

Full Length Article

Development of highly stable lamella using polyelectrolyte complex nanoparticles: An environmentally friendly scCO₂ foam injection method for CO₂ utilization using EOR



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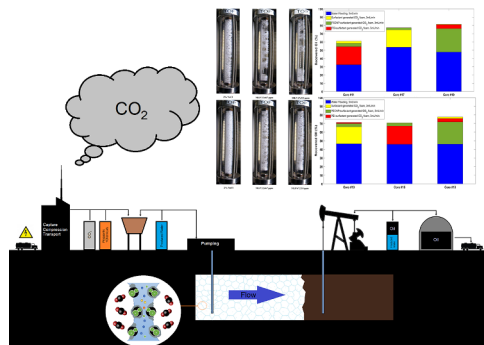
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GRAPHICAL ABSTRACT

Enhanced oil recovery with scCO₂ foam fluids stabilized by PECNP/Surfactant at the lamella interface helps to store and sequester CO₂ in underground formations. The presented mixture reduces the amount of fresh water usage and produced water disposal in EOR process.



ARTICLE INFO

Keywords:

Enhanced oil recovery
CO₂ foam
Polyelectrolyte complex nanoparticle
Foam stability
Produced water
CO₂ storage

ABSTRACT

CO₂ foam flooding is a proven technology that enhances oil recovery and geological storage by improving the mobility of the injected CO₂ in depleted reservoirs. Surfactant drainage, disintegration and rock adsorption have long affected the stability of CO₂ foams in saline formations. To generate a more stable foam front in the presence of crude oil and to overcome the capillary forces destabilizing the foam lamella, polyelectrolyte complex nanoparticles (PECNP) conjugated with surfactant oligomers are introduced to the lamella generated by an aqueous phase containing high salinity to improve the EOR performance and produced water compatibility of supercritical CO₂ (scCO₂) foams. The formation of vesicular structures containing electrostatically hinged complexes of PECNP and surfactant was verified via transmission electron microscopy (TEM) while the

Abbreviations: scCO₂, supercritical CO₂; CCUS, carbon capture utilization and storage; PEI, polyethyleneimine; DS, dextran sulfate; PECNP, polyelectrolyte complex nanoparticle; MLP, Mississippian limestone play; RO-DI water, reverse osmosis-deionized water; CMC, critical micelle concentration; MMP, minimum miscibility pressure; TEM, transmission electron microscopy; IFT, interfacial tension; TDS, total dissolved solids

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<https://doi.org/10.1016/j.fuel.2019.116360>

Received 1 August 2019; Received in revised form 3 October 2019; Accepted 4 October 2019

Available online 22 October 2019

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structural changes associated with molecular complexation were identified using Raman spectroscopy. Accordingly, optimized ratios of PECNP:surfactant were employed to generate the most stable scCO_2 foam in high salinity produced water and improve the recovery of the foam flooding process. The effect of PECNP-conjugated surfactant on stability, durability, and interfacial properties of scCO_2 foam were examined. A set of core-flooding experiments in a wide range of salinity proved the capability of scCO_2 foam systems enhanced using PECNP-surfactant to offer the highest apparent viscosity and incremental oil recovery. A variety of injection scenarios tested on oil-saturated limestone core samples indicating that the highest incremental oil recovery and the lowest residual oil saturation are achieved by prioritizing PECNP:surfactant scCO_2 foam flood in optimized electrolyte concentrations.

Nomenclature		ΔP	pressure difference between the two ends of the core holder (psi)
ϕ	gas volume fraction	A	cross section area of the core (cm^2)
$\Delta\pi_e$	equilibrium part of surface pressure variation (mN/m)	Q	volumetric flow rate of fluid flow (cm^3/s)
$\Delta\pi_{ne}$	non equilibrium part of surface pressure variation (mN/m)	L	core length (cm)
E_e	equilibrium surface dilatational elasticity (mN/m)	PV	pore volume (cm^3)
U_b	velocity of compression (m/s)	k	permeability (D)
A_i	initial surface area (m^2)	K	flow consistency index ($\text{Pa}\cdot\text{s}^n$)
t	time (s, min)	n	flow behavior index
τ	relaxation time (s)	η	viscosity (cP)
μ_{app}	apparent viscosity of fluids (cP)	$\dot{\gamma}$	shear rate (s^{-1})

1. Introduction

The Paris Climate Accord aims at holding global temperature rise to well below 2°C for this century by limiting greenhouse gas emission into the atmosphere [1]. CO_2 emission from power plants and industrial facilities is widely regarded as major contributor to global warming and rising global temperature [2]. However, fossil fuels still play a dominant role in global energy sector, global oil production has increased to more than 2.5-fold over the last 50 years, and crude oil has become the largest energy source on planet, accounting for around 39% of fossil energy [3]. To reduce detrimental environmental impacts of anthropogenic CO_2 emissions, various technologies for CO_2 storage have been proposed [4–6]. Compression, injection and partial storage in geological formations with the purpose of EOR is a viable approach in oil recovery from subsurface resources [7–9].

