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Hybrid surfactant-nanoparticles assisted CO_2 foam flooding for improved foam stability: A review of principles and applications

Miras Issakhov [a], Mariam Shakeel [b], Peyman Pourafshary [b, *], Saule Aidarova [a], Altynay Sharipova [c]

[a] Kazakh-British Technical University, Almaty, Kazakhstan
[b] School of Mining and Geosciences, Nazarbayev University, Nur-Sultan, Kazakhstan
[c] Satbayev University, Almaty, Kazakhstan

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ABSTRACT

Miscible carbon dioxide (CO_2) flooding is a well-established and promising enhanced oil recovery (EOR) technique whereby residual oil is recovered by mixing with injected CO_2 gas. However, CO_2, being very light and less viscous than reservoir crude oil, results in inefficient sweep efficiency. Extensive research is ongoing to improve CO_2 mobility control such as the development and generation of CO_2/water foams. The long-term stability of foam during the period of flooding is a known issue and must be considered during the design stage of any CO_2 foam flooding project. The foam stability can be improved by adding surfactants as stabilizers, but surfactants generated foams have generally a shorter life because of an unstable interface. Furthermore, surfactants are prone to higher retention and chemical degradation in the porous media, particularly under harsh reservoir conditions. Research has shown that nanoparticles (NPs) can act as an excellent stabilizing agent for CO_2/water foams owing to their surface chemistry and high adsorption energy. The foams generated using NPs are more stable and provide better mobility control compared to surfactant-stabilized foams. One limitation of using NPs as foam stabilizers is their colloidal stability which limits the use of low-cost NPs. Combining surfactants and NPs for CO_2 foam stabilization is a novel approach and has gained interest among researchers in recent years. Surfactants improve the dispersion of NPs in the aqueous phase and minimize particle aggregation. NPs on the other hand create a stable barrier at the CO_2/water interface with the help of surfactants, thus generating highly stable and viscous foams. This paper presents a comprehensive review of the basic principles and applications of stabilized CO_2 foams. A brief overview of CO_2 foam flooding is discussed first, followed by a review of standalone surfactant-stabilized and NPs-stabilized CO_2/water foams. The application of hybrid surfactant-NPs stabilized CO_2 foams is then presented and areas requiring further investigation are highlighted. This review provides an insight into a novel approach to stabilize CO_2/water foams and the effectiveness of the method as proved by various studies.
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1. Introduction

Miscible carbon dioxide (CO_2) flooding is one of the most practiced and promising enhanced oil recovery (EOR) techniques with large-scale applications for more than forty years (Lee et al., 1991; Worthen et al., 2013a). The influential factors for CO_2 flooding as an EOR technique include physical nature, ability to achieve multiple contact miscibility (MCM), and a low solubility with water, providing higher oil recoveries than waterflooding (Orr et al., 1982; Schramm and Mannhardt, 1996; Sohrabi et al., 2015). Some other beneficial factors that make CO2 an appropriate choice for EOR include crude oil viscosity reduction, oil swelling, vaporization of heavier oil components on contact with gaseous phase, and reduction in crude oil interfacial tension (IFT) by dissolved CO_2 gas in the oil (Rezaei et al., 2021b). A CO_2 water alternating gas (WAG) project was initiated in the San Andres Unit of East Vacuum Field, New Mexico in 1985 and is still ongoing, increasing the recovery factor from the main producing formation of the unit by 12.5% of

* Corresponding author.
E-mail address: peyman.pourafshary@nu.edu.kz (P. Pourafshary).

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original-oil-in-place (OOIP) (Moffitt et al., 2015). However, the CO_2 EOR technique has some inherent limitations mainly because of its very low viscosity (0.02–0.07 cp at 25 °C and 950–1450 psia) compared to most crude oils encountered in subsurface formations (Worthen et al., 2015). The low viscosity and density of CO_2 can cause severe mobility control issues such as viscous fingering and channeling (Lake and Venuto, 1990), CO_2 gravity override tendency (Koval, 1963), the preferential flow of gas through high permeability channels, and unstable front displacement. As a result, the early gas breakthrough may occur which is a potential cause for an EOR project failure, particularly in reservoirs containing viscous crude oil (Aryana and Kovscek, 2012; Lee and Heller, 1990; Sanders et al., 2010). Several researchers have designed and implemented hybrid CO_2-based EOR methods to overcome mobility issues associated with CO_2 flooding and to improve residual oil recovery by various means such as foam generation, sweep improvement, IFT reduction, and crude oil emulsification (Al-Anssari et al., 2018; AlQuraishi et al., 2019; Dezfuli et al., 2020; Han and Gu, 2014; Kuhlman et al., 1992; Massarweh and Abushaikha, 2021; Nematzadeh et al., 2012; Nik Salwani et al., 2019; Ren et al., 2018; Sagir et al., 2016). CO_2 foam flooding is one such technique in which CO_2 gas is converted to a viscous foam under high pressure and high shear rate and then injected into the reservoir (Nguyen et al., 2000; Rossen et al., 2010). The injected foam increases the apparent gas viscosity and reduces the gas mobility by immobilizing large gas volume inside the pores (Hirasaki and Lawson, 1985). Foam-assisted WAG is a potential EOR technology that improves macroscopic sweep efficiency in reservoirs, increasing oil recovery. However, in a crude oil environment, foam destabilizes quickly at high temperatures, limiting the applicability of this approach (Denkov, 2004; Irani and Solomon, 1986; Jensen and Friedmann, 1987).

The stability of CO_2/water foams can be improved by adding surfactants. Several successful pilot applications are available in the literature to show the performance of surfactant-stabilized foams (Patzek, 1996). Surfactant improves foam lifetime and stability by the development of barriers created by thin liquid films. The application of surfactants is limited by various subsurface factors such as high retention, high temperature, and salinity (Grigg and Mikhalin, 2007). Besides surfactants, nanoparticles (NPs) have also become popular in terms of increasing the stability of CO_2 foams under harsh reservoir conditions because of their remarkable stability and excellent surface properties (Emrani and Nasr-El-Din, 2015; Worthen et al., 2013b). In most of the studies, silica NPs have been used due to their hydrophilic nature, low toxicity, and high solubility in water. Silica NPs also have applications in other areas such as wettability alteration and fines migration control (Muneer et al., 2020, 2021; Zhao et al., 2021). NPs have an added advantage of lower adsorption onto the rock surface compared to surfactants (Singh and Mohanty, 2016; Worthen et al., 2012). The foams stabilized using NPs are reported to have longer lifetimes of up to one year compared to the surfactant-stabilized foams which are stable only for a few hours (Alargova et al., 2004). NPs have several orders of magnitude higher adsorption energy compared to surfactants resulting in better stability (Aroonsri et al., 2013; Binks and Horozov, 2005). Hence, a combination of surfactants and NPs is an effective way to enhance the applicability of CO_2 foams.

2. CO_2/water foam flooding

The CO_2/water foam is produced by various mechanisms such as lamellae creation, snap-off, etc. (Ransohoff and Radke, 1988). The concept of gas mobility control by using foam was first presented in 1958 by Boud and Holbrook (1958). Afterward, extensive research had been carried out to study the driving mechanisms of the foam flooding EOR technique (Chang and Grigg, 1999; Fried, 1960; Wellington and Vinegar, 1988). The CO_2 foam consists of 70–90% gas and thus requires less amount of water compared to the WAG technique (Yu et al., 2012a). The foam helps to provide a stable frontal advance because of its highly effective viscosity and higher contact area which results in better sweep efficiency. However, the long-term stability of a CO_2 foam is another major challenge because generally CO_2 foams are less stable and collapse quickly (Rossen, 1996). The major factors responsible for unstable foams involve the formation of the hole, coalescence of foam bubbles, Ostwald ripening, and lamellae drainage and disintegration (Worthen et al., 2012, 2013b). Generally, higher incremental oil recoveries during foam flooding are observed for CO_2 foams which have higher formability and are more stable (Dickson et al., 2004; Kim et al., 2016; Worthen et al., 2013a, 2015; Zhang et al., 2011). More stable foams can result in better sweep efficiency.

3. Surfactant-stabilized CO_2/Water foams

To enhance the stability of CO_2 foam, different chemicals are added to it such as surfactants and gels (Guo et al., 2012; Schramm, 1994, 2000). Several pilot-scale field tests showed the potential of surfactant-stabilized CO_2 foam in terms of sweep improvement and recovery of residual oil (Rognmo, 2019). The advantage of surfactant comes from the saponification and IFT reduction which improves foam stability, increases microscopic and macroscopic sweep efficiency, and recovers more residual oil (Yu et al., 2012a). In addition to enhanced foam stability, surfactant addition results in wettability alteration and thus accelerates oil flow by minimizing the capillary forces (Rezaei et al., 2020). During foam flooding in the porous media, the gas phase flow is stopped in some areas by the generation of thin liquid films that are known as lamellas. The foam stability comes from the hydrophilic surfactants molecules' ability to adsorb on the gas-water interface and foam mobility is controlled by continuously regenerated lamellae by surfactant in micropores of the reservoir (Johnston and da Rocha, 2009; Rossen, 1996; Rossen, 2017). Surfactants can effectively increase foam viscosity which results in more stable and piston-like oil front displacement (Derikvand and Riazi, 2016).

Sun et al. (2014) conducted experiments on silica sandpacks to evaluate the stability and oil recovery improvement of sodium dodecyl sulfate (SDS) surfactant-stabilized nitrogen gas foam. The foam half-life, measured by noting the time it takes for the foam to reduce 50% of its original height, was around 5 min whereas the incremental oil recovery by surfactant-stabilized foam was around 12% from a homogeneous sandpack and 6% from a heterogeneous sandpack. Fig. 1 shows the oil recovery profile for SDS-stabilized foam from a two-layer heterogeneous sandpack, indicating a higher diversion of foam into a high permeability layer.

A comprehensive nitrogen foam stability with oil displacement study was performed by Al Yousef et al. (AlYousef et al., 2017a) using an anionic surfactant, alpha-olefin sulfonate (AOS), as a foam stabilizer. Foam half-life was estimated from the static foam stability test and was found to be ~3.5 h and 12.5 h in the absence and presence of oil, respectively. The stabilized foam helped to improve the oil recovery and caused a 6.5% OOIP increase in the recovery factor, as shown in Fig. 2.

A surfactant-stabilized CO_2 foam treatment was designed and implemented in a heterogeneous formation of the San Andres Unit of East Vacuum Field in the 1990s where more than 60% of the injected gas was being channeled through a high permeability zone into one producing well out of 8 producers (Martin et al., 1995). To satisfy rock adsorption criteria, around 90000 lbs of surfactant was injected during the WAG injection period, followed by a rapid cycle of 2500 ppm surfactant alternating gas to produce 80% foam in the

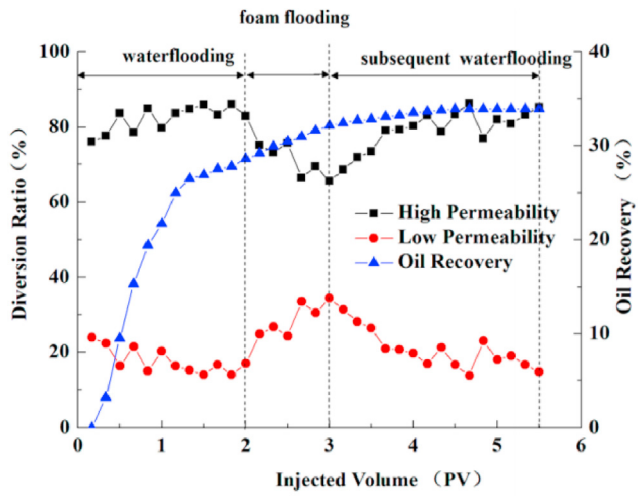

Fig. 1. Oil recovery and diversion ratio for SDS-stabilized foam injection in a heterogeneous sandpack (Sun et al., 2014).

