of sodium hydroxide solution (10% silica-rich bentonite with 2 M NaOH) at 85°C for 90 minutes, to produce sodium silicate solution. The achieved solution was filtered to dispatch the residue and any unfavorable impurities, and the obtained sodium silicate was treated with nitric acid (10 M HNO3) dispersed in 30 ml of ethanol for neutralization. The neutralized liquid phase was then centrifuged (Rotanta 460, 1000 min1-1 Hettich Instruments) at a rate of 2000 rpm for 20 minutes to separate the solid silica. Eventually, to achieve the silica NPs, the residue silica from the centrifugation process was dried at 105°C for 3 hours [40].

2.3 Silanization of silica NPs

A stable nanofluid can be reached when the electrostatic repulsive forces are greater than the van der Waals attraction forces between adjusted NPs, which keeps each nanoparticle individually suspended in the colloidal phase and prevents or at least mitigates rapid aggregation of NPs. Augmentation of silica NPs' surface with a silane group can significantly enhance the colloidal stability via increasing the repulsive forces between particles in a silanization process [30, 31, 34]. The silane used for surface modification of silica NPs was 3-aminopropyl triethoxysilane ($H_2N(CH_2)_3Si(OC_2H_5)_3$), which was used as supplied without further purification or changes. In this context, a pre-hydrolyzed solution was initially formulated through the dissolution of 7.34 g of silane in a mixture of 150 mL of ethanol and 1.8 mL of DI water. These amounts of silane, ethanol, and DI water are sufficient to modify 10 g of silica NPs, considering the number of hydroxyl groups in each gram of silica [41]. Moreover, the pH of the hydrolysis phase was controlled at pH = 2 by adding drops of HCl to shift the system from the point of no net electrical charge (i.e., the isoelectric point) of silica. Simultaneously, a dispersion of 10 g silica NPs in

0.5 L of ethanol was sonicated at an energy rate of 180 watts for 5 minutes using an ultrasonic homogenizer (300 VT, Biologics). Subsequently, the hydrolysis solution was pipetted into the NPs dispersion, and the whole aqueous phase was thoroughly agitated overnight. The aqueous phase was then filtered, and the silica nanoparticles were centrifuged to effectively separate the solid phase. Finally, the effluent NPs were impregnated with an excess amount of ethanol to remove the reversibly attached silane and dried at 80°C for 36 hours to achieve surface-modified (Hybrid) silica NPs (Fig. 2). Mechanistically, due to hydrolysis, the hydrolysable group of the silane is covalently linked to the free hydroxyl group of the silica NPs, letting the functional group (NH2) governs the physicochemical property of nanoparticle's surface.

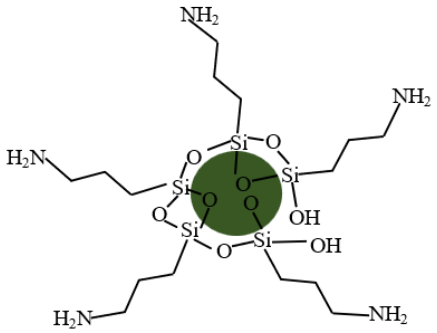

Figure 2. Surface-modified (Hybrid) silica NPs with 3-aminopropyl triethoxysilane.

2.4 Fluid Formulation

Carbonate rock and calcite are both reactive surfaces that can be dramatically dissolved in water. Formation water in carbonate oil reservoirs is typically equilibrated with carbonate ions [42]. Thus, to mimic the real scenario in carbonate reservoirs and to evaluate the sole effect of nanofluid treatment on the surface properties and oil recovery without the impact of surface dissolution on the achieved results, the DI water should be equilibrated with carbonate before use in this study. To achieve this, a calcite piece was submerged in DI water, with continuous monitoring of pH and stirring. Equilibrated water was achieved when no further change in pH was observed, indicating that no more dissolution occurs due to reaching the equilibrated state. After filtration, the equilibrated water is then used to formulate different fluids in this study.

Nanofluids were formulated through ultrasound dispersing of various weights of NPs in different base fluids, including water and brines at various total salinities (0.1 – 2 wt% according to API ratio, which is 80% NaCl and 20% CaCl2). The ultrasound mixing was conducted at a rate of 180 W for 5 minutes via an ultrasonic homogenizer (300 VT, Biologics). Moreover, preventing the potential overheating of the nanodispersion during sonication [43, 44] is essential by using multiple short sonication periods. The brines were previously formulated with different total salinities (0.1 – 2 wt%) according to the API ratio. For instance, the 0.1 wt% brine was formulated via dissolving 0.02g of CaCl2 and 0.08g of NaCl in 99.9g of water using a magnetic stirrer [3, 45].

