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Lowering Fresh Water Usage in Hydraulic Fracturing by Stabilizing scCO₂ Foam with Polyelectrolyte Complex Nanoparticles Prepared in High Salinity Produced Water

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Abstract

Polyelectrolyte complex nanoparticle (PECNP) systems compatible with produced water were developed to improve supercritical CO₂ (scCO₂) foam stability and to reduce fluid loss for fracturing applications. Foam viscosity, stability, fluid loss properties and cleanup of injected liquid through the formation were enhanced by PECNP-surfactant systems prepared in produced water medium. Taking advantage of produced water as energized fluids for fracturing requires enhanced compatibility of gas/liquid mixture. Two produced water recipes of 33,333 and 66,666ppm TDS were used to prepare 1 w/w% surfactant solutions. PECNP was formed as a mixture of positively- and negatively- charged polyelectrolytes. Experimental setup was designed to determine the aqueous foam stability at actual reservoir conditions. Rheological measurement was performed to measure the stability of the bulk foam under shear and to evaluate the foam texture properties. The improved viscosity of different proportions of PECNP-Surfactant (9:1, 8:2, 7:3, and 6:4) in aqueous foam mixtures was observed as compared to surfactant stabilized CO₂ foam. The flow consistency index observed in the shear thinning region was also increased from 1184.3 to 2916.4 Pa sⁿ in 33,333ppm and from 1035.7 to 1683.1 Pa sⁿ in 66,666ppm brine solutions. The view cell results revealed the high stability and longevity of scCO₂ foam employing various proportions of surfactant to nanoparticle as oppose to surfactant generated foam in which the foam height shortened faster. The presented scCO₂ generated foam can preserve the foam cellular structure in absence of crude oil. The PECNP-Surfactant system successfully lowered the interfacial tension to up to 74% and 93% for 33,333 and 66,666ppm brine salinity, respectively. Fluid loss was measured to evaluate fluid leak-off from a core when the high flow velocity along the core exists. The fluid loss for both CO₂ and water leak-off were also lowered employing PECNP- Surfactant containing foam.

Introduction

Hydraulic fracturing (HF) is one of the most enduring and reliable technologies developed to increase and maintain the well productivity. Alongside horizontal drilling, the aim of hydraulic fracturing is to enhance the hydrocarbon production from low permeability formations (Michael Berry Smith 2014). Fracture design, propagation and clean up are crucial stages in HF processes (Osiptsov 2017). After the

clean-up, proppant remains in the fracture. The fracture which once was held open by fluid pressure, needs to be filled with granular materials to maintain the permeability in order to avoid the pressure drop as result of fluid loss (Barbati et al. 2016). The technology is now very well developed in a way that more than 60% of all the wells drilled are fractured to increase the production rate with stimulation. From the early development of hydraulic fracturing process in 20th century, chemical fluids were used to open/propagate the fractures and to carry the proppants to the fracture (Barbati et al. 2016). Variety of chemical components were used to reduce the friction loss along the flow lines and their proppant carrying capability is still examined by researchers (Al-muntasheri et al. 2014). Initially, hydrocarbons such as kerosene, crude oil or gasoline were selected as viscous agents and fraction reducers followed by fatty acids to increase the viscosity of fracturing fluids (Al-muntasheri et al. 2014; Barati and Liang 2014; Daneshy 1990). Synthetic polyacrylamides as thermally stable polymers were employed to improve the viscosity and temperature resistivity in deeper wells (Al-muntasheri et al. 2014), however, the permeability of proppant-packs may be significantly damaged using these materials. Breakers need to be added to polymer based fluids to improve the conductivity and to degrade the polymer residue in the fracture (Brannon and Pulsinelli 1990). Moreover, slick water with high velocity of injected water fails to carry high concentration of proppant to the fracture (Al-muntasheri et al. 2014).