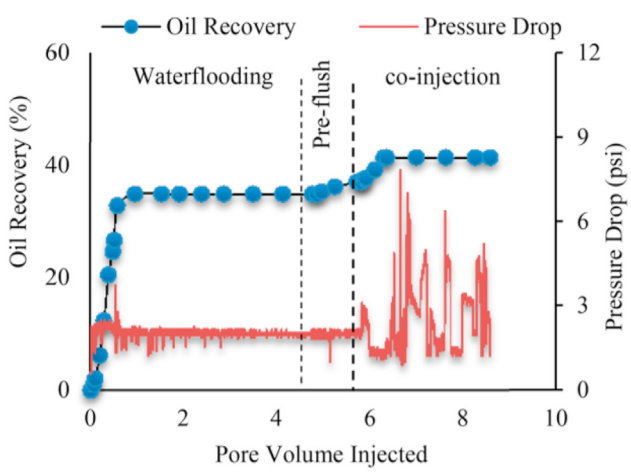

Fig. 2. Oil recovery and pressure drop profile for AOS-stabilized nitrogen foam (AlYousef et al., 2017a).

channel. More than a 30% reduction in CO_2 mobility was observed after foam treatment while a 50% decrease in CO_2 production was reported in one offending well. The generated foam diverted the injected fluid to other producers in the flood pattern and resulted in ~19000 STB of augmented oil production.

Another surfactant-generated CO_2 foam pilot project was launched in an extremely heterogenous sandstone field in Texas to improve the volumetric sweep efficiency of CO_2 (Chou et al., 1992). 40–85% drop in gas injectivity was observed by in-situ foam generation, thereby reducing gas production in the offending well while improving oil production in the rest of the producing wells in the test pattern by more than 90% compared to pre-foam treatment production. From the analysis of four foam treatments conducted at different times during 2 years, the maximum duration for which CO_2 injectivity was reduced (maximum time for which foam treatment was effective), was around 6 months and was found to be directly related to the surfactant concentration injected. Because of better sweep efficiency during foam treatment, almost 31% incremental oil was produced from one offset producer compared to the scenario if WAG had been continued instead of surfactant-CO_2 foam treatment.

Application of surfactant-alternating CO_2 foam flooding in Wall Creek sandstone reservoir located in Salt Creek field Wyoming also provided successful results by providing CO_2 conformance control and increasing oil production from an inverted five-spot arrangement (Patil et al., 2018). The response of surfactant-stabilized CO_2 foam generated in-situ was instantly seen by a decrease of 40% in the gas injection rate required to maintain a constant tubing head pressure (THP). The CO_2 overriding tendency was effectively reduced by the foam treatment, diverting the gas to low permeability areas, and as a result, above 25000 bbl of additional oil was recovered in contrast to the forecasted production of the base case scenario of WAG injection. Several other studies have also shown promising results of surfactant-stabilized CO_2 foam treatment in controlling excess CO_2 production, reducing gas recycling, increasing CO_2 sweep area by providing diversion towards less affected wells, and improving oil recoveries. Some laboratory experiments and field trials of this method available in the literature are presented in Table 1, demonstrating incremental oil production (Hoefner and Evans, 1995; Jonas et al., 1990; Sanders et al., 2012).

However, a major challenge for surfactants as CO_2 foam stabilizers is that they form a very weak adsorption layer at the CO_2-brine interface due to the low solubility of surfactant in CO_2 compared to water, resulting in inefficient foam stability (San et al., 2017; Worthen et al., 2013b). CO_2-philic surfactants have weak solvation with CO_2 because of low van der Waals forces which in turn limits lamellae stabilization in foams (Dickson et al., 2004; Worthen et al., 2012). The stability of surfactant-stabilized gaseous foams is reduced in the presence of high salinity formation brine and crude oil because of an increased rate of coalescence of lamellae at the gas-water interface (Yekeen et al., 2018; Zhu et al., 2004). Crude oil adversely affects the stability of surfactant-stabilized foams by processes such as snap-off, thus obscuring the efficient generation of thin liquid films (Almajid and Kovscek, 2016).

Surfactants are also prone to high adsorption onto the rock surface and the foams involving surfactants need to be regenerated continuously, thereby elevating the chemicals cost (Heller et al., 1985; Ransohoff and Radke, 1988; Wang, 1984; Yekeen et al., 2017). Henry et al. (1996) reported field trial results of CO_2 foam stabilized by surfactants to lower CO_2 cycling. The test was successful in terms of reducing CO_2 recycling, but the foaming efficiency slowly reduced as the foam dried out and water was injected two times to regenerate the foam by rehydration, making the test economically unfeasible. Similarly, the surfactant-stabilized CO_2 foam pilot test conducted in the East Vacuum Field was successful in terms of achieving technical objectives of mobility control and incremental oil production, however, the project economics was adversely affected by high surfactant cost and delay in incremental oil production, making it economically unattractive to be implemented at the full field-scale (Martin et al., 1995). Furthermore, surfactants tend to undergo chemical degradation in high temperature and high salinity reservoir environments (Kim et al., 2004). All these factors elevate the project cost, making it economically unfeasible.

4. Nanoparticles-augmented foam flooding

Several research studies have shown the effectiveness of using NPs to enhance the stability of CO_2 foams and emulsions in recent years (Adkins et al., 2007; Jikich, 2012; Martinez et al., 2008; Yu et al., 2014). The thermal stability of emulsions can be considerably enhanced with the application of NPs. Zhang et al. (2011) reported an improvement in oil/water emulsion stability using silica NPs based on a phase behavior analysis. In a study by Dickson et al. (2004), functionalized silica NPs were used to generate stable CO_2 foam while the effects of NPs size, concentration, and brine salinity on foam stability were studied by Binks and Horozov (2006).

Table 1
Some studies showing improvement in oil recovery by surfactant-stabilized CO_2 foam.

Study	Field	Surfactant	Incremental Oil by Surfactant-Stabilized CO_2 Foam Injection	Remarks
Jonas et al. (1990)	Sand unit of Rangely Weber, Colorado	Chevron chaser CD-1040	Slight improvement in oil production	Oil production slightly improved in other producers of the pattern owing to gas diversion caused by foam while a 42% reduction in chase CO_2 injectivity was observed for at least 2 months after foam treatment.
Hoefner and Evans (1995)	East Mallet Unit of Slaughter field, Texas	Rhodapex CD-128	~22–31%	50% decrease in CO_2 production from the problem well.
Hoefner and Evans (1995)	McElmo Creek Unit of Greater Areth field, Utah	Rhodapex CD-128 and Chase CD-1045	10%	40% reduction in produced gas volume compared to injected CO_2 volume after surfactant-alternating CO_2 flooding.
Sanders et al. (2012)	Canyon Reef field, Texas	ELEVATE™	30%	Vertical sweep efficiency was increased because of foam propagation deeper into the formation and the injectivity during surfactant-alternating CO_2 injection was reduced by 50% compared to standalone CO_2 flooding.
Alcorn et al. (2018)	East Seminole field, Texas	Not mentioned	15% OOIP	CO_2 mobility post-SAG treatment was reduced by a factor of 340 in laboratory corefloods.

Aroonsri et al. (2013) investigated the critical shear rates required to generate silica NPs-stabilized CO_2 foam in Berea core samples while flowing through matrix and fractures. Singh et al. (2015) demonstrated the ability of inexpensive fly ash nanoparticles to increase the stability of CO_2 foam and emulsions.

A critical surface property of a nanoparticle is its hydrophilic/CO_2-philic balance (HCB) which aids in controlling the interfacial activity of the particles by achieving the desired contact angle at the interface (Worthen et al., 2012). The ease of flow and negligible retention of small-sized uniform functionalized NPs inside the porous media, their ability to change the oil/water interfacial contact angle by forming a particle monolayer at the interface, and the opportunity to externally control the de-stabilization and stabilization of emulsions by manipulating magnetostrictive and magnetic properties of the NPs are some of the attributes which make them an attractive stabilizer for foams and emulsions (Jonathan et al., 2007; Melle et al., 2005). NPs such as silica, alumina, sulfates of metals, and carbon all are capable of stabilizing foam bubbles by irreversibly adsorbing at the CO_2-brine interface. Furthermore, higher energy would be required to destabilize such foams owing to the larger adhesive forces at the fluid-fluid interface (Aroonsri et al., 2013; Zhang et al., 2009). The adsorption energy of NPs at the CO_2-water interface can be calculated by Equation (1) (Worthen et al., 2012).

$$E = \pi r^2 \gamma_{\alpha\beta} (1 \pm cos\theta)^2 \quad (1)$$

where θ is the interfacial contact angle of the particle and $\gamma_{\alpha\beta}$ is the CO_2-water interfacial tension. Equation (1) shows that the adsorption energy of a particle having a radius of 80 nm at a CO_2-brine interface with an IFT of 20 dyn/cm and making a contact angle of 90° at the interface would be 90000 kT at 50 °C (k is the is Boltzmann constant and its value is 1.38E-23 and T is temperature in kelvin. While using Equation (1), a unit conversion is required to convert the adsorption energy from Joules to kT using the Boltzmann constant and desired temperature). This value of adsorption energy is quite higher compared to that of surfactants, making NPs more effective foam stabilizing agents.

4.1. Improved foam properties (formability and stability)

In a laboratory study by Zhang et al. (2009), phase behavior and transport properties of oil-water emulsions stabilized using functionalized silica NPs were investigated. The NPs produced quite stable emulsions and the emulsion integrity and viscosity were successfully maintained while transporting through glass bead columns. Similarly, Espinosa et al. (2010) showed that a supercritical CO_2 foam generated using silica NPs was more stable and 2 to 18 times more viscous compared to the foams without NPs when flowed through a glass beads column. They also concluded that higher NPs concentration was needed to ensure foam stability under high salinity conditions. Mo et al. (2012) also confirmed improved stability of NPs-assisted CO_2 foam in both glass-beads column and reservoir cores. The nanoparticles-stabilized foam properties such as stability and formability depend on several factors including nanoparticle type, concentration, degree of hydrophobicity, brine salinity, hardness, temperature, and injection rate. Table 2 provides a summary of studies showing the effect of the aforementioned critical factors on foam stability.

4.1.1. Effect of nanoparticles' concentration

In the experiments of Zhang et al. (2009) the stability of oil-in-water emulsions formed using 5 wt% and 10 wt% silica NPs was maintained for up to two months compared to less than 5 days for 0.1 wt% and 1 wt% concentration. Based on a phase behavior scan, a column-flood was performed by injecting toluene-in-water emulsion stabilized with 10 wt% silica NPs to displace already present deionized water. A piston-like displacement of deionized water by the emulsion slug was observed with negligible dispersion. The estimated emulsion apparent viscosities during the front displacement were found to be 30–40 cp which were in close agreement with the shear viscosity obtained by the rheometer. The transport experiment also revealed that the NPs-stabilized emulsion was able to flow through the glass-beads column without breaking.

Dickson et al. (2004) developed supercritical CO_2-water emulsions utilizing various concentrations of silica NPs ranging from 1 to 50 wt% and determined the emulsion stability as a function of different parameters e.g., the density of CO_2, NPs concentration, and degree of hydrophilicity of nanoparticles. The results showed a direct relationship between NPs concentration and emulsion stability. Similar results were reported in other literature (Fuller et al., 2006; Hunter et al., 2008; Lopetinsky et al., 2006; Yu et al., 2012b). An experimental study by Mo et al. (2012) also showed that a high concentration of silica NPs were required to increase the stability and quantity of produced CO_2 foam. The CO_2 foam mobility was obtained by flowing the NPs-stabilized CO_2 foams through Berea sandstone cores and reduced from 52 md/cp to almost 2 md/cp when the NPs concentration increased from 0 ppm to 5000 ppm (Fig. 3). Consequently, a 15-folds increase in foam resistance factor was observed for foam generated with 5000 ppm silica NPs, compared to 1000 ppm NPs case. The comparable trend was also

Table 2
Some studies showing effect of critical factors on nanoparticles-stabilized CO_2 foam.

