Oil recovery with nickel nanoparticles and weak acid

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Abstract

In this work, nickel nanoparticles and weak acid were evaluated for enhanced oil recovery. Medium crude oil from northeast part of Mexico was selected for the experiments as well as siliciclastic rock from the same region of Mexico. Firstly, contact angles with brine and oil over rock surface were measured. The rock was then impregnated with nickel nanofluid for 24 hours and dried. Contact angles with brine and oil over rock surface were again measured and compared with previous tests. The results show an improvement towards water-wetting after the rock was submerged in nanofluid. Enhanced oil recovery was carried out in a Co-reFlood system. Two cores with similar properties were used for the same test. The cores were first saturated with brine and then with oil. Recovery with brine was achieved and after no more oil was flowing out the core, nanofluid was injected. Extra recovery of oil was ob-tained with nanofluid injection. After no more oil was flowing out the core, weak acid was injected, and more oil could be recovered, achieving an overall recovery factor of 74%.

Keywords: Enhanced oil recovery, nanoparticles, weak acid, permeability curves.

Recuperación de petróleo con nanopartículas de níquel y ácido débil

Resumen

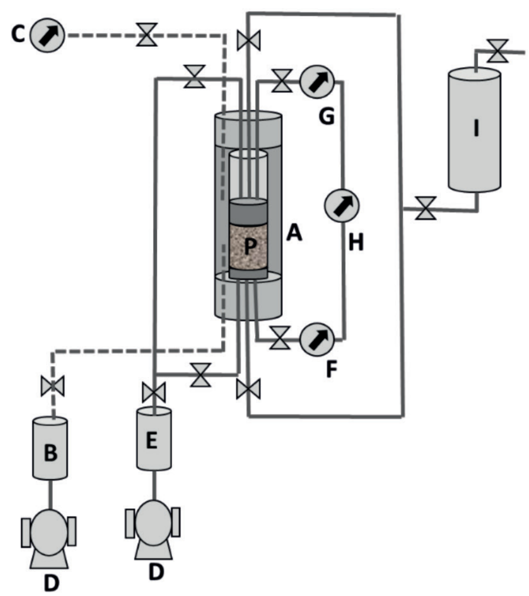
En este trabajo, se evaluaron nanopartículas de níquel y ácido débil en la recuperación mejo-rada de petróleo. Para los experimentos se seleccionó petróleo crudo medio de la parte noreste de México, así como roca siliciclástica de la misma región de México. En primer lugar, se midieron los ángulos de contacto con salmuera y petróleo sobre la superficie de la roca. A continuación, la roca se impregnó con nanofluido de níquel durante 24 horas y se dejó secar. Se volvieron a medir los ángulos de contacto con salmuera y aceite sobre la superficie de la roca y se compararon con las pruebas anteriores. Los resultados muestran una mejora en la humectabilidad de la roca con preferencia por el agua después de que la roca se sumergió en nanofluidos. La recuperación mejorada de petróleo se llevó a cabo en un sistema CoreFlood. Se utilizaron dos núcleos con propiedades similares para la misma prueba. Los núcleos se saturaron primero con salmuera y luego con aceite. Se logró la recuperación con salmuera y después de que no fluyera más aceite del núcleo, se inyectó el nanofluido. Se obtuvo una recuperación extra de aceite con inyección de nanofluido. Después de que no saliera más aceite del núcleo, se inyectó ácido débil y se pudo recuperar más aceite; logrando un factor de recuperación global del 74%.

Palabras clave: Recuperación mejorada de petróleo, nanopartículas, ácido débil, curvas de permeabilidad.