Foam and energized fluids are composed of one compressible component such as carbon dioxide or nitrogen that are considered to overcome the formation damage, low viscosity and clean-up efficiency of conventional fracturing fluids in tight and ultra-tight unconventional formations (Tong et al. 2017). Better fracture stimulation was reported using CO₂-based energized fluids (Garbiset al. 1986). CO₂ is mixed with fluids injected to deeper wells to form a low water content fracturing fluid (Anandan et al 2017). Despite the environmental concerns of CO₂ pollution in atmosphere (Keith 2009) and heavy emphasize on its capture (Rezaei et al. 2017; Rownaghi et al. 2016), storage (Jun et al. 2017; Moodie et al. 2017) and sequestration (Jun et al. 2017; Allam et al. 2003), if properly managed, CO₂ is abundant, nonflammable, essentially non-toxic for variety of applications such as refrigeration (Polzot et al. 2015), material synthesis and processing (Allam et al. 2003; Tomasko et al. 2003), medicine (Lin et al. 2014), chemical industry (Dzyuba and Bartsch 2003) and of course, oil industry for oil recovery enhancements (Verma 2015). Due to thermodynamic immiscibility, discrepancies in cohesive energy density of oil and CO_2 and having lower density than oil and water, the affinity of CO_2 /water has been subject of variety of studies to stabilize the gas/liquid mixture while flowing through low permeable formations (Aroonsri et al. 2013). In their stable form, foams offer high apparent viscosity, low leak-off and faster fracture cleanup (Anandan et al. 2017; Tong et al. 2017). scCO₂ in water (C/W) foams are stabilized with nanoparticles or surfactants through CO₂-water interfacial adhesion (Worthen et al. 2013). Surfactants, in general, form protective layers at gas/liquid interface to prevent the coalescence between the bubbles (uniform dispersion) and to make gas and liquid phase compatible in the mixture (Dreiss and Feng 2017). Some issues with surfactants such as imbalanced head/tail solubility in CO2/aqueous phase impacts the resulting emulsion stability (Peach and Eastoe 2014). Foamed liquids with CO₂ compatible viscoelastic surfactants (VES) offer stable fracturing fluids with viscous behavior under shear which helps to break in the fracture in addition to leaving no residue behind (Barati and Liang 2014). When VES is dissolved in water, micellar structures are formed, so the water viscosity is enhanced, while increasing the VES concentration leads to formation of rod-shape structures sensitive to oil or hydrocarbons dissociate their structure in spherical micelles when oil meets the aqueous foam (Barati and Liang 2014; Dreiss and Feng 2017), however, high fluid leak-off and excessive viscous behavior at high temperatures were reported for VES enhanced fracturing fluids (Al-muntasheri et al. 2014; Sullivan et al. 2006). To address this issue, nanoparticles are employed to enhance the VES elastic portion. Nanoparticles at interface are proven to be more effective in stabilizing the foams (Yang et al. 2017). Nanoparticle can act as barrier to bubble coalescence upon their irreversible adsorption to the interface layer and thus reduction of contact area between the two phases occurs (Emrani et al. 2017). Addition of nanoparticle to VES results in micellar accumulation and structural condensation leading to thermal stability and elasticity (Yang et al. 2017). Another method to stabilize the VES in interfaces is to reduce the chain dynamic movement through electrostatic forces(Bower et al. 2016). Polyelectrolytes are promising candidates to stabilize the VES chain dynamics. Polyelectrolytes are polymers containing electrolyte groups capable of dissociation in aqueous solutions for ionic stabilization, adsorption and exchange applications (Hosseini, Hooman; Dornbusch, Donald 2014; Hosseini, Hooman 2016; Hosseini et al. 2016). To form the nanoparticles, polyelectrolytes with opposite charges can bind to form collide particles capable of hindering VES relaxations and lamella stabilization. A new type of polyelectrolyte complex nanoparticle for stability improvement of CO₂ foam in oil recovery applications was previously introduced by our group (Ghahfarokhi 2017). The polyelectrolyte complex nanoparticle (PECNP) mixture with supercritical CO₂ (scCO₂) at low salinity 2% NaCl brine successfully lowered the extent of core damage while the percentages of recovered oil in place and pressure drop across the sand pack increased during the cleanup simulation(Kalyanaraman et al. 2017). These nanoparticles were also modified and to be stable in high salinity brine while making scCO₂ foams generated for EOR applications stable (Nazari et al. 2017). Recently, PECNP enhanced scCO₂ foam was successfully tested for well stimulation in particular in coordination with low salinity brine and it revealed a promising improvement in stability and viscosity of resulting foam (Anandan et al. 2017). Since it is critical to manage and treat the large volumes of water containing high concentration of total dissolved solids (TDS) returning to the surface as a result of HF and Enhanced Oil Recovery (EOR) processes (Gregory et al. 2011; Kalyanaraman et al. 2017; Nazari et al. 2017; Tetteh et al. 2017), it is highly desirable to develop a fracturing foam systems compatible with high salinity brine. The objective of this work is to develop polyelectrolyte complex nanoparticle (PECNP) systems compatible with produced water and capable of improving scCO₂ foam stability to reduce fluid loss for fracturing applications.