Study	NPs type/Size/ Concentration	Brine composition	Foam Quality	Flow rate (cc/min)	T (°C)	Foam properties
Fu and Liu (2021)	Silica NPs/7 nm/500 −7000 ppm	5% NaCl	70%	12	20	Apparent foam viscosity increased from 5.2 cp at 500 ppm to 15.4 cp at 3000 ppm and then remained constant at 16 cp at 5000 and 7000 ppm. Foam texture and lifetime improved considerably by increasing NPs concentration.
	Silica NPs/7 nm/ 5000 ppm	3%−11% NaCl	10% −90%	12	20	Apparent foam viscosity increased from 11.3 cp at 3% NaCl to 34.5 cp at 11% NaCl. The highest foam half-life of more than 96 h was obtained for the foam generated using 11% NaCl.
	Silica NPs/7 nm/ 5000 ppm	5% NaCl	70%	12	20	Apparent foam viscosity increased from 8.2 cp at 10% foam quality to16 cp at 70% foam quality and then dropped to 4.5 cp at 90% foam quality. The optimum foam quality was found to be 70% in this case.
	Silica NPs/7 nm/ 5000 ppm	5% NaCl	70%	6 to 18	20	Apparent foam viscosity and foam texture both improved with increasing total flow rate.
	Silica NPs/7 nm/ 5000 ppm	5% NaCl	70%	18	20 to 72	Apparent foam viscosity decreased dramatically from 25 cp at 20 °C to 5.5 cp at 43 °C and then dropped gradually to 3 cp at 72 °C. Foam half-life was also reduced from 12 h at 20 °C to less than 1 h at 72 °C. As temperature increases, a higher injection rate is required for foam generation.
Yu et al. (2012b)	Silica NPs/100 −150 nm/1000 −50000 ppm	DI water	–	–	25	The critical NPs concentration required for foam generation was 4000 ppm. Beyond this concentration, the generated foam height started to decrease because of NPs aggregation. The foam height for the 4000 ppm case decreased by only 7% after 2.5 h, indicating a stable foam.
	Silica NPs/100 −150 nm/5000 ppm	0 −50000 ppm NaCl	–	–	25	The foam texture improved by increasing brine salinity from 0 to 5000 ppm. However, the particle size began to increase upon a further increase in brine salinity and the foam height and stability considerably decreased at higher salinities.
	Silica NPs/100 −150 nm/5000 ppm	20000 ppm NaCl	–	–	25 to 60	CO2 foam height decrease with increasing temperature and no foam was generated at 60 °C. This is because CO_2/brine IFT as well as NPs mobility increase with increasing temperature resulting in bubble coalescence.
Espinosa et al. (2010)	Silica NPs/5 nm/100 −1000 ppm	DI water	83%	6	25	No foam was generated at 100 ppm concentration. 75% increase in normalized mixture viscosity was observed by increasing NPs concentration from 500 to 1000 ppm.
	Silica NPs/5 nm/ 500 ppm	DI water	83% −90%	6	25	No apparent trend was observed between foam quality and apparent viscosity. However, as the foam quality increased from 83% to 92%, apparent viscosity decreased possibly due to the lesser volume of nanofluid in the mixture.
	Silica NPs/5 nm/ 1000 ppm	20000 −40000 ppm	83%	6	25	Normalized mixture viscosity decreased by 50% when brine salinity increased from 20000 ppm to 40000 ppm.

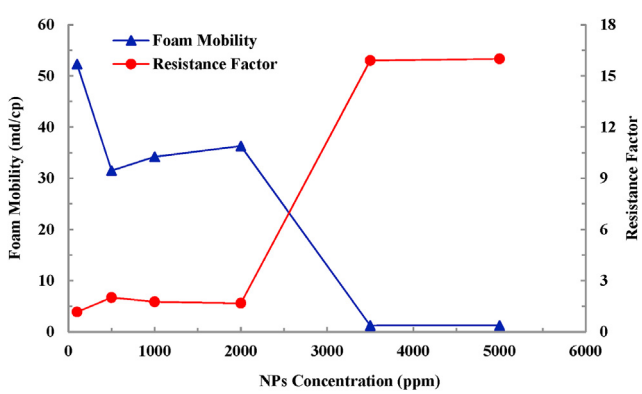

Fig. 3. Effect of NPs concentration on CO_2 foam mobility and resistance factor (Mo et al., 2012).

observed by Yu et al. (2012a) that foam mobility decreased with increasing NPs concentration. This can be attributed to the improved stability of lamellae formed at the CO_2/NPs interface with higher NPs concentration, thereby exhibiting a higher resistance to coalescence while flowing through the pore spaces.

4.1.2. Effect of brine salinity and composition

Various studies have been conducted to study different parameters affecting the generation of NPs-stabilized CO_2 foams and mobility control extent (AlOtaibi et al., 2013; Dickson et al., 2004; Espinosa et al., 2010; Yu et al., 2014). The effect of monovalent, divalent, and multiple ions on the properties of NPs-stabilized CO_2 foams and the flow through porous media was investigated by San et al. (2017). The foam was produced by simultaneous injection of silica nanofluids of different salinities and supercritical CO_2 into sandstone core samples and the generated foam was observed through a sapphire observation cell. The results showed that with increasing NaCl brine salinity, foam quality, stability and texture were enhanced. By increasing NaCl concentration from 1 to 10%, mobility of the generated foam as calculated using pressure drop data was reduced by 80% while for $CaCl_2$ brine, the mobility reduction with increase in divalent ions concentration was around 75% (Fig. 4). After one week, more than two-third of the generated foam volume remained stable for 10% NaCl nanofluid while all the foam was collapsed in the case of 1% NaCl nanofluid. Their study showed a more pronounced effect of divalent ions (Ca^{2+}) compared to monovalent ions (Na^{+}) on CO_2 foam formation and stability as 10% NaCl and 1% $CaCl_2$ generated foams with similar mobility, consistency, and stability. The adsorption tendency of NPs at the gas-water interface is increased by the compaction of the electric double layer around the NPs surface and gas-water interface in a high salinity environment, causing changes in interfacial contact angles (Kostakis et al., 2006). An increase in contact angle by increasing brine salinity was observed by Binks et al. (2007) because of reduced repulsion between adjacent silanol groups. This phenomenon makes the NPs more hydrophobic in nature and generates highly stable CO_2 foams because of an increase in NPs adsorption energy at the CO_2/water interface (Churaev and Derjaguin, 1985). However, there exists a threshold salinity beyond which NPs start to agglomerate. San et al. (2017) observed a continuous increase in pressure drop across the core while injecting 15% NaCl silica nanofluid/CO_2 and lower than 80% concentration of NPs in the effluent, indicating NPs agglomeration and plugging of the rock.

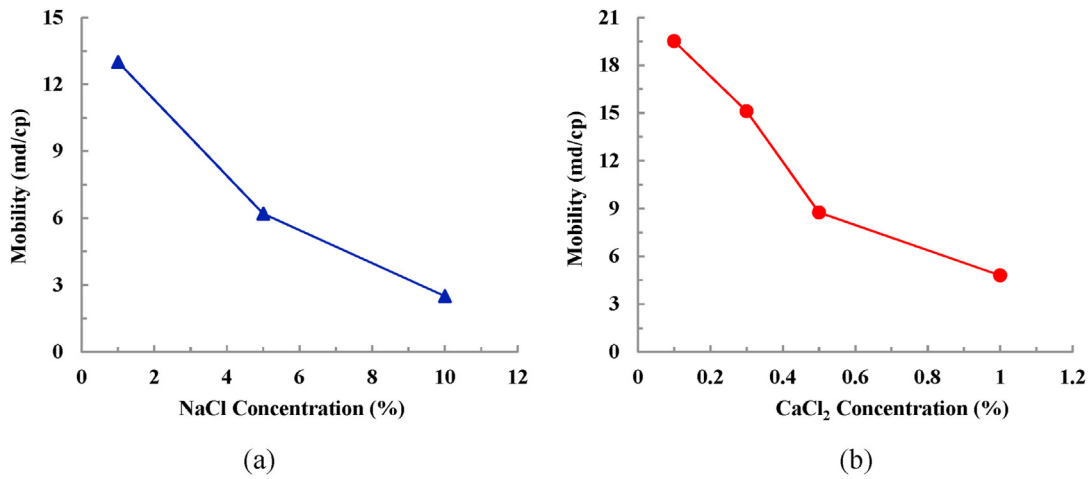

Fig. 4. Effect of (a) Monovalent ions, and (b) Divalent ions concentration on NPs-stabilized CO_2 foam mobility (San et al., 2017).

4.1.3. Effect of nanoparticles' hydrophobicity/surface modification

Different researchers produced CO_2-in-water and water-in-CO_2 emulsions and foams stabilized using functionalized or surface-modified nanoparticles (Adkins et al., 2007; Dickson et al., 2004; Golomb et al., 2004, 2006). Worthen et al. (2012) performed glass-beads column tests to generate CO_2 foams using different stabilizers including specially designed hydrophobic silica NPs, polymer-coated NPs, and nonionic surfactant. A capillary viscometer was used to measure foam viscosity. The foam stability was assessed visually in a high-pressure observation cell. The results indicated that silica NPs with an optimum hydrophobicity (50% SiOH) were able to strongly adsorb on the CO_2-water interface without being solvable in CO_2 and generate highly stable, dense white CO_2 foams which were almost 100% stable after 23 h.

Despite being initially viscous, the foams produced with polymer-coated NPs were stable only for short times and collapsed completely after 20 h due to the smaller size of NPs and poor association of polymer chains with CO_2. The surfactant-stabilized CO_2 foams, on the other hand, destabilized quite quickly because of continuous movement of surfactant molecules across the interface and 40% of the generated foam was collapsed after 22 h as estimated based on foam height. The higher stability of foams generated using 50% SiOH NPs in contrast to polymer-coated NPs can be explained in terms of particle size. As previously discussed, the adsorption energy of 150 nm sized 50% SiOH NPs would be almost 900 times higher compared to 5 nm sized polymer-coated NPs while keeping other parameters constant in Equation (1). Such high adsorption energy makes particles irreversibly attached to the CO_2-water interface and provides long-term stability to the foams (Binks, 2002). These adsorbed NPs at the interface act as a physical barrier and prevent the foam bubbles from coalescence, thereby slowing down the foam disintegration (Hunter et al., 2008). Surfactant molecules, on the other hand, keep on entering and leaving the interface, making the foams less stable (Adkins et al., 2010a).

The effect of the degree of hydrophobicity of silica NPs on CO_2 foam generation and stability was also studied by Yu et al. (2014). Silica NPs with three different extents of hydrophobicity were used, namely AS-silica – strongly hydrophilic, C-silica – intermediate hydrophilic, and AW-silica – slightly hydrophobic. The results showed an increase in foam volume and a finer foam texture with increasing particle hydrophobicity. The apparent gas viscosity of CO_2 foam generated with AW-silica NPs was increased by 54%, compared to the CO_2-water system, which was the maximum apparent viscosity among the three types of NPs studied (Fig. 5).

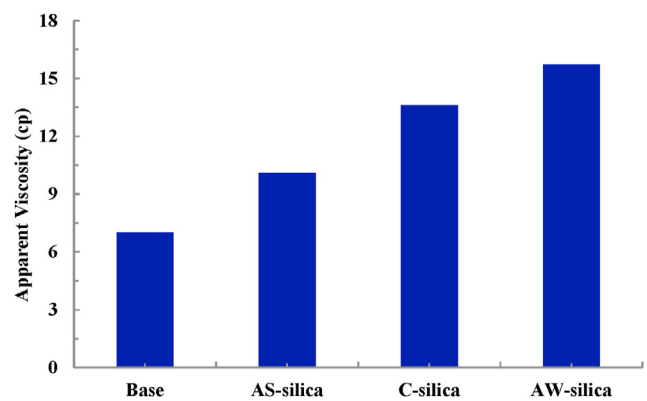

Fig. 5. NPs-stabilized CO_2 foam apparent viscosity as a function of particle's degree of hydrophobicity (Yu et al., 2014).

4.1.4. Effect of injection rate

The normal practice to generate CO_2 foam in dynamic conditions is by co-injecting supercritical CO_2 gas and dispersed nanofluid into the reservoir (Adkins et al., 2010a; Worthen et al., 2013a). Total injection rate is a critical factor in addition to NPs concentration that affects the CO_2 foam formability and mobility (de Vries and Wit, 1990; Khatib et al., 1988; Lee et al., 1991). Yu et al. (2012a) generated dynamic silica NPs stabilized CO_2 foam by conducting glass-bead pack flooding tests and analyzed the properties of the generated foam such as apparent viscosity and mobility by visual inspection through a sapphire tube. A critical injection rate of 3 cc/min was found to be required for a stable foam generation and an oscillating pressure drop trend was observed probably due to forming and breaking of CO_2 foam bubbles during flow through porous media. The apparent viscosity of the nanoparticles-stabilized CO_2 foam was almost 1.5–2.5 times more whereas the foam mobility was reduced by 8–10 folds compared to the foam without NPs.