2.5 Carbonate Surface Modification into Oil-wet

Carbonate rocks are typically strongly water-wet; however, the invasion of oil over thousands of years has altered the wettability in carbonate oil reservoirs, resulting in mixed-wet and strongly oil-wet conditions. Therefore, to simulate the scenario in hydrocarbon reservoirs, calcite substrates were treated with chemicals to alter their wettability to a strongly oil-wet condition. Then, the role of nanofluids in rendering the wettability of such oil-wet surfaces water-wet was investigated. To achieve this, an aqueous phase was formed by dissolving 0.143g of stearic acid in 50 mL of decane. This 1M stearic acid was utilized to modify the surface wetness of pure CaCO3 substrate into a hydrophobic condition [45]. Mechanistically, the adsorption of stearic acid onto the carbonate surface is based on hydrogen ions moving to carbonate ions on the surface; thus, stearic ions chemisorb onto the surface center of calcium ions, which results from surface dissociation of calcite when flushed with water before being immersed in stearic acid [46]. Experimentally, calcite substrates were first washed with acetone and then with water and dried with nitrogen gas. Subsequently, calcite samples were immersed in a vessel filled with a stearic acid solution at a concentration of 10 mL stearic acid, equivalent to 1g of CaCO3 sample. The treating vessel was then heated in a vacuum furnace at 70°C overnight. The calcite samples were then thoroughly cleaned with acetone and water and

stored in a clean, dry place for contact angle measurements or further treatments.

The modification of core plugs into an oil-wet state was conducted by inducing stearic acid into the core plugs. To achieve this, limestone micro core plugs with a diameter of 4.8 mm, a length of 17 mm, and an average porosity of 19% were immersed in stearic acid. Experimentally, each core plug was cleaned with acetone to remove any potential contaminants and dried in an oven at 50°C for 3 hours. The core plugs were then submerged entirely in the stearic acid and heated at 70°C with continuous stirring for 48 hours. Ultimately, the core plugs were flushed with acetone and then DI water and dried at 50°C for 4 hours.

2.6 Nanoparticles Characterization

Silica NPs were sustainably synthesized from waste bentonite as a green source for silica. The chemical structure of the produced silica NPs before and after modification with silane was characterized by Fourier Transform Infrared Spectroscopy (Shimadzu IR Affinity-1). This analysis is a valuable tool to distinguish between the various Si species [47]. Moreover, the crystalline structure of silica NPs, both before and after modification with silane, was also investigated via XRD analysis using a diffractometer (AERIS, Malvern Panalytical, United Kingdom) to determine the amorphous nature of silica NPs. Scanning electron microscopy (SEM, JEOL JSM-7800F) was also used to prob the aggregation and adsorption behavior of various silica NPs. Furthermore, the stability of silica NPs in the aqueous phase was evaluated via zeta potential measurements, which is a direct method for assessing nanofluid stability. In addition, the particle size distribution and the rate of particle growth with time were examined via Dynamic light scattering (DLS) measurements [48]. both zeta potential and particle size distribution were performed on a Malvern Zetasizer Nano ZS90.

2.7 Surface Treatments with Nanofluids

To evaluate the influence of hybrid silica NPs on the surface properties of calcite, particularly the wettability, calcite substrates were submerged in the nanofluids at various desired NPs concentrations and treatment times. In this context, the calcite sample was fixed vertically in the treatment vessel, and a predetermined weight percentage of 10 mL nanodispersion for each gram of the sample was piped gradually to the vessel, submerging the sample for a desired treatment period. Similarly, to examine the effect of silica NPs on the wettability of the oil-wet core plugs, each core plug was submerged in a nanofluid at a specific time, temperature, and NPs concentration. At the end of the nano-treatment (treatment with nanofluid), each core was flushed with cleaning agents, including acetone and DI water, to remove any reversibly attached NPs; then, it was dried at 50°C for 3 hours.

2.8 Contact Angle Measurements

The contact angle is a direct measurement of wettability, which is the affinity of a surface for oil or water [49]. In this context, the wettability of various calcite surfaces at subsurface conditions (high temperature and high pressure) was examined via the pendant drop method utilizing a tilted plate technique [50, 51]. Fig. 3 displays the configuration of the contact angle apparatus. It comprises a pressure vessel (optical cell), a high-precision syringe pump (Teledyne D-500) to inject the CO_2, a high-precision syringe pump (Teledyne D-260) to inject the water, and a microscopic high-speed camera (Basler scA 640–70 fm, pixel size = 7.4 μm; frame rate = 71 fps, Fujinon HF35HA-1 Machine Vision Camera Lens 1:1.6, 35mm, C-Mount, 1.5 Megapixel), a heating tape to reach the desired temperature.

Before each contact angle measurement, the calcite sample was rinsed with acetone and flushed with water to remove any reversibly adsorbed NPs, then, after drying with nitrogen gas, the sample was treated in the air plasma (Harrick plasma, PDC-001-HP (115V) for 2 minutes to provide identical conditions for all measurements. Calcite samples were subsequently placed in the optical high-pressure vessel on the sloped base, and the pressure vessel was sealed. At this point, decane is fed to the cell gently at a low flow rate to prevent potential dislocation of the sample from the tilted plate until the cell is filled with decane. Then the oil inlet valve is closed. The heating tape turned on, and the vessel was heated to the experimental temperature (25, 50, and 70°C). Simultaneously, the pressure in the cell was raised to the experimental pressure (0.1, 5, 10, 15, and 20

MPa) by injecting CO_2 gas by the CO_2 pump. After reaching the predetermined thermodynamic parameters, the pressure vessel was left to equilibrate and stabilize for 3 hours, allowing it to reach a steady-state condition. Furthermore, the tested brine was thermodynamically equilibrated at the specific experimental conditions in a CO_2 equilibrium reactor [30]. Ultimately, the CO_2-saturated brine was fed through the other pump at a very low flow rate (0.001 L/h); thus, a droplet (6 - 8 µL) of brine was dispensed onto the nano-treated calcite sample using a needle. The tilted setup (tilting angle = 14°) of the sample allows the direct measurement of advancing (θa) and receding (θr) at the leading and trailing edges, respectively. The entire process was recorded using a microscopic camera, and the contact angles were measured from extracted images that were analyzed by J image software. The standard deviation of the measurements was ±3° based on the repeatability of results.

