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Ca-DTPMP nanoparticles-based nanofluids for the inhibition and remediation of formation damage due to $CaCO_3$ scaling in tight gas-condensate reservoirs

Maribel Franco-Aguirre[a], Richard D. Zabala[b], Sergio H. Lopera[c], Camilo A. Franco[a,*], Farid B. Cortés[a,**]

[a] Grupo de Investigación en Fenómenos de Superficie – Michael Polanyi, Facultad de Minas, Universidad Nacional de Colombia Sede Medellín, Kra 80 No. 65–223, Medellín, Colombia

[b] Gerencia de Desarrollo de Yacimientos, Vicepresidencia Técnica de Desarrollo, Ecopetrol S.A, Cra 7 # 32-42, Piso 15, Edificio San Martin, Bogotá, Colombia

[c] Grupo de Investigación en Yacimientos de Hidrocarburos, Facultad de Minas, Universidad Nacional de Colombia Sede Medellín, Kra 80 No. 65–223, Medellín, Colombia

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ABSTRACT

The oil productivity of tight gas-condensate reservoirs can be affected by the precipitation/deposition of inorganic scales such calcium carbonate ($CaCO_3$), which leads to a reduction mainly in permeability and porosity of the porous media. Therefore, the main objective of this study is to develop for the first time a nanofluid based on the interaction between active nanoparticles such as Ca-diethylenetriamine pentamethylene phosphonic (Ca-DTPMP) and remaining synthesis fluid (RSF) obtained from the synthesis process, to simultaneously inhibit and remove the formation damage due to the precipitation/deposition of $CaCO_3$ scales. The synthesis of the Ca-DTPMP nanoparticles was performed varying the phosphonate concentration between 0.01 and 0.5 M. The obtained nanoparticles were characterized through N_2 physisorption at −196 °C for obtaining the surface area (S_{BET}), field emission scanning electron microscopy (FESEM), and dynamic light scattering (DLS) measurements. The mean nanoparticles size of the obtained materials ranged between 36 and 69 nm and was lower for the nanoparticles synthesized with a lower concentration of DTPMP. Nanofluids containing the synthesized nanoparticles of Ca-DTPMP were prepared with RSF solutions in deionized water as a carrier fluid for different Ca-DTPMP/RSF ratios of 10, 50, 200 and 500. The ability of the nanoparticles and nanofluids to inhibit the $CaCO_3$ scaling was evaluated in batch-mode experiments at 70 °C by measuring changes in the calcium ion (Ca^{2+}) concentration in the solution. The nanofluid with better performance was that prepared with 50 mg/L of Ca-DTPMP/0.3 nanoparticles and a Ca-DTPMP/RSF ratio of 10, with an inhibition efficiency of 67%. Further, coreflooding tests were carried out using the nanofluid with better performance from the batch – mode experiments. Displacement tests were conducted under tight gas-condensate reservoir conditions at a temperature of 110 °C (230 °F) and confining and pore pressures of 34.47 MPa (5000 Psi) and 6.89 MPa (1000 Psi), respectively. Inhibition and remediation of $CaCO_3$ scaling were evaluated. The nanofluid was soaked in the porous media for 8 h. Based on the results of the relative permeability and oil recovery curves, it is possible to conclude that the synthesized nanofluid promotes the inhibition and removal of the formation damage due to $CaCO_3$ inorganic scales. The nanofluid injection leads to an increase of the oil permeability of 57% in comparison with the base system, suggesting that the nanofluid acts as inhibitor agent, as remediation treatment, and as stimulation product of oil wells. Also, the treatment showed a perdurability of more than 60 pore volumes and increasing of oil recovery of 4 and 24% regarding the base and the damaged systems, respectively.

1. Introduction

The productivity/recovery of oil and gas reservoirs is commonly affected by different types of formation damage, which reduces the porous media permeability and leads to inefficient and uneconomic production operations (Bennion, 2002). In tight reservoirs, the formation damage is more harmful due to the low permeability and reduced pore space of the system (Elkewidy, 2013). The most common types of

* Corresponding author.
** Corresponding author.
E-mail addresses: caafrancoar@unal.edu.co (C.A. Franco), fbcortes@unal.edu.co (F.B. Cortés).