The rheology of fracturing fluid is studied to examine the fracture conductivity and geometry and also to evaluate the ability of proppant suspension, transport, deposition and flow back (Nath et al. 2017; Tong et al. 2017). The behavior of non-Newtonian fracturing fluid is evaluated by power law model. Different proportions of PECNP/Surfactant in high salinity brine foam were visually examined in view cell and dynamic fluid loss tests. The proposed system is capable of commercial development in produced water to ensure the creative management of flow back and protection of ground and surface water resources.

Materials and Methods

High salinity brine was prepared according to the brine recipe of the Mississippian Limestone Play (MLP) reported in Table 1, 200,000ppm aqueous solution of CaCl₂.2H₂O, MgCl₂.6H₂O, SrCl₂.6H₂O, Na₂SO₄, NaCl and KCl was prepared in reverse osmosis (RO) water. Subsequently, dilution with reverse osmosis (RO) water to sea level concentrations, 33,333ppm (33.3k) and 66,666ppm (66.7k) was performed.

Table 1: Mississippian Limestone Play (MLP) brine composition							
Salt	NaCl	Na_2SO_4	KCl	MgCl ₂ .6H ₂ O	SrCl ₂ .6H ₂ O	CaCl ₂ .2H ₂ O	Total
Concentration (mg/L)	163,661	1,224	715	21,759	1,535	46,886	235,782

Surfactant HDP-0761-12-2AM was prepared by Harcros Chemicals Inc. This surfactant was used

to form 1 w/w% reference solutions in 33.3kppm and 66.7kppm brine samples. HDP-0761-12-2AM was employed to stabilize the liquid-scCO₂ mixture at 1350 psi and 40 °C. The polyelectrolyte complex nanoparticle (PECNP) system was made in accordance to the procedure introduced by Kalayanaraman et al. and Nazari et al (Kalyanaraman et al. 2017; Kalyanaraman et al. 2016). Branched Polyethyleneamine (PEI) with average molecular weight of 25,000 was purchased from Sigma Aldrich. The PEI density is 1.03 g/ml at 25 ℃ and the corresponding viscosity ranges between 13,000 cP and 18,000 cP at 50 ℃. Dextran sulfate (DS: Sodium Salt) with an average molecular weight of 500,000 was also purchased from Sigma Aldrich. The critical micelle concentration (CMC) was determined for the surfactant solution in the brine, and all the samples were maintained above the CMC. pH for solution of PEI in brine (33.3kppm and 66.7kppm) was adjusted to 8 and 8.5 based on the previously published work by our group (Anandan et al. 2017; Kalyanaraman et al. 2017). The best value of pH is determined based on vial test measurement and stability of foaming solution with air as a dispersed phase. Hydrochloric acid (HCl) is added to the mixture to reduce the basicity of PEI solution in high salinity brine and to optimize the density of amine functional groups on PEI chains. HCl addition also helps to break helical and coiled polyamine chains(Pei et al. 2016). At this alkaline level (pH= 8.5) the cloudy mixture turns to clear homogenous solution.

Particle Size and Zeta Potential Measurements: The diameter of ionic particles in each sample was measured by taking the average of the three readings with NanoBrook Omni Particle sizer and zeta potential analyzer, Brookhaven Instruments. The mean particle size of each sample along with the electrophoretic mobility were employed for determining the zeta potential. For the zeta potential measurements, the samples were diluted 20 times in 1mM KCl and the average of three readings were considered for analysis.