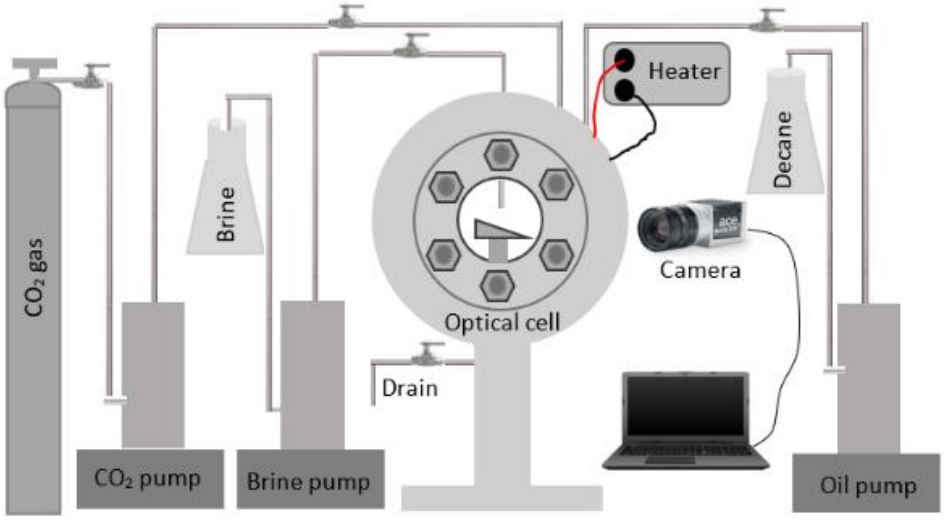

Figure 3. Experimental configuration for contact angle measurements.

2.9 Spontaneous Imbibition (SI)

Spontaneous imbibition is a process where water, as a wetting fluid, is drawn into a porous rock [52]. No external pressure or pumping is applied in this process; thus, it is considered a qualitative calculation of the wettability [53]. The influence of silica NPs on water imbibition into limestone cores and consequently the wettability of the porous media was investigated. Experimentally, the core plug was immersed in water while hanging under an electronic scale. The measurement is based on recording the change in weight with time, which results from water imbibition into the core. The equilibrium time indicates the point at which no further change in weight can be observed. Eventually, the dimensionless ratio of the weight of imbibed water at any time (WT) to the weight of imbibed water at equilibrium (WE) was plotted with time (WE/WT versus time) for each treatment test [54].

3. Results and Discussion

In the best cases, studies should design experimental conditions that reflect the reservoirs' harsh conditions of in-situ reservoirs, including temperature, pressure, and both surface and fluid chemistry; thus, the achieved results can be adopted as potential subsurface scenarios. Initially, the sustainably synthesized pure and hybrid silica NPs were characterized using FTIR, XRD, SEM, zetasizer, and DLS. Then the spontaneous imbibition and contact angle at CO_2-EOR conditions were measured. All experiments were conducted with a minimum of three independent test sets.

3.1 Characterization of NPs

3.1.1 FTIR and XRD

In this study, silica NPs were sustainably synthesized from bentonite, which is produced in large amounts as a by-product from drilling

processes. Furthermore, the produced silica NPs were silanized with 3-aminopropyl triethoxysilane in a process, including hydrolysis and condensation reactions to produce hybrid NPs with enhanced surface properties. Consequently, the chemical structure of both pure and hybrid silica NPs was characterized via FTIR spectroscopy (Fig. 4).