4.1.5. Effect of temperature

San et al. (2017) investigated the effect of temperature on NPs-stabilized CO_2 foam characteristics and observed a reduction in foam stability with increasing temperature. As the temperature increased from 25 °C to 65 °C, the foam lifetime reduced by almost 90% while foam mobility increased by 58% (Fig. 6). The effect of temperature on foam lifetime and mobility was more significant for

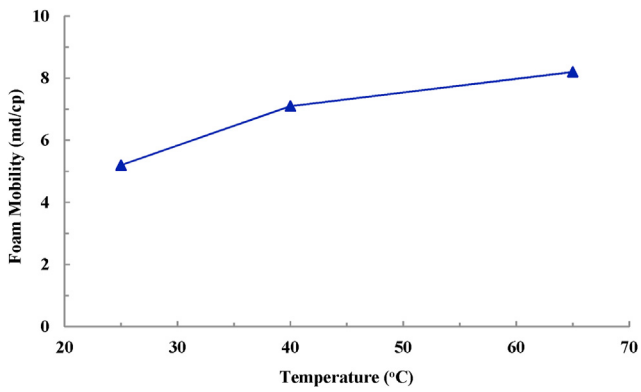

Fig. 6. Effect of temperature on NPs-stabilized CO_2 foam mobility (San et al., 2017).

an increase in temperature from 25 °C to 40 °C compared to when temperature increased from 40 °C to 65 °C. Sharma et al. (1985) also concluded similar findings that the half-life of the foam considerably decreased by increasing the temperature from 20 °C to 40 °C while it changed very slightly with a further increase in temperature to 80 °C. With increasing temperatures, the drainage rate increases, and the rate of coarsening also increases because of the higher permeability of foam films to gas which leads to enlargement of foam bubbles and ultimate collapse of foam (Farajzadeh et al., 2009; Kapetas et al., 2016; Saint-Jalmes, 2006).

4.2. Incremental oil recovery by NPs-Stabilized CO_2 foams

Several lab-scale experimental studies have been conducted to analyze the effect of using NPs as foam stabilizers on oil recovery. Generally, a higher incremental oil volume is recovered by a stabilized CO_2 foam injection compared to traditional CO_2/brine flooding. A detailed study of NPs-stabilized CO_2 foam for enhanced oil recovery was conducted by Fu et al. (2018) in which silica NPs were used as stabilizing agents and coreflooding experiments were performed on Berea sandstone samples. The objectives of this study were to investigate NPs capability of generating stable CO_2 foams while flowing through porous media in presence of oil and reducing residual oil saturation after waterflooding. The performance of NPs-generated CO_2 foam was also evaluated as a function of pressure and temperature. Fig. 7 shows a schematic of the experimental setup used in this study to generate silica NPs-stabilized CO_2 foam which consisted of two syringe pumps connected to two accumulators containing dispersed nanofluid and supercritical CO_2.

The pumps were used to inject the fluids into the core. Co-injection and mixing of the fluids into the core sample created a high shear force, making the NPs to be adsorbed at the CO_2-water interface and generate stable foams. A differential pressure transducer was used to measure and record the pressure gradient across the core. To study the generated foam properties such as stability and consistency, a sapphire visual cell was used and the temperature was regulated by placing the whole setup, excluding the pumps, in an air bath. The same setup was modified for residual oil recovery by removing the sapphire observation tube and connecting a gas-oil separator at the outlet of the core holder. The CO_2 foam generated using silica NPs resulted in 3–6% more residual oil recovery compared to the case without NPs for the same PVs injected. Around 12% higher residual oil in terms of waterflood residual oil was recovered by NPs-CO_2 formulation after increasing the pressure by 1300 psi (Fig. 8a) which can be credited to the improved foam stability with increasing pressure, providing better sweep and frontal displacement. Similar results have also been reported in other studies (Liu et al., 2005; Yu et al., 2012b). Regarding the temperature effect on residual oil recovery by NPs-stabilized CO_2 foam, it was observed that the residual oil recovery decreased by 10% when the temperature increased by 35 °C (Fig. 8b). This decrease in oil recovery is caused by reduced CO_2 foam stability with increasing temperature which is also supported by other studies in the literature (Liu et al., 2005; San et al., 2017).

Rognmo et al. (2018) studied and compared the efficiency of supercritical CO_2 foam stabilized using surface-modified silica NPs and a surfactant alcohol ethoxylate (C12–C16) to improve oil recovery by conducting corefloods on Bentheimer sandstone outcrop cores. The NPs-stabilized foam remained stable while displacing oil as confirmed by 3–5 times more pressure drop during co-injection of CO_2 and NPs in contrast to injecting CO_2 without foam stabilizer. Furthermore, 2 times higher incremental oil recovery was obtained by injecting NPs-CO_2 foam in tertiary injection mode after waterflooding compared to co-injection without NPs. An interesting observation was that by increasing NPs concentration from 1500 ppm to 5000 ppm, the incremental oil recovery did not increase considerably. However, the increase in oil production started earlier after injecting 0.1 pore volume (PV) for 5000 ppm nanofluid case while oil production increased after injecting 0.5 PV of 1500 ppm NPs-CO_2 foam. This comparison shows a lag or hysteresis of foam generation due to the adsorption of NPs on the rock surface. Fig. 9 shows the comparison of incremental oil recovery and average pressure gradient for the CO_2/brine, 1500 ppm, and 5000 ppm NPs-stabilized CO_2 foam.

The performance of NPs to stabilize CO_2 foam was also assessed in secondary injection mode where co-injecting NPs and supercritical CO_2 provided around 15% higher incremental oil recovery compared to the base case of CO_2-brine co-injection (Rognmo et al., 2018). The breakthrough of CO_2 was also delayed in the presence of NPs, indicating an active foam generation process in-situ which resulted in a favorable mobility ratio and enhanced volumetric sweep efficiency.

In a comparative study by Bayat et al. (2016), the performance of different NPs to stabilize CO_2 foams and improve oil recovery was analyzed. The NPs studied were silica (SiO_2), alumina (Al_2O_3), copper oxide (CuO), and titanium dioxide (TiO_2). To assess foam stability and half-life as a function of NPs type and concentration, the nanofluid dispersions were introduced in a chromatography column and CO_2 was flowed through the nanofluids at a rate of 10 cc/min to generate foams. In addition, the average bubble size of generated foams was determined on a bubble scale by using a Hele-Shaw cell and conducting microscopic analysis. The oil recovery performance of different NPs-stabilized foams was evaluated by conducting coreflood tests on quartz porous media. Fig. 10 shows the experimental setup used by Bayat et al. (2016). The results showed that irrespective of the NPs type, an optimal NPs concentration of 0.008 wt% was required to achieve the maximum CO_2 foam stability. Furthermore, silica NPs yielded the most stable foam with a half-life of 28.1 min (Fig. 11a). Based on the results, the NPs can be arranged in the following order of CO_2 foam stability.

$$SiO_2 > Al_2O_3 > TiO_2 > CuO$$

This trend can be related to the higher interaction energy of silica NPs which results in higher inter-particle repulsive forces, thereby increasing dispersion stability and resulting foam half-life. The average foam bubble size as obtained from image analysis was found to be 25–50% smaller for silica NPs-generated CO_2 foams compared to other NPs. The oil displacement tests also revealed similar results that the highest ultimate oil recovery of ~72% was obtained by silica NPs-stabilized CO_2 foam while alumina NPs

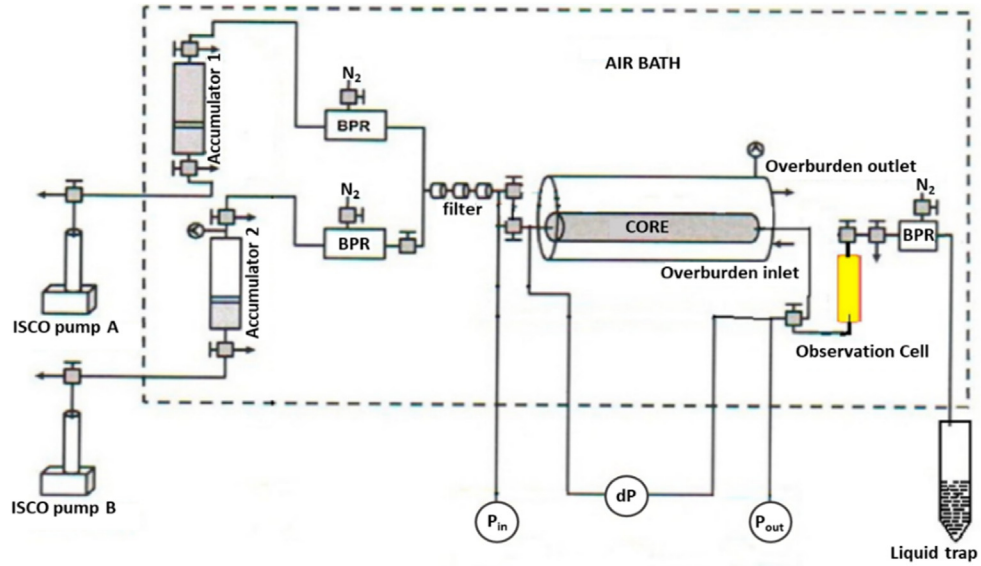

Fig. 7. Schematic of the set-up used for NPs-stabilized CO_2 foam generation and residual oil recovery (Fu et al., 2018).

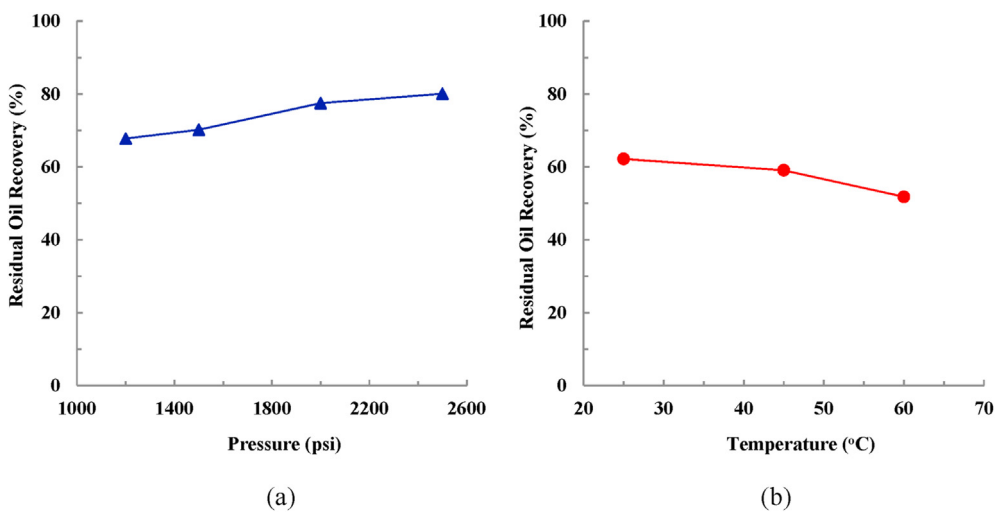

Fig. 8. Effect of (a) Pressure, and (b) Temperature on residual oil recovery by NPs-stabilized CO_2 foam injection (Fu et al., 2018).

provided the second-highest ultimate oil recovery of ~66%. Fig. 11b presents the incremental oil recoveries and residual oil saturation at the end of NPs-CO_2 foam flooding for each NPs type used in the study. The foams generated using TiO_2 and CuO nanoparticles yielded comparable ultimate recoveries of 58% and 57%. The residual oil saturation in the sand pack after NPs-CO_2 foam flooding was also the lowest for silica NPs (28%) whereas it was highest in the case of CuO NPs (41%). Although all types of NPs were successful in generating stable foams and recovering oil, the best performance was exhibited by silica NPs.

Table 3 summarizes more studies from the literature showing the EOR potential of NPs-stabilized CO_2 foams. The research shows nanoparticles are promising in generating quite stable foams even in the presence of oil and can potentially recover higher oil volumes compared to CO_2-brine flooding. Nanoparticles-stabilized CO_2 foams have shown encouraging results in several laboratory-scale studies. However, further research is required to make this approach economically applicable on pilot and field scales.