Vial tests: The surfactant in brine solution and PECNP mixtures were prepared, added and mixed in different proportions (PECNP:Surfactant 1:9, 2:8, 3:7) and predetermined amount (10ml) of final solution is transferred to 25 ml vials for foam decay test. The mixture of surfactant/PECNP/brine and air was agitated heavily for almost 30 times for perfect mixing of air/liquid. Experimental setup was designed to quantify bulk foam height as a function of time to determine the aqueous foam stability. The scaled vial is placed in an oven with constant temperature of 40 °C (Figure 1). By the aim of Go-Pro camera set inside the oven the foam height in the vial was recorded every 5 minutes, while the system was isolated at 40 °C.



Figure 1: Simple vial test for PECNP/Surfactant mixtures in high salinity brine mixed with air as preliminary test before actual test with scCO₂

Foam Rheology: The rheometer setup consists of feed cylinders, pumps, the main rheometer unit connected to PC software and a waste pump collector (Figure 2). To make an isothermal environment in lines, valves and pumps, recirculating cooler (ISOTEMP 1016D) was turned on and the temperature was set on 6°C. Pump A is refilled with CO₂ and temperature and pressure were set to a supercritical state of 40°C and 1350 psi. Pump B was also filled with the foaming liquid. Lines containing scCO₂ and foaming solution were connected and the produced foam flowed through the rheometer cup and from there to the waste collector pump (Pump C). The proportion of scCO₂ to foaming mixture was chosen to be 9 to 1 based on previous observations by our group(Anandan et al. 2017; Nazari et al. 2017). Rheometer utilizes constant (2000 s⁻¹) and variable (2000 s⁻¹ to 100 s⁻¹) shear rates. The measurements were carried out in dynamic (constant flow of foam solution), static (stagnant foam liquid in the cup) and ramp (variable shear

rate in static mode). During the static and ramp modes 45 to 120 data points were collected with 30-second time intervals. The Rheoplus software was used to set the rheological adjustments.



Figure 2: Process flow diagram for rheometer setup

Foam IFT Measurements: Interfacial tension analysis for high salinity brine, surfactant solution and $scCO_2$ foam were performed according to pendant drop method by a tensiometer capable of analysis in $scCO_2$ conditions. The pendant drop chamber and corresponding inlet/outlets were rinsed with RO water multiple times and the main chamber was filled with desired solution while isothermal temperature of 40°C was set by applying heating jackets around the pipes and chamber. The chamber liquid was pressurized to 1350 psi and $scCO_2$ bubble was generated through the desired liquid in chamber. The DROPimage software and high-resolution camera were employed to measure the interfacial tension. Process flow diagram for high pressure – high temperature tensiometer is represented in Figure 3.



View Cell Testing: View cell measurement was carried out in a high-pressure, high-temperature (HPHT) CO₂ foam flooding setup capable of core flooding, fluid loss and foam stability measurements (Figure 4). The system was isolated at 40°C. The left transfer cylinder was filled with foaming solution and scCO₂ was added to mixture from CO₂ line before inline mixing and the gas/liquid mixture was directed through the sapphire view cell. After sufficient time (to complete foam mixing), the view cell was isolated from the rest of the system and foam decay was measured. For foam-oil stability measurements, the right transfer cylinder was filled with oil and cylinder pressure was maintained at 1350 psi for exposure at scCO₂ condition. After isolation of foam was performed in view cell, oil was immediately introduced from the right transfer cylinder to view cell to measure the stability of foam in the presence of crude oil.



Figure 4: Process flow diagram for HPHT CO₂ foam flooding setup, capable of core flooding, fluid loss and foam stability measurements. Pathway A represents foam flow through view cell setup, Pathway B represents foam flow through dynamic fluid loss setup

Dynamic Fluid Loss: Dynamic fluid loss measurements were performed in the setup presented in Figure 4. The fluid loss module is presented in Figure 5 as core sat adjacent to fluid flow and the ability of fracturing fluid flow and leak-off in low permeability rocks were measured. The scCO₂ foam was generated and directed to the fluid loss setup where the tight core is exposed to foam flow. Two pathways directed the flow through the cell, one was adjacent to the core and the other through the core (fluid loss). The volume of gas and liquid coming out of the core were recorded versus time.