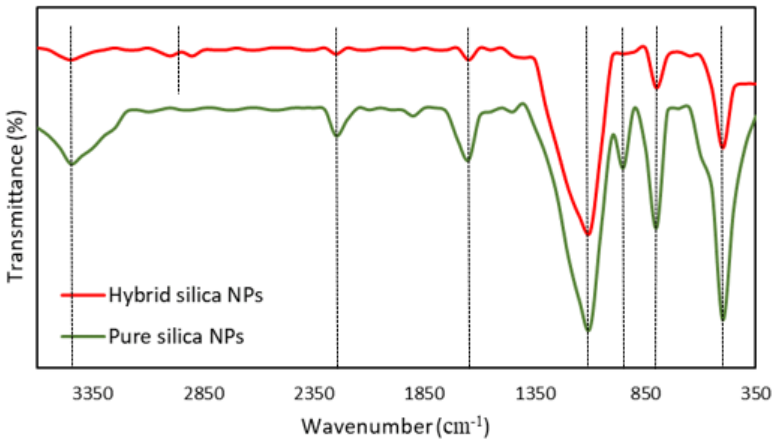

Figure 4. Comparative FTIR spectra of pure and hybrid SiNPs

FTIR measurements indicated that both pure and hybrid NPs have distinctive silica peaks at 575, 800, and 1110 cm-1, conforming to $Si-O-Si$ proportional tensile vibration and bending vibration. While the peak at 950 cm-1 represents the bending vibration of $Si-OH$. Moreover, the peak of 1630 cm-1, which is more evident in the pure silica NPs, is related to the physical adsorption of $-OH$ groups on the surface. Significantly, the peak at 2900 cm-1 indicates the presence of a low-energy group (silane) on the hybrid silica NPs, which explains the absence of this peak in pure silica. Furthermore, the peak of 3440 cm-1 in both pure and hybrid silica NPs is related to the symmetrical stretching vibration of hydroxyl groups. These observations are consistent with the published data [33, 55-57].

X-ray diffraction (XRD) patterns of both pure and hybrid silica NPs are shown in Fig. 5. The patterns indicated that both the pure and hybrid silica NPs displayed a broad peak around $2\theta = 23°$, revealing an amorphous nature of silica NPs (Sheet ICDD PDF2 00-039-1425) before and after treating with silane. Nevertheless, hybrid silica NPs showed lower noise compared to pure silica NPs. The reported outcomes are consistent with the reported data in previous works [33, 57, 58].

3.1.2 Scanning Electron Microscope (SEM)

SEM images were used to prob the adsorption behavior of various silica NPs on calcite substrate. To achieve this, SEM images of pure and hybrid silica NPs have been taken in duplicated magnification and at the same surface's nano-treatment conditions (Fig. 6). The main purpose of scanning the images at exactly the same magnification (7.75kx, 6keV, 20µm, analysis) and treatment conditions (50°C, 0.1MPa, 0.01wt% silica NPs) was to observe and compare the adsorption behavior of pure and silane-treated (hybrid) silica NPs on calcite surfaces regardless the influence of other thermodynamic parameters and nanofluid composition [30, 59].

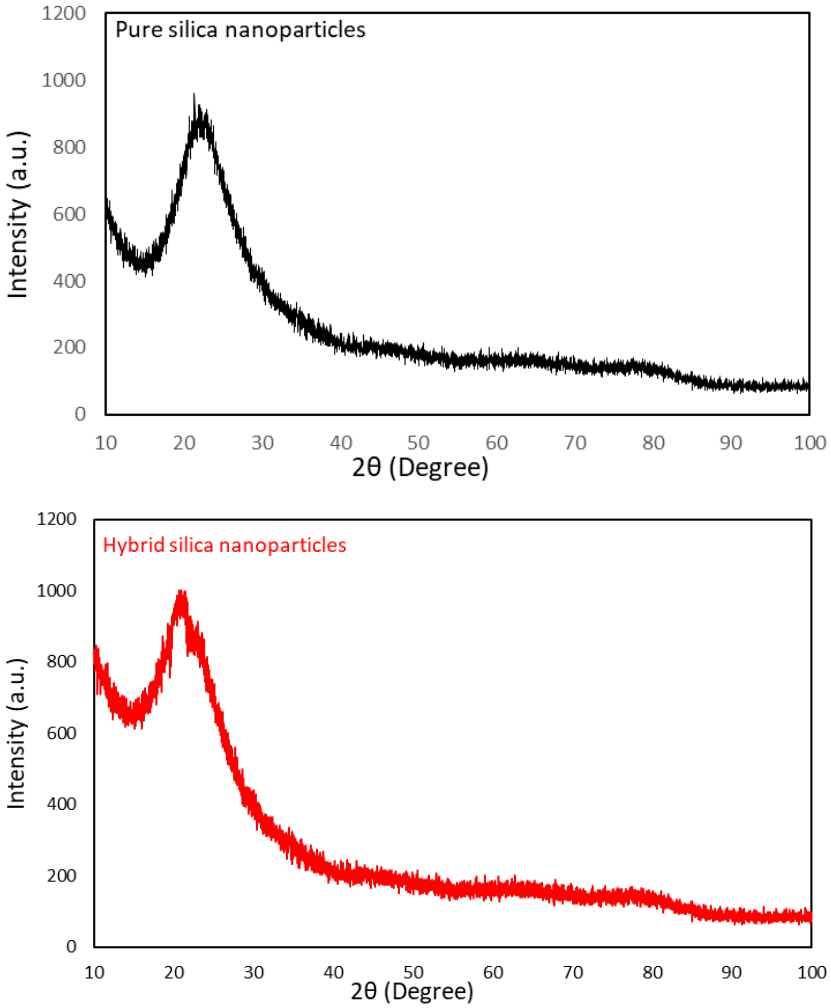

Figure 5. X-ray diffraction spectra for pure (upper) and hybrid (lower) silica NPs