Research shows that low-cost NPs, such as bare silica, as well as NPs with a high degree of hydrophobicity or hydrophilicity, are not efficient foam stabilizing agents because of being less adhesive to the CO_2-water interface (Fameau and Salonen, 2014; Stocco et al., 2011). As a result, specially designed and surface-modified NPs are required to achieve desired foam strength and stability, which can potentially increase project economics (Zhang et al., 2021). Karakashev et al. (2011) observed no foam generation by NPs as nanoparticles were unable to cause a considerable reduction in gas-water IFT. NPs tend to agglomerate and plug the cores under harsh reservoir conditions such as high salinity and temperature and thus can create injectivity issues (Ehtesabi et al., 2015; Sun et al., 2017). High salt concentration causes the screening effect of electrical double layers and reduces particle-particle repulsion, which results

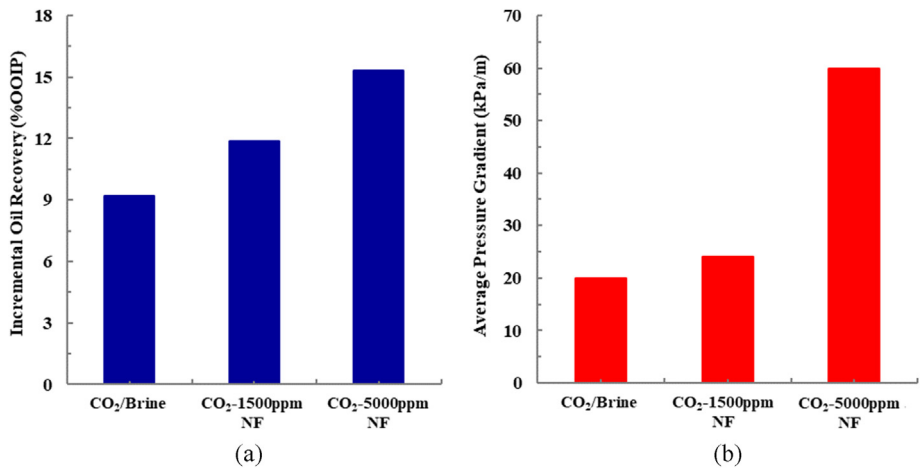

Fig. 9. Comparison of (a) Oil recovery, and (b) Pressure gradient showing higher incremental oil production by NPs-stabilized CO_2 foam injection (Rognmo et al., 2018).

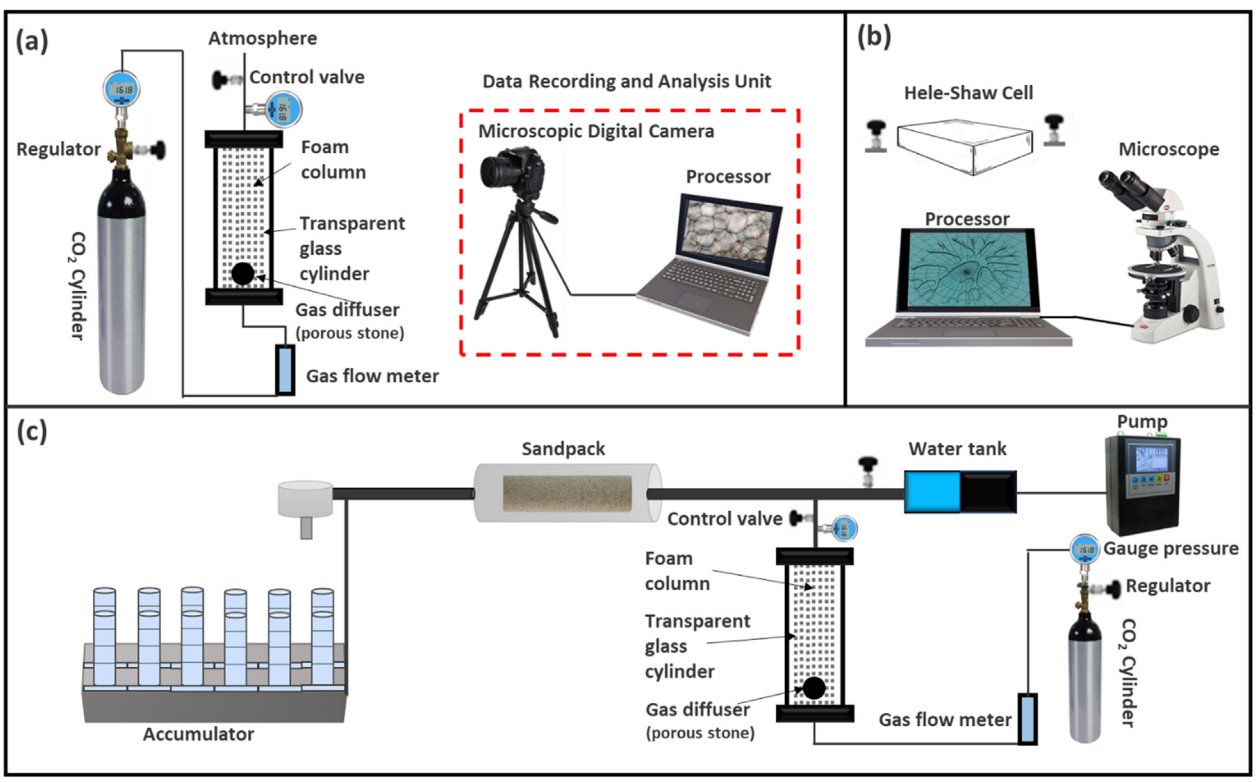

Fig. 10. Experimental setup used for (a) NPs-CO_2 foam generation and stability analysis, (b) Foam bubble size estimation, and (c) Coreflooding tests (Bayat et al., 2016).

in NPs agglomeration. Similarly, the number of collisions of NPs increases by increasing temperature, making the particles to aggregate (Hashemi et al., 2012). The environmental effects of NPs are also still not well understood, limiting their practical applications in the oilfields (Bakshi et al., 2015).

5. Surfactant-nanoparticles assisted CO_2 foam flooding

Surfactants are often used to increase the dispersibility and stability of nanofluids. By adding certain surfactants to nanofluids, the degree of NPs aggregation can be considerably reduced because of reduced inter-particle interactions due to adsorption and coating of surfactant molecules onto NPs surfaces (AttarHamed et al., 2014; Kvítek et al., 2008). The synergetic mechanisms of surfactants and NPs on the CO_2-water foam generation and stability are not yet investigated in detail. Table 4 summarizes some foam-stabilization studies using surfactant, nanoparticles, and hybrid formulation using both.

5.1. Synergetic mechanisms of surfactants and nanoparticles

IFT reduction by surfactants (Shaw, 1980), rearrangement of the NPs caused by a change in interfacial contact angle due to surfactant adsorption (Hunter et al., 2008; Vignati et al., 2003; Wang

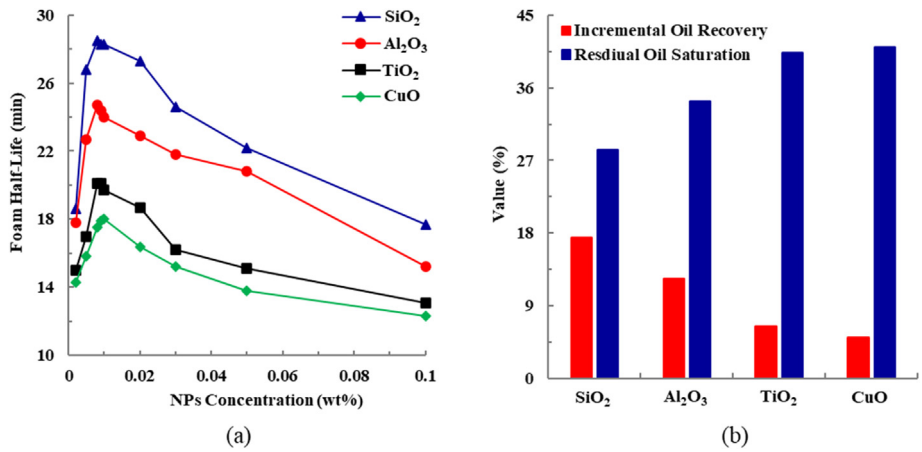

Fig. 11. (a) NPs-stabilized CO_2 foams' half-life and (b) Incremental oil recovery and residual oil saturation as a function of NPs type.

Table 3
Some studies showing improvement in oil recovery by NPs-stabilized CO_2 foam.

Study	Porous media	Nanoparticles	Incremental Oil	Remarks
Nguyen et al. (2014b)	Glass micromodel	50% methyl-coated silica NPs	10% OOIP more incremental production compared to CO_2 gas flooding	More paths were opened during NPs-CO_2 injection and a homogenized sweep pattern was obtained, providing three times more oil recovery in contrast with CO_2 gas flooding.
Yu et al. (2013)	Berea sandstone	Silica NPs	36–49%	90% decrease in CO_2 mobility was observed in presence of NPs and higher incremental oil was produced from low permeability sample due to more volume of foam generated.
Mo et al. (2014)	Berea sandstone, limestone, and dolomite	Silica NPs	39.6% in sandstone, 33.2% in limestone, and 26.5% in dolomite	Although NPs-stabilized CO_2 foam flooding produced incremental oil from limestone and dolomite samples, however 45–63% reduction in permeability was observed after cleaning the core with tetrahydrofuran (THF) mainly due to core plugging by NPs.
Husin (2015)	Sandstone and limestone	Silica NPs	5.5% and 6.7% more recovery in sandstone and limestone, respectively, compared to CO_2 gas flooding	Permeability reduction in limestone was observed after NPs-stabilized CO_2 foam injection.

et al., 2004), and improved interfacial rheology because of long inter-locked surfactant chains between NPs (Adkins et al., 2010b; Farhadi et al., 2016; Kaptay, 2003), are the potential mechanisms responsible for better formability and foam stability in presence of NPs and surfactants mixture. The synergetic benefits of using both surfactants and NPs as foam stabilizing agents also come from the higher foam stability and longer lifetime of foams in presence of adsorbed NPs at the gas/water interface, as schematically shown in Fig. 12.

5.2. Foamability and stability of surfactant-NPs-stabilized CO_2 foam

The utilization of nanoparticles and surfactants to stabilize CO_2 foam for an EOR application was studied by Guo and Ariana (Guo and Aryana, 2016) and an improvement in incremental oil recovery was observed using the new stabilized foam. The formability of the CO_2 foam and its dynamic stability were measured as a function of time to characterize the foam. The factors affecting the stability and viscosity of CO_2 foam including nanoparticles type, size, type of surfactant, and pressure applied to generate foam were analyzed, and the best combination was selected. Based on bulk foam tests and microfluidic foam density study, the best results in terms of foam stability, formability, and viscosity were obtained for a combination of silica nanoparticles and nano clay with a mixture of alpha-olefin sulfonate (AOS) and lauramidopropyl betaine (LAPB) surfactants. This combination of NPs and surfactants provided the maximum absolute stability as measured by the half-life of the generated CO_2 foam which was around 210 min. Almost 9 months of a lifetime was reported by Martinez et al. (2008) for N_2 foam stabilized using silica NPs dispersion. Adkins et al. (2007) compared stability of CO_2 foam stabilized using a combination of silica NPs and surfactants with the foam stabilized using a surfactant alone. The surfactant-NPs stabilized foam remained stable and experienced no bubbles coalescence over several days while the foam stabilized using surfactant destabilized very quickly with the bubbles coalescing within 3–4 h.

Worthen et al. (2015) performed a comprehensive study for CO_2 foam stabilization using functionalized silica nanoparticles at various scales including NPs stability and injectivity tests, foam generation by co-injection of nanofluid and CO_2 in both glass-beads columns and reservoir cores, assessment of foam viscosity improvement, and finally a numerical simulation modeling of NPs-assisted CO_2 foam flooding at field scale. The surface-modified NPs injectivity tests showed very low retention in the porous media when flowed through a Boise sandstone core. The NPs-stabilized CO_2 foams were generated in the glass-beads columns of 1.2 and 22 Darcies permeability and for two concentrations of NPs i.e., 0.5% and 1%. All the generated foams were white with a maximum viscosity of 10 cp against a shear rate of 90 s^{-1} irrespective of the permeability and NPs concentration. The synergy of adding LAPB surfactant to NPs-stabilized foam was also evaluated and a 1–2 orders of magnitude increase in foam viscosity was observed

Table 4
Studies showing foam stabilization using surfactants, NPs, and a combination of both.