Figure 5: Fluid loss module from different views used in HPHT CO₂ foam apparatus

A Kentucky sandstone outcrop core with specification detailed in Table 2 was provided by Kocurek Industries and it was used for fluid loss proposes.

Table 2: Physical properties for Kentucky sandstone core, data provided by Kocurek Industries.					
Core	Gas Permeability	Brine Permeability	Porosity	UCS Strength	
Kentucky Limestone	1 to 5 mD	0.18 mD	14%	8000 psi	
Core					

Results and Discussion

Vial Test

The vial test is a primary experiment to examine the compatibility and initial stability of foaming solutions with the gas phase. The stability of foaming mixture with air as gas phase is improved by addition of variety of PECNP to surfactant ratios. The PECNP foam height declines with lower rate in 33.3kppm and 66.7kppm brine concentrations and foam degradation occurred in a longer time accordingly (Figure 6).



Figure 6: Air foam stability test for different ratios of PECNP to Surfactant in two different brine concentrations (a) 33.3kppm and (b) 66.7kppm

The mixtures preserved their initial height for at least 20 minutes in 33.3kppm brine solution and for 50 minutes in 66.7kppm brine solution. The 1:9 ratio of PECNP:Surfactant exhibits a consistent improvement in foam stability for both brine concentrations.

Zeta Potential Test

PECNP in 33.3kppm solutions represent lower mean size, polydispersity and average count rate which are due to lower ionic interactions in the solution (Table 3). When the concentration of the brine solution increases to 66.7kppm, nanoparticles form larger aggregates due to strong ionic interactions in brine solution which lead to coalescence and growth of particles. The average zeta potential is positive, which is in agreement with the optimum pH (8.5) and composition ratio of PEI:DS:Brine (3:1:0.1) (Anandan et al. 2017; Ghahfarokhi 2017). The zeta potential increases with salinity concentration and the positive charge of nanoparticles help to electrostatically stabilize the surfactant with sulfonate negative functional groups, thus the lamella stability is improved. Due to charge magnitude and particle size, it is expected to achieve higher lamella stability for PECNP systems in 66.7kppm brine.

Particle Size Measurements	33.3kppm brine	66.7kppm brine
Viscosity (cp)	0.85	1.05
Mean Size (nm)	106.26	373.41
Average Count Rate (kcps)	269.20	711.86
Mean Polydispersity	0.26	0.417
Zeta Potential Measurements	33.3kppm brine	66.7kppm brine
Average Zeta Potential (mV)	13.46	14.50
Average Mobility (µ/s)/(V/cm)	1.10	0.99
Sample Count Rate (kcps)	230	241

Table 3: Zeta potential and particle size measurements from dynamic light scattering analysis

Interfacial Tension Analysis (IFT)

The perfect scCO₂ compatibility of surfactant and PECNP with both brine concentrations is evident in Figure 7. As presented in Figure 7a, interfacial tension for the seawater-like salinity brine (33.3kppm) mixture with scCO₂ is lower than RO water mixed with scCO₂ due to ionic interactions which act as stabilizing agents in the lamella, therefore, the favorability of this concentration for colloidal dispersion of scCO₂ is anticipated. To enhance the stabilizing effect, surfactant and surfactant/PECNP mixtures were mixed with scCO₂ and surface tension reduction of up to 74% was recorded compared to Brine- scCO₂ for 1:9 ratio of PECNP:Surfactant (Figure 7a). Brine with 66.7kppm concentration represents higher interfacial tension due to excessive ionic interactions (Figure 7b) since surfactant can form stable micelles in this highly concentrated ionic media and the degree of PECNP/Surfactant compatibility with 66.7kppm brine is higher than solutions made in 33.3kppm brine (93% decline in IFT compared to original 66.7kppm brine solution) due to the presence of large PECNP and high positive charge on them in 66.7kppm brine. The best composition of PECNP:Surfactant for 66.7kppm brine solution was 4:6 (Figure 7b).



igure /: Interfacial tension analysis for scCO₂ bubble generated in RO water and PECNP/Surfactant mixtures in (a) 33.3kppm and (b) 66.7kppm brine solutions