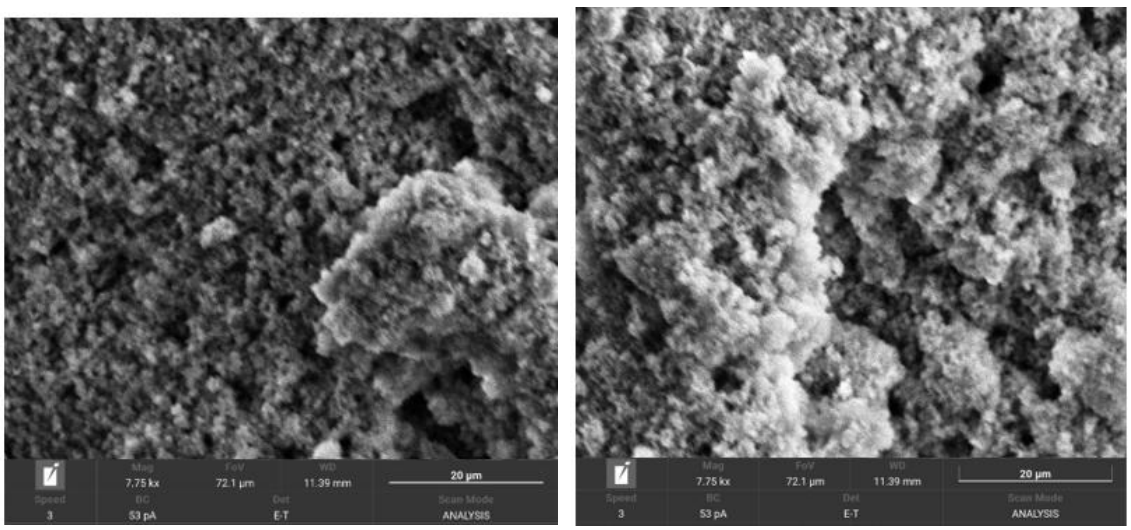

Figure 6. SEM images of pure (left) and hybrid (right) silica NPs.

Reviewing the SEM images reveals that the attachment scenarios of pure and hybrid NPs were nearly identical. However, larger nanoclusters were observed in the case of hybrid NPs, which are potentially related to the uncontrolled aggregation of silica NPs during treatment with silane [33]. It

is thus essential to measure the zeta potentials, particle size distributions, and aggregation rates of various silica NPs with time.

3.1.3 Zeta Potential, Particle Size Distribution, and Aggregation Rate

The zeta potential of pure and hybrid silica NPs at various salinities (0 and 0.5 wt% API brine) is depicted in Fig. 7, with measured values of -35mV, -25mV, -12.5mV, and -22.5mV for pure and hybrid NPs in DI water, and pure and hybrid NPs in 0.5 wt% API brine, respectively. Despite the dramatic screening effect of the salt electrolyte on the surface charges of pure silica NPs, which reduced them from -35mV to -12.5mV, surface charges of hybrid silica NPs showed significant tolerance for the salt electrolyte since it only changed by 3mV (e.g., reduced from -25mV to -23 mV). Such a phenomenon gives the hybrid silica NPs great potential in subsurface applications where the salinity varies significantly from one point to another [8].

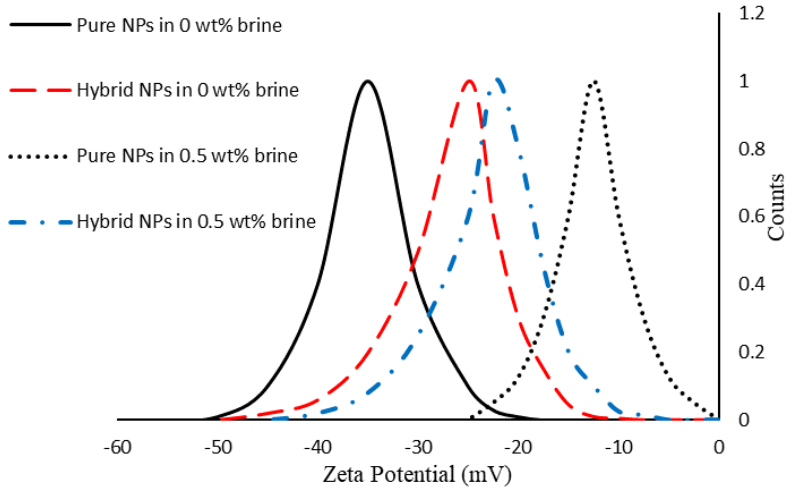

Figure 7. Zeta potentials of pure and hybrid silica NPs (0.01 wt%) at various salinities (0 and 0.5wt% API brine).