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formation damage in tight reservoirs include induced damage, relative permeability reduction, scaling of inorganic compounds, fines migration, asphaltene precipitation and deposition, and geomechanical damage (Qutob and Byrne, 2015; Franco et al., 2017). Particularly, in the most important tight gas-condensate reservoir in Colombia, the Cuapiagua field, the precipitation/deposition of inorganic scale is one of the main sources of formation damage (MacAdam and Parsons, 2004), affecting both producer and injector wells (Zhang et al., 2001). Mainly, calcium carbonate ($CaCO_3$) scales represent a severe problem due to its precipitation in different points and stages of the production system (MacAdam and Parsons, 2004; Zhang et al., 2001; Crabtree et al., 1999; Oddo and Tomson, 1994; Chen et al., 2005), mostly related to the mixture of two incompatible waters, or due to the ions that exceed their solubilities at reservoir conditions (MacAdam and Parsons, 2004; He et al., 1999; Khormali et al., 2014; Boak, 2013; Merdhah and Yassin, 2007). Accordingly, essential variables that influence the scale precipitation and inhibition efficiencies have been identified and include water chemical composition, $CaCO_3$ saturation index (SI), bulk temperature, pH, scale quality, as well as type and amount of treatment (MacAdam and Parsons, 2004; Kiaei and Haghtalab, 2014; Xyla et al., 1992). The CaCO3 scales have been well studied separately for each one of the phenomena (inhibition and remediation) since it represents a significant economic impact due to the production losses (Zhou, 2002). In this way, two types of chemical treatments based on polymeric and non-polymeric compounds have been mainly used for the inhibition of $CaCO_3$ scaling. These types of inhibitors can be divided into two groups by their mechanism of action: *i*) threshold effect inhibitors, which inhibit the formation of $CaCO_3$ at very low concentrations and are also known as sub-stoichiometric inhibitors (Khormali et al., 2014), and *ii*) chelating inhibitors, substances that form soluble complexes with Ca^{2+} cations, preventing the precipitation of these anions (Khormali et al., 2014). Threshold effect inhibitors work by distorting the crystal lattice and prevent its growth (Zhou, 2002). It is worth to mention that the most important technical aspects to consider for the inhibitor selection are the adsorption phenomena onto porous media (Shamsijazeyi et al., 2013), the lifetime of the treatment (Zabala et al., 2014), and the treated area according to the treatment injectivity (Franco et al., 2017). Accordingly, phosphonates have been proposed as threshold effect inhibitors to delay and to inhibit scale formation of $CaCO_3$ (Khormali et al., 2014; Abdel-Aal and Sawada, 2003; Amjad, 1997; Chen et al., 2011; Xia and Chen, 2015; Zhang et al., 2010). Some authors have evaluated the adsorption phenomena of these treatments on the active sites of the rock and thus how this affects the crystals growth (MacAdam and Parsons, 2004; Boak, 2013; Abdel-Aal and Sawada, 2003; Amjad, 1997; Nowack, 2003). Also, some authors have assessed the performance of phosphonate compounds at a high concentration of Ca^{2+} (Kan et al., 1994; Rahman et al., 2005).

However, when the formation damage due to inorganic scales is already found in the reservoir, different techniques are used such as milling or water jetting (Crabtree et al., 1999), and chemical dissolution (Nasr-El-Din et al., 2000). Milling and water jetting are costly and are often not recommended in tight reservoirs as additional formation damage can be caused. In the case of chemical dissolution, the treatment is mainly performed with acids such as ethylenediaminetetraacetic acid (EDTA) and hydrochloric acid (HCl) due to the high carbonate solubility in these compounds (Crabtree et al., 1999; Martell and Calvin, 1952). Nevertheless, these treatments are costly due to the scale reprecipitation.