Rheological Measurements

Figure 8 illustrates the rheological measurements in static time sweep (static: no flow of scCO₂ foam in the chamber) for variety of PECNP/surfactant enhanced scCO₂ foams in two concentrations of brines. The average apparent viscosity calculated at constant shear rate of 2000 s⁻¹ is found to be the highest for the PECNP-surfactant foam compared to the baseline surfactant solution (\sim 23cp). The 1:9 ratio of PECNP:Surfactant in 33.3kppm brine represents the highest viscosity which maintains the lead over other ratios in entire time period, while in 66.7kppm brine, the highest time sweep value belongs to the highest concentration of PECNP (4:6 ratio of PECNP:Surfactant). In 66.7kppm solution, addition of higher portions of PECNP is needed to elevate the viscosity and to stabilize the excessive ionic interactions in a highly concentrated brine. Near to constant viscosity of foaming solution over the time in static measurement was recorded. The consistent viscosity of foaming solution represents uniform texture and homogenous distribution of gaseous phase in high salinity brine which agrees with view cell observations. Stability of gas/liquid interface under constant shear is clearly observable in Figure 8 which illustrates the prefect phase stability by surfactant and PECNP system.



Figure 8: Viscosity versus time for 90% CO₂ foam quality generated using 1:9, 2:8, 3:7 and 1:6 ratios of PECNP:Surfactant prepared in (a) 33.3kppm and (b) 66.7kppm brine. (Static Constant Shear Measurement)

Figure 9 reveals the rheological measurements in static shear sweep mode for variety of PECNP/surfactant enhanced scCO₂ foams in two different brine salinities.



Figure 9: Viscosity versus shear rate of 90% CO₂ foam quality systems prepared using 1:9, 2:8, 3:7 and 4:6 ratios of PECNP:Surfactant in (a) 33.3kppm and (b) 66.7kppm brine. (Static Shear Sweep Measurement)

Non-Newtonian flow behavior is observed for shear rate sweep of foaming mixtures. Decline in viscosity over shear rate is a shear thinning phenomenon that occurs for foam flow through formation fractures (Reidenbach et al. 1986). The same trend for time sweep governs the shear rate sweep. By preserving the viscosity over the shear rate, the ability to transport proppant through the fracture is improved for the fracturing fluid, therefore, for 33.3kpmm brine solution, the 1:9 ratio of PECNP:Surfactant exhibits higher viscosity over the linear shear thinning region (Figure 9a). The 1:9 ratio of PECNP:Surfactant offers the highest value of viscosity and flow consistency index in 33.3kppm solution (Figure 9a and Table 4), whereas, for 66.6kpmm brine solution, the 4:6 ratio of PECNP:Surfactant represents the maximum viscosity and flow consistency index (Figure 9b and Table 4). Flow consistency index is the highest for the scCO₂ foam generated by the PECNP-surfactant systems. It is evident that high salinity brine ionic species and surfactants present in the solution are aimed to help the stabilization of the interface in combination with variety of nanoparticle ratios. The 1wt% surfactant solution offers lower viscosity compared to PECNP:Surfactant systems proving the fact that addition of nanoparticles successfully enhances the rheological properties and electrostatic forces in the interfacial region.

33.3 kppm System	K (Pa s ⁿ)	n
Surfactant-scCO ₂	1184.3	0.402
PECNP:Surfactant-scCO ₂ (3:7)	1387.9	0.394
PECNP:Surfactant-scCO ₂ (2:8)	1261.6	0.407
PECNP:Surfactant-scCO ₂ (1:9)	2916.4	0.276
66.7 kppm System	K (Pa s ⁿ)	n
Surfactant-scCO ₂	1035.7	0.368
PECNP:Surfactant-scCO ₂ (4:6)	1683.1	0.380
PECNP:Surfactant-scCO ₂ (3:7)	1443	0.371
PECNP:Surfactant-scCO ₂ (2:8)	1163.9	0.405
PECNP:Surfactant-scCO ₂ (1:9)	1464.6	0.385

Table 4: Flow consistency index (K) and flow behavior index (n) for variety of PECNP/Surfactant scCO₂ foam systems