A reasonable particle size distribution allows the transportation and penetration of NPs in the porous media of subsurface formations. Furthermore, constant particle size or limited nano-cluster growth over time indicates a stable nanodispersion [60], which is crucial for successful application in subsurface projects, particularly CO_2-EOR [15, 61]. Consequently, the particle size distribution of pure and hybrid silica NPs in DI water and 0.5wt% API brine was systematically examined (Fig. 8). Moreover, the rate of particle size growth with time was also investigated for the same samples (Fig. 9). DLS analysis (Fig. 8) starkly declares that pure silica NPs dispersed in DI water maintained a narrow size distribution with an average particle size of 188 nm. Meanwhile, hybrid silica NPs dispersed in DI water showed a slightly wider size distribution with a larger average particle size of 330 nm, which is primarily due to the early aggregation of NPs during treatment with silane [62]. What is interesting is the vital resistance of hybrid silica NPs to rapid aggregation when dispersed in a 0.05 wt% API brine, keeping almost the same distribution with an average particle size of 375 nm. In contrast, DLS analysis reported a massive increase in average particle size of pure silica NPs when dispersed in brine, with an average particle size of 690 nm and a dramatically wide size distribution. This is primarily due to the screening impact of the salt electrolyte on the repulsive forces between approaching NPs [48, 60, 63, 64].

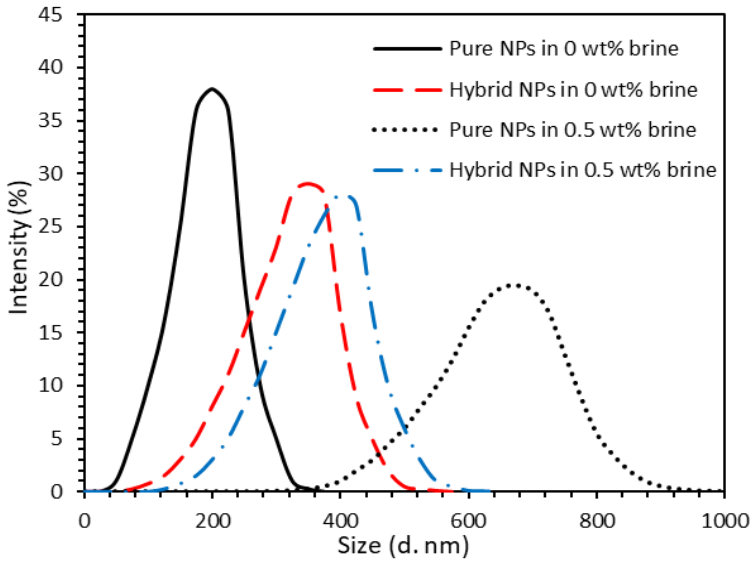

Figure 8. The particle size distribution of 0.01 wt% pure and hybrid silica NPs dispersed in DI water, and 0.05wt% API brine.

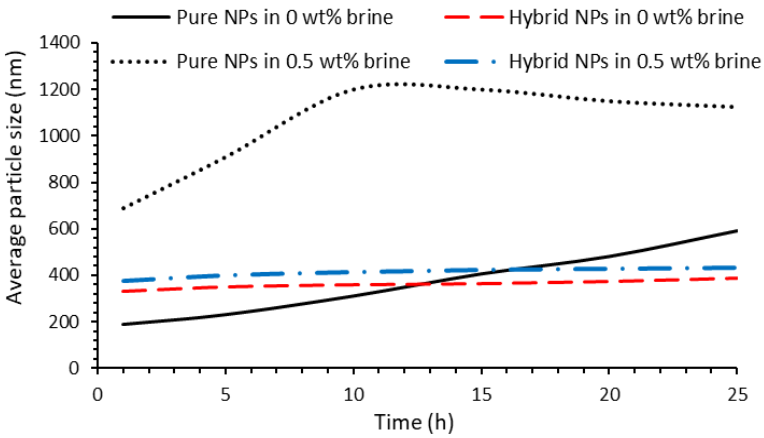

Figure 9. Average particle size over time of 0.01 wt% pure and hybrid silica NPs dispersed in DI water, and 0.05wt% API brine.

The observations from Figures 7 and 8 were confirmed by Fig. 9, which demonstrates the rate of growth in NPs size over 24 h. Consistent with zeta potential and particle size distribution measurements, the average particle size of pure NPs grows rapidly with time, particularly for NPs dispersed in brine, reaching 1210 nm within 10 h. Note that the subsequent reduction in the growth of size after 18 h is related to the sedimentation process of larger aggregates [30]. These results highlight the significant potential of hybrid silica NPs in subsurface applications, particularly CO_2-EOR and carbon and hydrogen storage [33, 45, 65].

3.2 Contact Angle Measurements

The interaction of the gas-liquids-rock system has been examined via wettability evaluation using contact angle measurements at CO_2-EOR conditions. Advancing (θa) and receding (θr) water contact angles under different circumstances are presented in Figs. 10 – 12. Experimentally, the impact of increased pressure (0.1, 5, 10, 15, and 20 MPa) on the water contact angle and thus wettability of various calcite substrates was systematically measured.