Hence, today the oil and gas industry has the challenge of improving the performance of the treatment used for each one of the process of inhibition as well as remediation of inorganic scales formation damage (Crabtree et al., 1999). Recently, the nanotechnology has been explored in this field due to their exceptional properties and successful field trials for formation damage inhibition (Franco et al., 2017). For example, the nanoparticles/nanofluids can reach inaccessible reservoir zones due to their nanoscale size. Also, nanoparticles can be fixed on the porous media surface during the soaking period of the treatment, favoring the nanoparticles – rock interaction due to the high surface energy of the nanomaterial (Franco et al., 2017; Zabala et al., 2014, 2016). Posteriorly, the reservoir can release the nanoparticles to the production water at the minimum concentration required for inhibiting the precipitation of $CaCO_3$ and thus prolong the lifetime of the treatment (Zabala et al., 2014, 2016). In this order, few researchers have focused their attention on the use of nanoparticles and nanofluids for the inhibition of $CaCO_3$ scaling (Kiaei and Haghtalab, 2014; Zhang et al., 2010; Shen et al., 2008; Haghtalab and Kiaei, 2012), and it has been achieved mainly using nanoparticles synthesized from phosphonic acid as the active compound. Shen et al. (2008) synthesized particles of Ca-diethylenetriamine penta methylene phosphonic acid (Ca-DTPMP) with submicron size and studied the transport and their deposition on porous matrices of calcite and sandstone. Also, Zhang et al. (2010) developed a route for the synthesis of metal nanoparticles of phosphonate assisted by surfactants. In both Shen et al. (2008) and Zhang et al. (2010) studies, it was found that the employed nanoparticles have excellent transport, diffusion, retention and releasing properties in porous media, and therefore the inhibition can be achieved over long distances from the injection point (Zhang et al., 2010; Shen et al., 2008). Haghtalab and Kiaei (2012) studied the influence of different factors such as pH, temperature, sonication, surfactant concentration, and calcium phosphonate concentration in the morphology and particle size distribution of Ca-DTPMP nanoparticles. Kiaei and Haghtalab (2014) tested the efficiency of these particles in the inhibition and delaying of crystal growth of the $CaCO_3$ at 25 °C. They found that at this temperature, the efficiency increased as the concentration of inhibitor increased and as the particle size decreased. Although some researchers have reported the study of inhibition of $CaCO_3$ crystals growth using metal particles of phosphonate, as reported above, only a few studies have evaluated the formation damage by inorganic scales through core flooding tests. However, there are no studies including core-flooding evaluation in tight sandstone rocks at reservoir conditions of pore pressure, overburden pressure, and temperature. Displacement tests under reservoir conditions allow to obtain of the absolute and relative permeabilities of oil and water, as well as the oil recovery after treatment injection, which are essential factors for the scale-up of the technology and thus guarantee the success of this type of technology for tight gas-condensate reservoirs. Also, it is worth to mention that there are no reports in the specialized literature including the simultaneous remediation and inhibition of formation damage due to inorganic scales using nanotechnology.

Hence, the primary objective of this study is to synthesize and evaluate Ca-DTPMP nanoparticles-based nanofluids that allow both inhibition and remediation of the formation damage due to $CaCO_3$ scaling in tight reservoirs. The nanoparticles were synthesized by varying the concentration of phosphonate. Also, to improve the performance for the inhibition of crystal growth of $CaCO_3$, nanofluids were prepared using the remaining fluid from the synthesis process as part of the carrier fluid. Through batch-mode experiments of fluid-fluid interaction and coreflooding tests, the effect of nanofluids on the inhibition and remediation of formation damage in tight rock was investigated. The coreflooding test includes the construction of relative permeability and oil recovery curves at typical reservoir conditions of tight gas-condensate reservoirs. It is expected that this study opens a broader landscape about the use of nanotechnology in the oil and gas industry in the inhibition and remediation of formation damage as an efficient and cost-effective technology.

2. Experimental section

2.1. Materials and chemicals

Diethylenetriamine penta-methylene phosphonic acid (DTPMP, 50 wt%, Sigma Aldrich, USA), *n*-hexadecyl-trimethyl ammonium