View Cell Measurements

Foam stability and texture of cellular structures were revealed by view cell measurements. Upon foam formation, homogenous and fine-textured scCO₂ bubbles in aqueous medium were generated (Figure 10a). The interaction of charged nanoparticles and surfactant with gas/phase lamella prevents the coalescence of bubble, bubble drainage and rupture, so the minimum bubble size with uniform distribution

was created in the aqueous medium. Upon oil introduction (Figure 10b), the generated foam using surfactant started to deteriorate in the presence of hydrocarbon molecules, while, the nanoparticlesurfactant system continues to stabilize the lamella. Fracture cleanup is directly related to foam breakage in the presence of hydrocarbons. When foam decays, the liquid is drawn to the lower end of view cell which leads to oil advance toward the aqueous phase (Figure 10c) and eventually the foam completely breaks, and oil/water phases separate out in the view cell (Figure 10d). The advantage of presented formulation is to form a very stable foam to carry and transport the proppants to the fracture, but it becomes unstable or it disappears during cleanup when exposes to the produced oil and hydrocarbons.



Figure 10: View cell measurements carried out to measure the foam stability with and without oil. (a) Foam isolation in the view cell (b) Introduction of the oil (c) Foam drainage in the presence of oil (d) Total foam disappearance and oil dominance

Figure 11a represents the foam stability for 1% surfactant solution in 33.3kppm brine and nanoparticle added to surfactant with 1:9 and 2:8, 3:7 ratios of PECNP:Surfactant. PECNP successfully increases the foam stability 33.3kppm brine solution. Upon addition of more portions of polyelectrolyte nanoparticles (2:8, 3:7 and 4:6), the lamella becomes unstable in a medium with less ionic strength, however, it still represents higher stability than surfactant generated lamella, verifying the magnifying effect of nanoparticle-surfactant electrostatic interactions. 9:1 proportion represents the maximum enhancement achievable by PECNP system in 33.3kppm brine. Mixture stability in the oil presence was evaluated in 33.3kppm brine solutions (Figure 11b). The PECNP/surfactant enhances lamella while it breaks upon meeting the oil. Addition of nanoparticles to the system helps to destabilize the lamella upon oil exposure, however, higher ratios of Surfactant/PECNP exhibit strong resistance to breakage with providing even more stability to surfactant solution in brine. The fast breakage of foam enhances the cleanup of the fracture medium.



Figure 11: (a) Foam stability measurements for variety of PECNP/surfactant mixtures in 33.3kppm brine solutions. (b) Foam stability measurements in presence of oil for variety of PECNP/surfactant mixtures in 33.3kppm brine solutions

Figure 12a illustrates the superimposed plots for 1% surfactant and different proportions of PECNP:Surfactant mixtures (1:9, 2:8, 3:7 and 4:6) dissolved in 66.7kppm brine. The obtained curves clearly verify the quick foam decay and bubble rupture for nanoparticle/surfactant systems with 1:9, 2:8, 3:7 proportions over time as oppose to baselines (1Wt% surfactant solutions). For lower ratios of PECNP, the nanoparticle addition doesn't add stability to the foaming mixture, rather it destabilizes further the gas/liquid mixture. In fact, the positively charged particles fail to form a stable ionic complex with surfactant micelles in the interface with provided proportion, therefore, the stability of foam mixture can be improved by using higher proportion of surfactant to nanoparticles (4:6 and 5:5). Strong electrostatic interactions are insured by higher amounts of PECNP as opposed to surfactant because in high salinity brine with concentrated medium of ions, formation of stabilized complexes require higher concentration to overcome the repulsive counter ion interactions. Figure 12b illustrates the oil stability for 1% surfactant and different proportions of PECNP/Surfactant mixtures (1:9, 2:8, 3:7 and 4:6) dissolved in 66.7kppm brine. The exact opposite trend to Figure 12a is observable in Figure 12b where instant foam decay and bubble rupture in oil presence is detected for nanoparticle/surfactant systems with 4:6 ratio as oppose to the baselines (1% surfactant solution). The surfactant solution and surfactant in PECNP:surfactant complexes break quickly as they meet hydrocarbon chain molecules. The oil stability of foam mixture is guaranteed by using lower proportions of surfactant to nanoparticle because the ionic interface with lower ionic strength resist more to deteriorations due to hydrocarbon attractive interactions.