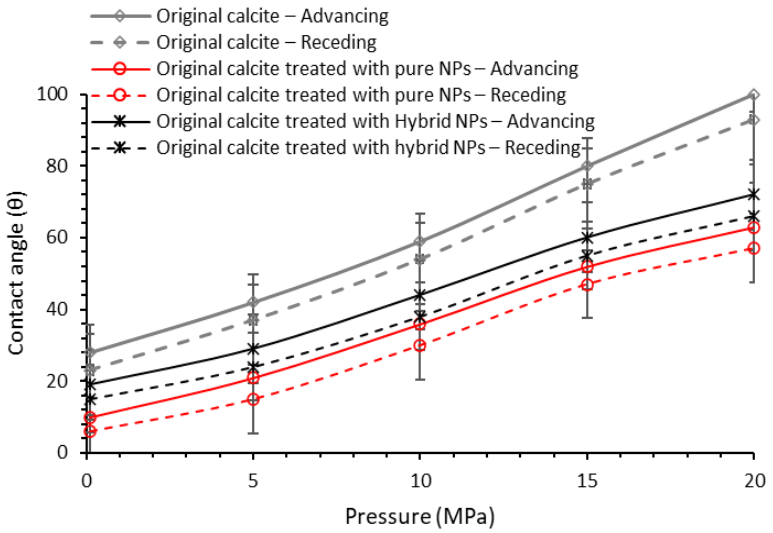

Figure 10. Water contact angle of the original calcite/decane/water system at various CO_2 pressures (0.1 – 10 MPa), and 50°C. Note that the solid and dotted lines refer to the advancing and receding contact angle, respectively.

Results in Fig. 10 indicated that at ambient pressure (0.1 MPa), the original calcite surfaces are strongly water-wet, regardless of NPs treatment. Moreover, treatment of calcite with silica NPs intensifies the water wetness properties of calcite, particularly when treated with pure silica NPs (i.e., at 0.1 MPs, θa reduced from 28° to 10° and 15° when treated with pure and hybrid silica NPs, respectively). These findings at ambient pressure are consistent with previous studies [28, 66] and confirm the strong water-wet nature of calcite. However, for the original calcite, increasing pressure to 5 and 10 MPa increases θa to 42° and 60°, respectively, shifting wettability to an intermediate state. A further increase in pressure, reaching 15 and 20 MPa, alters the wettability of calcite into an oil-wet condition (i.e., θa > 90°). Such an oil-wet condition, typically CO_2-wet as stated by Al-Anssari et al. (2017b), can dramatically promote the upward migration of carbon after injection in the CO_2-EOR process, posing a serious risk of CO_2 leakage due to suction and buoyancy forces acting on the carbon. However, interestingly, this is not the case when calcite was treated with silica NPs. As shown in Fig. 10, an increase in pressure up to 20 MPa will increase θa of calcite samples that are treated with pure or hybrid silica NPs to 62° and 71°, respectively, which are relatively intermediate water-wet and away from the limits of oil-wet status (θa > 90°). These observations promote the successful application of CCS projects after nano-flooding (i.e., treated with nanofluid) of carbonate formations.

The real scenario in oil reservoirs, even depleted ones, is quite different. The depleted oil reservoirs after primary and secondary oil recovery contain a tremendous amount of crude oil (i.e., more than 70% of the original oil in place), which means strongly oil-wet formations. Fig. 11 shows the impact of increased pressure on three different oil-wet calcite substrates (i.e., untreated, treated with pure NPs, and treated with hybrid NPs). Results revealed the dramatic ability of silica NPs to render oil-wet calcite water-wet even at elevated pressure (i.e., 20 MPa). In this context, θa of oil-wet calcite reached a critical value of around 175° at 20 MPs, indicating a high leakage risk. However, treating the oil-wet substrate with silica NPs keeps θa below 90°, thereby minimizing CO_2 leak risk. Most importantly, both pure and hybrid silica NPs showed nearly identical efficiency in rendering the surface water-wet. Pure silica NPs were slightly more efficient as a wettability modifier, which is mainly due to the faster aggregation and thus precipitation processes of NPs on the calcite surface. Such a rapid aggregation process is not recommended for long-term processes such as flooding into subsurface formations. Thus, the key to choosing the best nanofluid for long-term applications is stability.

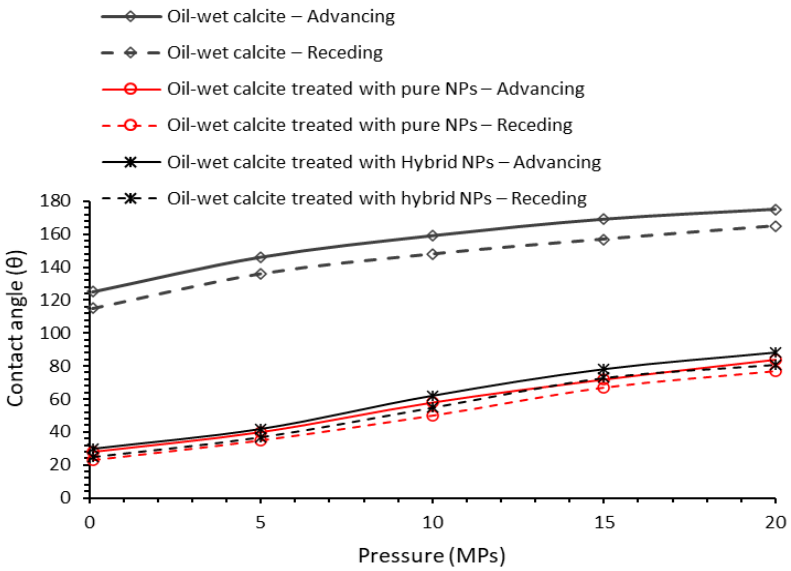

Figure 11. Water contact angle of the oil-wet calcite/decane/water system at various CO_2 pressures (0.1 – 10 MPa), and 50°C. Note that the solid and dotted lines refer to the advancing and receding contact angle, respectively.