CO_2 -enhanced oil recovery (EOR) is introduced as a promising tool for greenhouse gas emission reduction [10], since a CO_2 capture process from industrial facilities can provide the anthropogenic CO_2 required to inject and store in geological formations and to enhance the production [11]. Therefore, CO_2 for oil production with associated storage can reduce environmental impacts and contribute to Carbon Capture, Utilization, and Storage (CCUS) [12]. The US Department of Energy (DOE) has long been investing in next generation of CO_2 -EOR research for production and sequestration [13]. Accordingly, successful storage of CO_2 in geological formations have been reported across the US [8]. Additionally, CO_2 injection has been used to improve the recovery of oil reservoirs since the 1950s [14]. CO_2 miscible flooding, performed at reservoir pressures higher than the minimum miscibility pressure (MMP), results in a higher microscopic efficiency [15]. However, several issues were reported with CO_2 injection such as unfavorable mobility ratio, viscous fingering, gravity override and poor sweep efficiency [10,16,17]. Bernard and Holm initially presented CO_2 foam as an effective mobility control agent with selective mobility reduction, to improve the sweep efficiency of EOR processes [18]. Supercritical CO_2 as compressed CO_2 at extreme conditions (31.1°C and 7.4 MPa [19]) is known as a potential candidate for CO_2 storage with properties such as improved mass transfer and increased selectivity [20]. Foam offers the capability of mobility reduction where the foam quality lies between 45 and 90% [21,22]. Aqueous based scCO_2 foam is a colloidal dispersion consisting of scCO_2 in water or brine and foaming stabilizers [23]. Contributing fluids give rise to the final viscosity of foam [24],

eliminate pore plugging in formation [25], lower water-usage in water sensitive formations [23], and introduce a recyclable and eco-friendly approach with aqueous phase [26].

Typically, a large quantity of water (brine) injection accompanies CO_2 floods, leading to isolation of oil from CO_2 in the reservoir [27] and excessive produced water discharge on the surface [28]. Disposal, treatment and re-use are suggested techniques to handle the large volumes of produced water from oil fields [23,29–31]. Re-injection of produced water into the reservoir is the most optimized and ecofriendly approach to handle the produced water [32]. The water involved in this process can be re-injected to create a sustainable process and to prevent excessive fresh water usage and waste water disposal [28] as injection of recyclable fluids helps to create sustainable oil production cycle for non-hazardous energy-water nexus [33].

Carbonate reservoirs account for over 60% of the world's oil and gas reserves with average recovery of less than 40% [34] opening the door to examine the potential of advanced materials such as high internal phase emulsions for energy production. The stability of the surfactant generated CO_2 foam in the presence of crude oil is a determining factor in sweep efficiency and oil recovery [35] and ultimately underground CO_2 storage [36] as spreading oil into the foam lamellae destabilizes the CO_2 -water lamella interface [20]. Aqueous based CO_2 -EOR requires development of CO_2 -philic surfactants not sensitive to water medium for effective CO_2 mobility control in porous media [37]. Injection strategies were previously introduced with dissolution of surfactant in CO_2 [37], and better recovery was achieved when water was not injected. Conventional surfactants such as alpha olefin sulphonates are usually missing CO_2 -philic functional groups such as aliphatic/aromatic branches and methylene groups [38]. Non-ionic branched nonylphenol ethoxylate or tridecyl alcohol ethoxylate surfactants with variable ethylene oxide (EO) repeating units are increasingly used for mobility reduction due to brine soluble/ CO_2 soluble properties in high pressure [17,39,40].

Despite the advances in surfactant/foam EOR in recent years [41], the stability, excessive adsorption on the rocks [42] and imbalanced head/tail solubility in CO_2 /aqueous phase impacts the resulting emulsion stability achieved by surfactant generated foams [23]. Moreover, adsorption of the oil by the porous media changes the wettability of the rock and negatively affects the foam generation and regeneration [21]. Polyelectrolytes with electrostatic conjugation to the surfactants are considered promising additives for alternation of surfactant

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