Figure 12: (a) Foam stability measurements for variety of PECNP/surfactant mixtures in 66.7kppm brine solutions. (b) Foam stability measurements in presence of oil for variety of PECNP/surfactant mixtures in 66.7kppm brine solutions

Fluid Loss Measurements

Both 33.3kppm and 66.7kppm brine solutions represent a major decline in fluid loss coefficient (Figure 13 and Figure 14) compared to the baseline system. Total fluid loss volume (gas and liquid) and fluid loss coefficient (C_W) fall to 85% and 78% of their original value in 33.3kppm, respectively (Figure 13). Nanoparticles in form of PECNP effectively inhibit the leak-off by enhancing the formation resistance to flow using the 1:9 ratio of PECNP:Surfactant , thus, formation damage is less likely to happen and a longer fracture is more likely to propagate.



Figure 13: (a) Total fluid loss volume measurements for 1% surfactant and 1:9 ratio of PECNP: surfactant in 33.3 kppm brine solutions. (b) Fluid loss coefficient for 1% surfactant and 1:9 ratio of PECNP: surfactant in 33.3 kppm brine solutions

In the foaming mixtures made in 66.7 kppm brine solution, the total fluid loss is minimized using the 4:6 ratio of PECNP:Surfactant (Figure 14a). Fluid loss coefficient (C_W) shrinks compared to their original value, as an indicator for leak-off inhibition (Figure 14b). Formation resistance to flow is enhanced using both nanoparticle formulations and formation damage is less likely to happen by filter cake formation.



Figure 14: (a) Total fluid loss volume measurements for 1% surfactant and PECNP: surfactant 4:6 mixture in 66.7 kppm brine solutions. (b) Building wall coefficient for 1% surfactant and PECNP: surfactant 4:6 mixture in 66.7 kppm brine solutions

Conclusions

The PECNP - Surfactant system proposed in this work has successfully enhanced foam stability and improved its compatible with produced water. The presented mixture enhances the foam fracturing properties and cleanup. The stability of foaming mixture with air was improved by addition of variety of PECNP to surfactant ratios as a primary evaluation of compatibility. The zeta potential for presented PECNP systems increased with salinity and the positive charge of nanoparticles helped to electrostatically stabilize the surfactant. The perfect $scCO_2$ compatibility of surfactant and PECNP with varying brine concentrations was determined with interfacial tension analysis where surface tension reduction of up to 74% was recorded for 1:9 ratio of PECNP:Surfactant in 33.3 kppm brine solution and up to 93% decline in IFT was detected for 66.7 kppm brine solution using 6:4 ratio of PECNP:Surfactant. Improvement in viscosity, flow consistency index and flow behavior index for different PECNP-surfactant ratios were detected for both salinities. The flow consistency index observed in the shear thinning region was increased from 1184.3 to 2916.4 Pa sⁿ in 33.3 kppm and from 1035.7 to 1683.1 Pa sⁿ in 66,7 kppm brine solution. Achieving higher viscosity indicates a better ability to proppant transport, release and suspension compared to surfactant generated scCO₂ foam. The view cell results revealed a high stability and longevity of scCO₂ foam generated employing various proportions of surfactant to nanoparticle as oppose to foam systems generated by surfactant itself. The presented scCO2 generated foam can preserve the foam cellular structure in the absence of crude oil for both 33.3 kppm and 66.7 kppm brine concentrations, while it loses the stability for PECNP:Surfactant enhanced foams when it meets the oil. The nanoparticle systems with PECNP:Surfactant ratios of 1:9 and 4:6 represent the highest foam stability in the absence as well as instability in the presence of oil in 33.3kppm and 66.7kppm brine concentrations. Fluid loss properties and cleanup of injected fluid were enhanced by addition of PECNP-Surfactant nanoparticles prepared in produced water. Total fluid loss (gas and liquid) and fluid loss coefficient (Cw) declined to 85% and 78% of their original value, respectively, when prepared in 33.3kppm brine and 64% and 35%, respectively, when prepared in 66.7kppm brine, when nanoparticles in the form of PECNP are added to surfactant solutions as an indication of better control of formation damage.

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Nomenclature

- μ_{eff} : Effective viscosity, cP
- K: Flow consistency index
- n: Flow behavior index
- γ : Shear rate, 1/s
- τ : Shear stress

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