3.3 Spontaneous Imbibition

Nano-treatment of carbonate samples is mainly associated with the surface properties of the adsorbed NPs [25]. The fundamental difference between the treatment of calcite substrates and limestone cores with nanofluid is the area of rock surface that comes into contact with nanofluids and the potential effect of NPs on the internal structure of the porous media. Thus, the influence of various nanofluids on the spontaneous imbibition of original and oil-wet carbonate cores was investigated (Fig. 12).

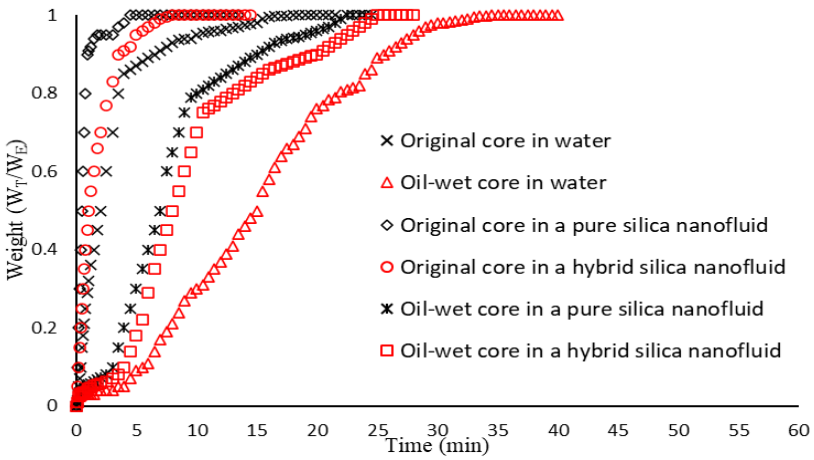

Figure 12. Curves of spontaneous imbibition for various cores and fluids.

Experimental data on the impact of various silica NPs (pure and hybrid) on the spontaneous imbibition of original and oil-wet carbonate cores are presented in Fig. 12. The rate of the spontaneous imbibition process is reported by the increase in the core weight due to water penetration into the core. Different trends can be identified based on the core's initial wetness status. Despite the strong water-wet nature of the original carbonate core, the presence of silica NPs enhances water imbibition into the core, revealing great potential for subsurface industries.

Mechanistically, due to their nanoscale size, the NPs act as seeding agents, driving water molecules into the smallest pores to overcome opposing capillary forces. Moreover, silica NPs significantly enhanced spontaneous imbibition of water into an oil-wet carbonate core. In such an oil-wet porous medium, NPs can detach the oil phase from the porous medium via a structural disjoining pressure, which mainly depends on the deposition of NPs on the edge of the solid/oil/water system. In both the original and oil-wet cores, despite the similar trend in NPs' effect on spontaneous imbibition, pure NPs showed slightly higher efficiency as a wettability modifier agent, consistent with contact angle measurements.

4. Conclusion

This research primarily characterizes and examines the sustainable synthesis and modification of silica nanoparticles and their influence as a wettability modifier in CO_2-EOR projects. Before conducting the nanofluid treatment, the surface properties of pure and silanized silica (hybrid) NPs were investigated. The presence of silane groups on hybrid silica NPs was confirmed via the FTIR test. Zeta potential and particle size distribution measurements showed that hybrid silica NPs are more tolerant to a saline environment, even at relatively high salinity (5 wt% brine), making them a prime candidate for subsurface applications. Moreover, in terms of wettability alteration, both pure and hybrid silica NPs showed a strong ability to convert oil-wet calcite to water-wet at reservoir conditions via contact angle reduction of 95°, and 107° at ambient and subsurface conditions, respectively. In this context, results showed that even natural calcite showed hydrophobic behavior at high pressure (i.e., > 10 MPs). However, treatment with silica NPs can significantly reduce the contact angle to a value below the oil-wet state (< 90°) even at very high pressure (i.e., 20 MPa). Further, a strongly oil-wet substrate inverts to a water-wet or intermediate state at CO_2 storage conditions (i.e., 15 – 20 MPs) when treated with pure or hybrid silica NPs. Pure silica NPs were slightly more efficient than hybrid silica NPs; however, hybrid NPs were more stable at severe reservoir conditions. Optimization between pure and hybrid silica NPs depends on the applications and the associated harsh conditions.

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Conflict of interest

The authors declare no conflicts of interest concerning this research.

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Author Contribution

Zain-Ul-Abedin Arain and Sarmad Al-Anssari proposed the research problem.

Mohammad Sarmadivaleh and Sarmad Al-Anssari developed the theoretical framework.

Zain-Ul-Abedin Arain, Sarmad Al-Anssari, and Mohammad Sarmadivaleh verified the analytical methods.

All authors participated in the discussion of the results and contributed to writing the manuscript.

AI Declaration Statement

The authors confirm that the manuscript has been written without the assistance of generative AI or AI-based writing tools.

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