Author	Stabilizers	Foam Viscosity	Foam Stability	Remarks
Surfactant-Stabilized Foams				
Emrani and Nasr-El-Din (2015)	Alpha Olephin Sulfonate (AOS)	–	Half-life: 3 h	CO_2 adsorbed into AOS solution and dynamic surface tension decreased until it reached a constant value after 2 h. The critical micelle concentration (CMC) value for the CO_2/AOS system was found to be 0.025 wt% in the solution of 1 wt% NaCl at ambient conditions. Dynamic adsorption and desorption of surfactant molecules at the interface destabilized the foam
Alargova et al. (2004)	Sodium dodecyl sulfate (SDS)	–	Foam life: a few hours	Sodium dodecyl sulfate (SDS), which is a strong foaming agent acted as a defoamer in this study. Few drops of 10 wt% SDS were added to a stable foam of 1.09 wt % SU-8 rods. Just after the addition of SDS, stable foam began to convert into liquid and after 30 min, 70% of the phase was destroyed. Foam life was orders of magnitude smaller than polymer microrods-stabilized foams
Guo et al. (2012)	Internal olefin sulfonate (IOS)	Higher than base brine	Half-life = 3.73 h, 3.65 h s and 3.61 h s for salt concentrations of 0, 0.5% and 1.0%, respectively.	Mobility-reduction factors (MRFs) for alkaline/surfactant system increased from 16.5 to 27.5 while the foam quality decreased. Lowering the IFT and achieving mobility control for EOR
Martinez et al. (2008)	Sodium dodecyl sulfate (SDS)	–	Foam life: less than 3 h	Foam life of fewer than 3 h was attributed to a small energy barrier of 3000 kT that led to the early rupturing of bubbles. Surfactant foams are less stable compared to nanoparticles-stabilized foams
Nanoparticles-Stabilized Foams				
Worthen et al. (2013a)	Surface modified silica NPs	120 times the viscosity of CO2-water foam	Foam life: 23 h	The apparent viscosity of foam increased 120 times compared to the CO_2-water system. Air-in-water foam was stable for 7 days, whereas CO_2-in-water foam remained stable for 23 days. An irreversible adsorption layer of nanoparticles at the interface hinders bubble coalescence and improves foam stability
Worthen et al. (2015)	Surface modified silica NPs	10- 15 cp	–	0.1 wt % functionalized silica nanoparticles increased the foam stability, and foam viscosity was increased to 10–15 cp. Nanoparticles resulted in around a 10-fold reduction in CO_2 mobility compared to without nanoparticles case. Furthermore, the addition of surfactant to the solution resulted in a 1000-fold reduction in foam mobility. Low pH conditions encountered during CO_2 foam flooding are favorable for NPs stability.
Kim et al. (2016)	Silica NPs	~16 cp	–	0.5 wt% of silica nanoparticles and 5 nm size provided the highest foam viscosity of around 16 cp during the coreflood test. Apparent viscosity of NPs-stabilized foams increased with decreasing particle size.
Zhang et al. (2011)	Surface-coated silica NPs and Iron-oxide NPs	18 times higher than CO_2-water mixture	–	A stable CO_2 foam was generated in combination with nanoparticles, and it increased the viscosity of foam 18-folds compared to only CO_2-foam, which can boost volumetric sweep efficiency.
San et al. (2017)	Silica NPs	The CO_2-foam mobility decreased from 13.1 to 2.6 mD/cp	168 h	5000 ppm silica nanoparticles enhanced the foam stability to 168 h for 10% NaCl, and the mobility of foam was decreased from 13.1 to 2.6 mD/cp. The stability of CO_2 foam was determined using salt and NPs concentrations, temperature, pressure, and the presence of bivalent ions.
Yu et al. (2014)	Silica NPs powder	15.55 cp	–	In 5000 ppm silica nanoparticles-stabilized CO_2-foam, the small and homogeneous bubble size was measured, along with a significant reduction in mobility at a phase ratio from 2 to 11. The introduction of silica nanoparticles to the system increased the viscosity from 7.23 cp to 15.55 cp.
Martinez et al. (2008)	Fused silica NPs functionalized with silanol group	–	9 months	Silica nanospheres were used with 34% of their surface is covered with silanol group. Application of 1 wt% nanoparticle is the solution to make large amounts of stable foam
Surfactant-Nanoparticles Stabilized Foams				
Emrani and Nasr-El-Din (2015)	Surfactant: AOS NPs: SiO_2, Fe_2O_3	–	Half-life: SiO_2-4 h, Fe_2O_3-7 h	The critical micelle concentration (CMC) value for the CO_2/AOS system was found to be 0.025 wt% in the solution of 1 wt% NaCl at ambient conditions. Silica nanoparticles of 100 nm and iron oxide nanoparticles of 50 nm were used in this study. The surfactant-NPs stabilized foam's height remained unchanged after 20 h because of reduced coalescence, resistance to hole formation, and mitigation of Ostwald ripening
Worthen et al. (2013b)	Surfactant: Caprylamido propyl betaine (CAPB) NPs: SiO2	>50 cp	Foam life: > 20 h	A stable foam of silica nanoparticles in the presence of CAPB was formed and the viscosity was measured to be 79 cp in bead pack and 36 cp in a capillary tube. The stability and texture of NPs-surfactant generated foam was controlled by tuning brine salinity
Worthen et al. (2015)	Surfactant: Lauramido propyl betaine (LAPB)	>100 cp	–	The synergy of NPs and surfactants reduced the CO_2 foam mobility by almost 1000 folds compared to the bare CO_2-water blend

Table 4 (*continued*)

Author	Stabilizers	Foam Viscosity	Foam Stability	Remarks
	NPs: Functionalized Si_2O_3			
Yu et al. (2012b)	NPs: Nanosilica powder Surfactant: CD 1045™	–	The foam was stable for 12 h	Silica nanoparticles of 100–150 nm size were used in the concentration range of 0.3–1 wt%, and a stable foam was generated when 0.5 wt% concentration was used at 1500 psi and 25 °C. Surfactant promotes CO2 foam generation and nano-silica enhances its stability.
Rezaei et al. (2021a)	NPs: Nanosilica powder Surfactant: CAPB, CTAB, and LABSA	~3000 cp for CAPB at 40% oil saturation	~29 min for CAPB ~16 min for CTAB and ~9 min for LABSA	Maximum ultimate oil recovery of 41% was obtained by using CAPB compared to the other two surfactants
Panahpoori et al. (2019)	NPs: TiO_2 Surfactant: CTAB	–	120 min	combination of nano-CTAB + N_2 gas foam injection into an oil-saturated core resulted in an additional 32% oil recovery
Razali et al. (2018)	NPS: SiO_2 (Hydrophilic and hydrophobic), ZnO, and TiO_2 Surfactant: SURF-X	10.01 cp	Half-life = 367 s	Hydrophilic silica nanoparticles improved the half-life 2 times better than the surfactant alone. Furthermore, 0.15 wt% nanoparticles increased the foam viscosity from 4.38 to 10.01 cp In a crude oil environment, foam destabilizes quickly at high temperatures, limiting its applicability for the EOR process.
Singh and Mohanty (2015)	NPs: Polyethylene glycol coated SiO_2 Surfactant: α-olefin sulfonate	–	Half-life > 48 days in the absence of oil, Half-life > 4 days in the presence of oil	10% incremental oil recovery was obtained by surfactant-NPs stabilized foam blend

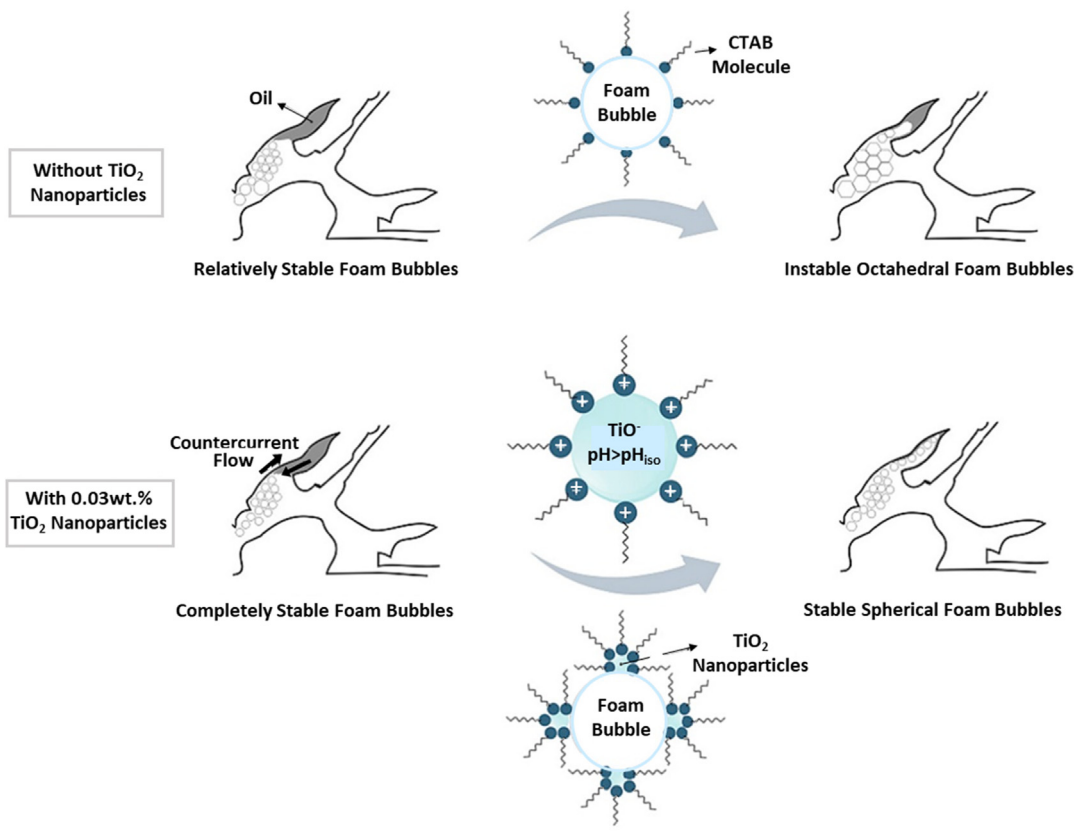

Fig. 12. Foam stabilization mechanisms of combined surfactant-NPs generated foam (Panahpoori et al., 2019).

compared to foams stabilized using only NPs (Fig. 13). This can be attributed to the stronger adsorption of NPs at the CO_2-water interface due to attraction between oppositely charged surfactant molecules (positive charge) and NPs (negative charge), enhancing the stability of generated foam (Worthen et al., 2013b).

After successful generation and transportation of NPs-stabilized foam in columns by Worthen et al. (2015), the foams were generated in the Boise sandstone cores for three concentrations of NPs (0.1%, 0.5%, and 1%). The maximum increment in apparent foam viscosity was around 95% for 1% NPs concentration at a shear rate of ~680 s^{-1} when compared to the base case without using NPs. The pressure drop profiles along with the core demonstrated successful

generation and propagation of the foam through the cores.

Silica NPs and anionic surfactants were used in a study by Singh et al. (Singh and Mohanty, 2015) in 2015 to improve foam stability in both the bulk phase and porous media. The design included evaluating static foam stability with surfactants and with silica NPs-surfactant with nitrogen gas scenarios in the absence and presence of crude oil, analyzing the surfactant-foam lamella with fluorescence microscopy, and controlling mobility in sandstone cores during oil displacement experiments. The foam half-life without using NPs was 48 h which increased to 68 h and more than 4 days by adding 0.1 wt% and 0.3 wt% nanofluids, respectively, as shown in Fig. 14. The addition of 0.3 wt% of nanoparticles improved the foam stability and reduced mobility by twofold. The results demonstrated that silica nanoparticles had very low retention, which enabled long-distance propagation in porous media without causing formation damage.

Razali et al. (2018) proposed the use of hydrophilic and hydrophobic nanoparticles in the presence of a low surfactant concentration to improve foam stability. The effects of SiO_2, ZnO, and TiO_2 NPs on foam stability in the presence of light crude oil at high temperatures of 110 °C were assessed. The surfactant concentration was kept constant at 0.5 wt%, while the NPs concentration was changed between 0.1 and 0.2 wt% in synthetic seawater in the presence of crude oil. The solution was stirred magnetically and ultrasonicated for 30 min to get a stable dispersion. Each sample's stability was tested visually and using the half-life method over several days. A viscometer was used to measure the viscosity of each sample at temperatures ranging from 25 °C to 80 °C. The best among all was hydrophilic silica NPs, which considerably improved the foam half-life twice as much as the surfactant alone (Fig. 15). On the contrary, the application of ZnO NPs reduced the foam half-life compared to the base case due to the reduced catalytic behavior. The size of foam bubbles was found to be more homogeneous in the presence of silica NPs, and liquid drainage was delayed due to the complex formation of silica chains. The addition of 0.15 wt% silica NPs boosted the foam's viscosity from 4.38 cp to 10.01 cp at ambient conditions, enhancing its stability with a half-life of 367 s.

Similarly, Babamahmoudi et al. (Babamahmoudi and Riahi, 2018) 2018 utilized silica NPs and anionic surfactant sodium dodecyl sulfate (SDS) and found an adequately dispersed solution with foam. It was noticed that combining nano-silica with SDS improved the foamability and stability of the solution by increasing the relative foam height by almost 25% (Fig. 16). Foam stability, on the other hand, deteriorated as oil saturation increased.

The stability and characteristics of foam were improved by increasing oil viscosity. In this work, three oils with viscosities and surface tensions ranging from 1.17 to 627 cp and 22–30.93 mN/m

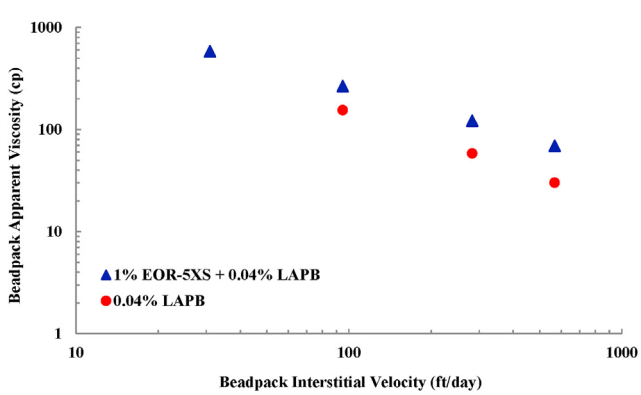

Fig. 13. Apparent surfactant-CO_2 foam viscosity with and without NPs (Worthen et al., 2015).

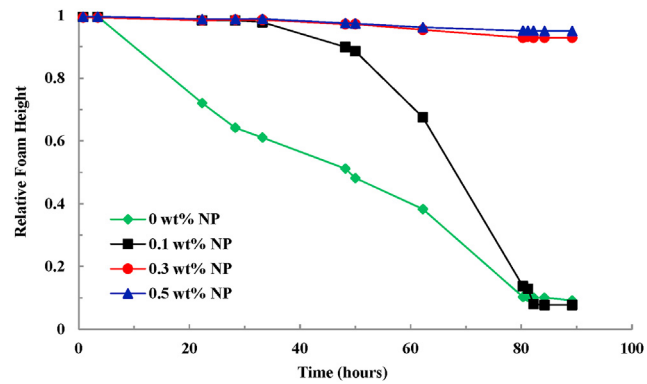

Fig. 14. Foam height as a function of 0.5 wt% surfactant and different concentrations of NPs (Singh and Mohanty, 2015).

were used. This study employed 0.1 wt% silica NPs and a Critical micelle concentration (CMC) of 1 wt% for SDS. When compared to light oil, high viscosity oil was less damaging to foam, resulting in larger average bubble sizes and faster-rising velocity.

In another study, Panahpoori et al. (2019) investigated the influence of varying concentrations of TiO_2 NPs (0.01–0.1 wt%) on foam stability in the presence and absence of cetyltrimethylammonium bromide (CTAB) surfactant by using nitrogen gas for foam generation. CMC, pH, contact angle, interfacial tension, zeta potentials, NPs size, and solution absorbance measurement were taken to evaluate the performance of the proposed hybrid method to enhance foam stability in the bulk phase. The CMC for CTAB was found to be 0.03 wt%. According to conductivity results, the maximum adsorption onto 0.03 wt% nanoparticles was found with 0.03 wt% CTAB which was kept constant for all experiments.

Recently, Rezaei et al. (2021a) presented a promising idea of a stabilized N_2 foam in a combination of silica NPs and three different surfactants under various temperatures and salinities. The effect of NPs and brine salinity was examined, and foam stability was evaluated with time. They investigated the stability of foam considering anionic, cationic, and amphoteric surfactants such as Cocamidopropyl Betaine (CAPB), linear alkylbenzene sulphonic acid (LABSA), and CTAB, respectively under a nitrogen gas environment. Experimental results showed that the application of CAPB surfactant in a hybrid approach provided the highest stability as compared to the other two surfactants. It was found that increasing salinity enhances the stability of foam, however, high salinity limits the application of nanoparticles as agglomeration starts due to high attractive forces in the system.

The best combination of 0.05 wt% CAPB +0.1 wt% silica NPs + 5 wt% NaCl was found that aided to form 2–3 times more stable foam in comparison to using other mentioned surfactants under similar conditions. Experimental results demonstrated that CAPB generated a stable foam till 50 °C, and then its stability decreased with an increase in temperature. However, when the temperature reached 70 °C, the CTAB surfactant showed excellent results as compared to CAPB and LABSA due to the high hydrophilic-lipophilic balance (HLB) value of CTAB molecules which makes them more soluble at high temperatures.

5.3. Improvement in oil recovery by surfactant-NPs-stabilized CO_2 foams

Al Yousef et al. (AlYousef et al., 2017a) explored the synergistic effect of nanoparticles and a surfactant to produce a stable and resilient foam that controlled CO_2 gas mobility in porous media. To test the ability of foam to improve oil recovery, two experiments

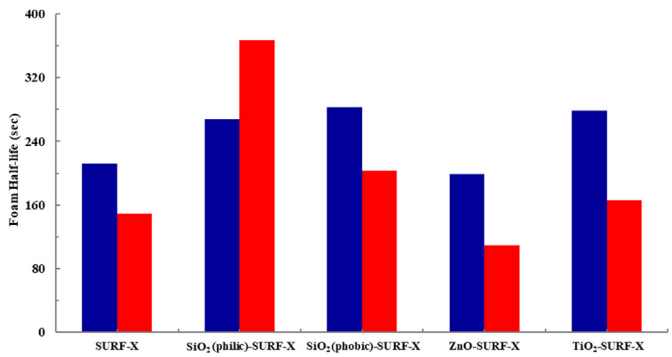

Fig. 15. Surfactant-CO_2 foam half-life as a function of NPs type (Razali et al., 2018).

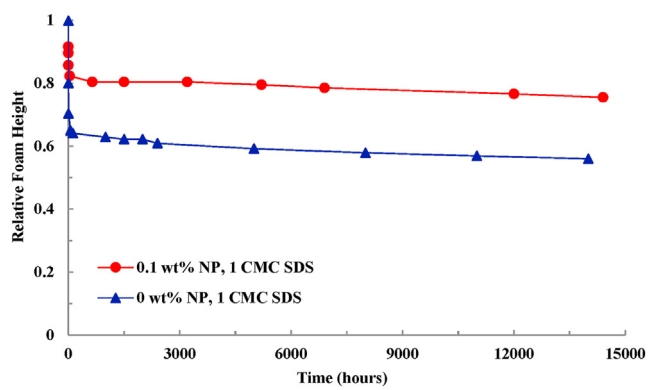

Fig. 16. Foam stability with and without silica NPs (Babamahmoudi and Riahi, 2018).

were carried out: one without nanoparticles and the other with nanoparticles. They utilized an anionic surfactant comprising of alpha-olefin sulfonate, isopropyl alcohol, and citrus terpenes and recovered 6.5% of OOIP with a maximum pressure drop of 7.5 psi in a co-injection surfactant injection setup as shown in Fig. 17. In comparison to surfactant alone, a dispersed mixture of functionalized silica NPs and surfactant were able to produce 9.76% of OOIP providing 3.26% additional oil recovery with a maximum pressure drop of 17 psi. This additional oil recovery was attributed to the utilization of silica NPs which reduced the gas mobility and increased foam viscosity. The influence of temperature was also studied, and it was observed that increasing the temperature from 25 to 50 °C had a negative impact on foam stability, resulting in a decrease in viscosity and a reduction in system pressure drop.

In another study, Zhao et al. (2021) utilized silica NPs of varying hydrophobicity with aerosol-OT (AOT) surfactant to enhance the stability of CO_2 foam. Their results revealed that hydrophobic NPs are far more efficient than hydrophilic NPs at creating and stabilizing CO_2 foam. Experiments on oil recovery were carried out in an oil-wet micromodel having channels of high permeability to simulate wormholes in unconsolidated sandstones. The experiments used two oil samples having different viscosities, called Type-I (215 cp) and Type-II (1850 cp). The NPs stabilized CO_2 foam resulted in an additional oil recovery following the waterflooding by 22.4% for Type-I and 21.9% for Type-II oil as compared to the only foam flooding which provided a recovery of 13.8% and 16.2% for Type-I and Type-II oils, respectively as indicated in Fig. 18. Highly stable foam, emulsification, water/oil IFT reduction, and wettability modification all contributed to the increased oil recovery.

Similarly, the oil recovery tests were conducted by Guo and Ariana (Guo and Aryana, 2016) for various designs of NPs-surfactant-CO_2 foam using a 2D microfluidic device, and the highest incremental oil recovery of 95% of original oil in place (OOIP) was obtained by the CO_2 foam generated using silica NPs together with a mixture of AOS and LAPB surfactants. The study showed higher stability of CO_2 foams produced by a combination of surfactants and NPs.

In a comprehensive experimental and modeling study of Worthen et al. (2015), oil displacement tests were performed by injecting already generated foam into Boise sandstone cores having residual oil saturation (S_{or}) of 30%. Four different scenarios were investigated including NPs-stabilized CO_2 foam injection, liquid CO_2 flooding, injection of 1 pore volume (PV) slug of NPs-stabilized CO_2 foam, and CO_2/brine flooding. The apparent viscosity results indicated 3 times and 30 times reduction in mobility by NPs-stabilized CO_2 foam compared to CO_2/brine flooding and liquid CO_2 flooding, respectively. Almost 24% reduction in S_{or} was observed for all scenarios however the NPs-stabilized CO_2 foam injection resulted in the additional benefit of mobility control and stable oil bank displacement. The results obtained from different stages were used to develop a mathematical model which was then incorporated into a numerical simulator to check the effectiveness of NPs-assisted CO_2 foam flooding on a reservoir scale. High and low permeability layers were introduced in the reservoir model to capture the front advancement accurately and to compare the NPs-stabilized foam flooding scenario with CO_2/brine flooding. The model results depicted a more stable front displacement and an improved sweep efficiency in the case of CO_2 foam generated using NPs. Hence, the results of their study showed that this technique has a huge potential for pilot and large-scale field applications, especially in heterogeneous formations.

Singh et al. (Singh and Mohanty, 2015) utilized three types of crude oils with different viscosities ranging from 9 to 382 cp. Coreflood results showed around 10% incremental oil recovery by surfactant-NPs stabilized foam blend. Nanoparticles remained lodged in lamellas, delaying liquid drainage and the merging of bubbles. In the work of Panahpoori et al. (2019), compared to distilled water injection, the given combination of nano-CTAB + N_2 gas foam injection into an oil-saturated core resulted in an additional 32% oil recovery. This was due to the use of nanoparticles, which improved foam stability and altered rock wettability.

The research conducted by Risal et al. (2019) looked at the combined effects of surface-modified SiO_2 NPs and SDS on the stability and pore-blocking capabilities of foams in a homogeneous glass-bead pack. Foam flow increased the pressure drop indicating the foam stability with blocking of pore space. Surface-modified silica NPs-stabilized foam performed excellently, recovering up to 18% of the remaining oil. Foam flooding was also carried out by Rezaei et al. (2021a) at 25 °C to quantify the performance of foam in carbonate core samples with silica nanofluid as an aqueous phase. Initially, synthetic seawater was injected at a constant rate of 1 cc/min, and later surfactant-nano stabilized foams prepared with different surfactants were injected, and a maximum of 41% ultimate oil recovery was obtained by using CAPB while LABSA provided the lowest oil recovery of 28.6%. Furthermore, tests indicated that the presence of oil was detrimental to foam stability especially under the application of surfactants having a low HLB. When the oil saturation in the core was high, the viscosity of the foam remained low. The viscosity of foam gradually increased when the oil saturation was reduced by injecting more foam, and CAPB-SiO_2 NPs stabilized foam gave the best stability in terms of increased displacing phase viscosity, resulting in excellent sweep efficiency. Table 5 presents some more experimental studies showing the effectiveness of hybrid surfactant-NPs-stabilized CO_2 foams for improved oil recovery from both sandstones and limestones. Hence, such foams have huge potential to recover residual oil while

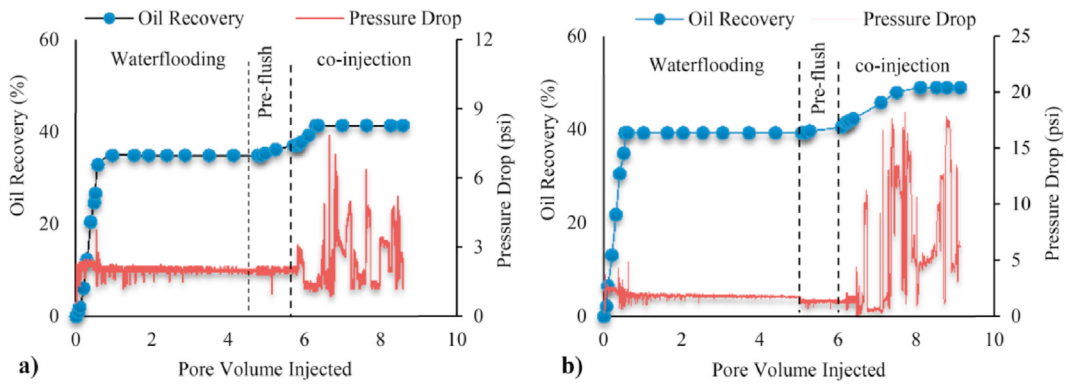

Fig. 17. Oil recovery comparison of (a) Surfactant-stabilized and, (b) Surfactant-NPs-stabilized CO_2 foam flooding (AlYousef et al., 2017a).

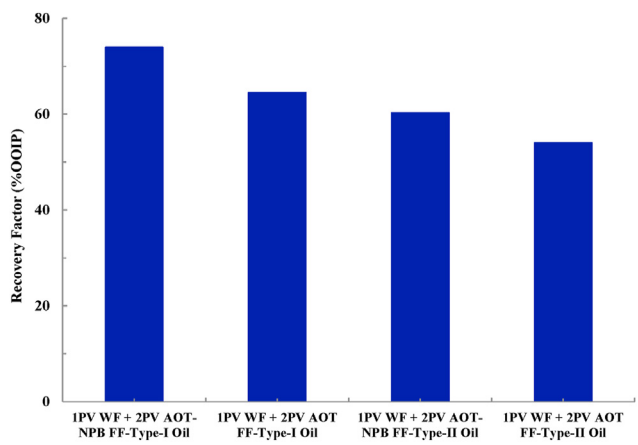

Fig. 18. Oil recovery comparison for surfactant-stabilized CO_2 foams in the presence and absence of NPs (Zhao et al., 2021).

ensuring sufficient sweep efficiency from heterogeneous oil reservoirs.

5.4. Recommended methodology for field pilot design of surfactant-NPs-stabilized CO_2 foams

Once an optimum nanoparticle and surfactant are designed for a certain reservoir based on preliminary testing such as NPs stability in the target brine, phase behavior studies, NPs-surfactant compatibility tests, bulk foam experiments, and foam rheology testing, a stepwise experimental design procedure should be followed for field trials of NPs-surfactant stabilized CO_2 foam flooding. The first step involves screening of most stable NPs-surfactant solutions through colloidal stability studies (Kim et al., 2015). The screened dispersions are then passed through injectivity testing to ensure flow through reservoir rock with minimum retention. The foam generation is first carried out in glass-beads columns and then corefloods are conducted with reservoir cores for a feasibility study

Table 5
Studies showing incremental oil recovery by surfactant-NPs-stabilized CO_2 foam.

Study	Porous media	Materials	Incremental Oil	Remarks
Nguyen et al. (2014a)	Chip scale Model	NPs: Functionalized silica NPs Surfactant: Sodium dodecyl sulfate (SDS)	17% IOIP	Silica NPs-stabilized CO_2 improved the oil recovery by an additional 10% as compared to CO_2 flooding. This increase in recovery was attributed to high sweep efficiency.
Sun et al. (2014)	The glass-etched micromodel and sandpacks	NPs: Silica NPs Surfactant: SDS	38–44%	The total incremental oil recovery for SiO_2/SDS foam flooding and following waterflooding was in the range of 38–44% from single and double core sandpacks.
Manan et al. (2015)	Porous stone	NPs: SiO_2, Al_2O_3 and TiO_2, CuO Surfactant: anionic alpha-olefin sulphonate (AOS)	14% of IOIP	Al_2O_3-NPs resulted in a maximum of 14% oil recovery due to excellent dispersion and injectivity.
Ibrahim et al. (2017)	Berea sandstone cores	NPs: SiO_2 Surfactant: viscoelastic surfactant (VES) and anionic AOS	45.7%	Adding VES to nanoparticles surfactant foam enhanced the stability and improved oil recovery by 7.7% as compared to the case without VES.
AlYousef et al. (2017b)	non-fractured and fractured Bentheimer sandstone	NPs: Modified silica NPs Surfactant: complex nanofluid (CNF) anionic surfactant	44.33%	Given hybrid-method provides an additional recovery of 44.33% in non-fractured rock as compared to 12.62% in fractured rock.

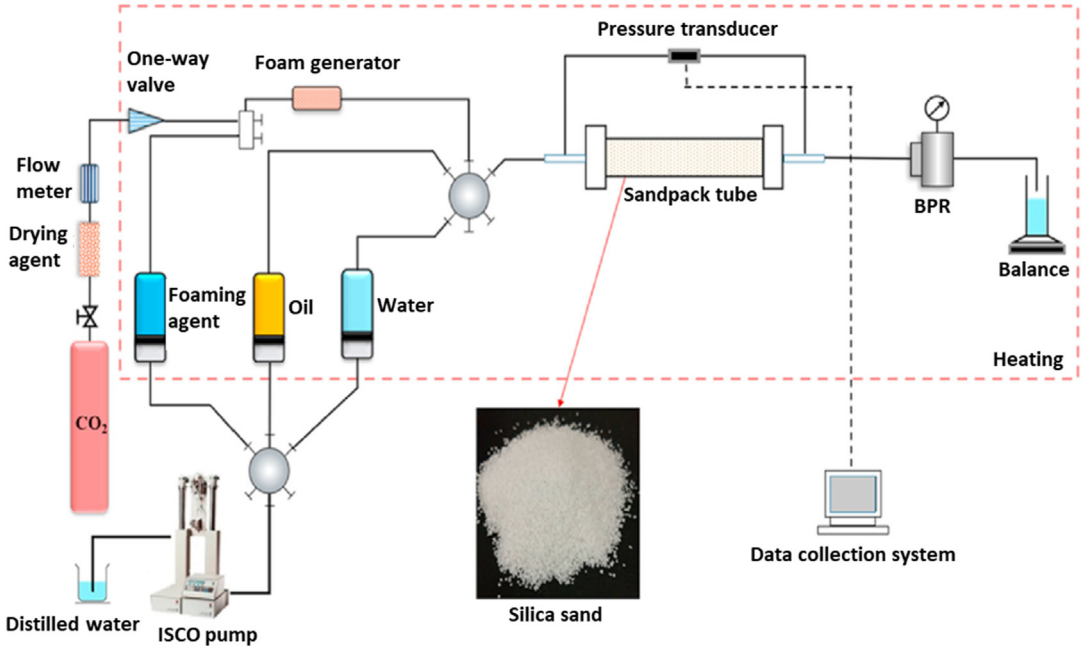

Fig. 19. Experimental set-up for surfactant-NPs-stabilized CO_2 foam generation and oil displacement tests (Lv et al., 2020).

(Espinosa et al., 2010; Worthen et al., 2013a). A schematic of the coreflood set-up most commonly used to generate CO_2 foams and evaluate oil recovery potential is shown in Fig. 19. The core-scale modeling is performed using data from columns and coreflood tests and the final history-matched model is up-scaled to field level to design a pilot field test (Prigiobbe et al., 2016).

6. Conclusions

This paper presented a comprehensive review of CO_2 foams stabilization with the aid of surfactants, NPs, and a combination of both. Miscible CO_2 flooding has a huge potential to improve residual oil recovery, but it results in an inefficient sweep efficiency. CO_2 foam flooding is an alternative to overcome mobility control issues by increasing the viscosity of the foam. However long-term stability of foams in the reservoirs is a challenge. Surfactant-stabilized foam flooding has been used to improve oil recovery from oil reservoirs by controlling displacing phase mobility. However, it is challenging to make a stable foam and keep it stable in porous media in the presence of oil. NPs have been widely used as emulsifiers and stabilizers for foams and emulsions because of their high adsorption energy, excellent surface properties, and their ability to irreversibly attach at the fluid-fluid interface. An overview of foams stabilized by both surfactants and NPs has revealed that NPs-surfactant-stabilized CO_2 foams are almost 2 to 20 times more stable compared to the foams stabilized using only NPs or surfactants. The increase in foam viscosity can lead to enhanced oil recovery from oil reservoirs and if this hybrid technique is optimized and deployed effectively, the rise in foam viscosity might lead to increase oil recovery from oil reservoirs due to synergy between NPs and surfactants.

It is concluded based on our review that NPs-surfactant stabilized CO_2 foams are promising EOR agents however a more extensive study is required for their field implementation since actual reservoir conditions of temperature, salinity, and operating pressure can significantly affect the activity of NPs and surfactants as foam stabilizers. The effect of crude oil presence on the stability of such hybrid foams needs to be studied in more detail as well as the capability of these foams to recover residual oil.

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Erratum regarding missing Declaration of Competing Interest statements in previously published articles

Declaration of Competing Interest statements were not included in the published version of the following articles that appeared in previous issues of Petroleum Research.

The appropriate Declaration/Competing Interest statements, provided by the Authors, are included below.

1. "Effect of operating pressure on the performance of THAI-CAPRI in situ combustion and in situ catalytic process for simultaneous thermal and catalytic upgrading of heavy oils and bitumen" [Petroleum Research, 2022; 7 (2): 155–164] https://doi.org/10.1016/j.ptlrs.2021.09.010

   Declaration of competing interest: The Authors have no interests to declare.

2. "Machine learning classification approach for formation delineation at the basin-scale" [Petroleum Research, 2022; 7 (2): 165–176] https://doi.org/10.1016/j.ptlrs.2021.09.004

   Declaration of competing interest: The Authors have no interests to declare.

3. "A minimalist approach for detecting sensor abnormality in oil and gas platforms" [Petroleum Research, 2022; 7 (2): 177–185] https://doi.org/10.1016/j.ptlrs.2021.09.007

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4. "Hybrid surfactant-nanoparticles assisted CO2 foam flooding for improved foam stability: A review of principles and applications" [Petroleum Research, 2022; 7 (2): 186–203] https://doi.org/10.1016/j.ptlrs.2021.10.004

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5. "A robust deep structured prediction model for petroleum reservoir characterization using pressure transient test data" [Petroleum Research, 2022; 7 (2): 204–219] https://doi.org/10.1016/j.ptlrs.2021.09.003

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6. "Review of wax sedimentations prediction models for crude-oil transportation pipelines" [Petroleum Research, 2022; 7 (2): 220–235] https://doi.org/10.1016/j.ptlrs.2021.09.005

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7. "Prediction of fold-of-increase in productivity index post limited entry fracturing using artificial neural network" [Petroleum Research, 2022; 7 (2): 236–245] https://doi.org/10.1016/j.ptlrs.2021.09.002

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8. "Application of machine learning algorithms to predict tubing pressure in intermittent gas lift wells" [Petroleum Research, 2022; 7 (2): 246–252] https://doi.org/10.1016/j.ptlrs.2021.09.006

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9. "Influence of wellhead pressure and water cut in the optimization of oil production from gas lifted wells" [Petroleum Research, 2022; 7 (2): 253–262] https://doi.org/10.1016/j.ptlrs.2021.09.008

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10. "Investigation of flow behavior of crude oils with emphasis to upper Assam Basin, India" [Petroleum Research, 2022; 7 (2): 263–268] https://doi.org/10.1016/j.ptlrs.2021.09.009

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11. "NMR chemical shifts of carbon atoms and characteristic shift ranges in the oil sample" [Petroleum Research, 2022; 7 (2): 269–274] https://doi.org/10.1016/j.ptlrs.2021.10.001

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12. "An assessment of trace metal pollution indicators in soils around oil well clusters" [Petroleum Research, 2022; 7 (2): 275–285] https://doi.org/10.1016/j.ptlrs.2021.09.001

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13. "Chemical speciation, bioavailability and risk assessment of potentially toxic metals in soils around petroleum product marketing company as environmental degradation indicators" [Petroleum Research, 2022; 7 (2): 286–296] https://doi.org/10.1016/j.ptlrs.2021.08.006

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