Introduction

Nanotechnology in the petroleum industry has gained enormous interest during the recent years, which is reflected in the amount of literature available. Nanoparticles for enhanced oil recovery (EOR) purposes seem gradually to become the cutting-edge technology (Engeset 2012, Cheraghian and Hendraningrat 2016). Kanj et al identified the usable size of nanopar-ticles in reservoir rocks through nanofluid core flooding experiments, using hydrophilic/ hy-drophobic synthesized nanoparticles. (Kanj, Funk, and Al-Yousif 2009) Nanofluids are col-loidal suspensions of nanoparticles in a base fluid, which is commonly water or organic liq-uids.(Ahmadi et al. 2016) Adding nanoparticles to fluids may significantly benefit enhanced oil recovery and improve well drilling, such as changing the properties of the fluid, wettabil-ity alteration of rocks, advanced drag reduction, strengthening sand consolidation, reducing the interfacial tension and increasing the mobility of the capillary-trapped oil (Cheraghian and Hendraningrat 2016, Cheraghian et al. 2014). Therefore, in some studies, the role of na-noparticles in EOR operations has been reported (Esfandyari Bayat et al. 2014, Ahmadi et al. 2016). If the nanoparticles do not aggregate to a larger size, they have the ability to flow through a pore size (typically measured in microns). Hence, the stability of the nanofluid becomes a critical parameter. (Hendraningrat and Torsæter 2015). The actual oil reservoirs can be water, intermediate or oil - wet. The initial rock wettability will affect oil recovery after waterflooding and plays a vital role in oil production. (Morrow, Lim, and Ward 1986). Emulsion flooding is a potential chemical enhanced oil recovery process for production of additional oil after water flooding. (Sharma et al. 2015) Typically, emulsion types ((Binks 2002, Bon and Colver 2007, Leal-Calderon and Schmitt 2008, Ershadi et al. 2015) are dependent on the hydrophobic and hydrophilic properties of the particles used, as the hydro-phobic particles are more efficient for stabilizing water-in-oil emulsions, while hydrophilic particles performs better with oil-in-water emulsions. Since nanoparticles can be partially wettable in oil and water phases, the particles are considered suitable for emulsification ow-ing to its favorable adsorption behavior at the oil-water interface. Pickering emulsions ((Pickering 1907, Yang et al. 2017, Binks and Lumsdon 2000, He and Yu 2007, Larson-Smith and Pozzo 2012) use solid nanoparticle alone as stabilizers instead of organic surfac-tants. They are a class of fluid that even shows much higher performance and stability than microemulsions. They accumulate at the interface between two immiscible liquids (oil and water phase) and stabilizes droplets against coalescence, thus potential fluids for EOR appli-cations. (Nwidee 2017, Aveyard, Binks, and Clint 2003, Binks 2002, Binks and Horozov 2006, Chevalier and Bolzinger 2013, Sharma et al. 2015) A comparison of Pickering emul-sions stabilized by particles and classical emulsions stabilized by surfactants (Ramsden 1904, Melle, Lask, and Fuller 2005) shows that Pickering emulsions displays better stability over other emulsions.

In this paper, the feasibility of nickel nanoparticles application as a chemical agent for EOR was investigated. Moreover, studies of permeability improvement with weak acid were car-ried out. As an acid flows through porous rock, it etches the rock and so increases the per-meability. This propagating reaction front suffers an instability, rather like the viscous fin-gering instability, in which the acid prefers to follow high-permeability channels which it has already etched.(Hinch and Bhatt 2006) When carbonate hydrocarbon bearing formations are acidized, a few dominating channels in the matrix are created and the majority of the treat-ment acid will flow along these channels. (Chang, Qu, and Frenier 2001).



A. CoreHolder
B. H2O tank for overburden pressure
C. Overburden pressure transducer
D. Positive displacement pump
E. High pressure stainless steel cylinder
F. Core inlet pressure transducer
G. Core outlet transducer
H. Differential pressure ttransducer
I. Acoustic Fluid Separator
P. Sample Plug

Figure 1. Core-flooding displacement experimental setup.

Experimental

Equipment

Brookfield DV2T Viscometer and Thermosel cell were used to measure the viscosity of oil at specific temperature. AP-608 Automated porosimeter-permeameter from Coretest Systems was used to measure porosity and permeability of plugs. Contact angles were measured using a Theta Lite Goniometer and OneAttension software. CFS-830 Core Flood System from Coretest Systems was used for displacement experiments, **Figure 1**.

Fluid's properties

Medium crude oil from northeast part of Mexico was selected for the experiments. Its density, API gravity and viscosity is shown in **Table 1**.

Fluid	Density, g/cm^3	API, º	Viscosity, cP
Medium oil	0.8	25.9	99

Table 1. Properties of fluids.

Nickel nanoparticles (synthesized at UNAM) were evaluated for enhanced oil recovery. Nanofluid consisting in a solution of 2500 ppm nickel nanoparticles in 36,000 ppm brine was used to recover medium oil from porous media. Weak acid (10%) was diluted in brine (36,000 ppm) and evaluated for enhanced oil recovery but also for increasing the permeability of the rock.

Rock properties

Siliciclastic rock cores were characterized in terms of porosity and permeability. Results for two rock cores are shown in **Table 2**.

	X1	X2
Length (cm)	5.030	5.583
Diameter (cm)	3.772	3.818
Weight (g)	133.987	154.081
Porosity (%)	9.333	7.419
Pore volume (cm^3)	5.246	4.742
Permeability (mD)	0.6565	0.568

Table 2. Properties of siliciclastic rock cores.

Coreflooding tests

Enhanced oil recovery was carried out in a CoreFlood system, **Figure 1**. All flow lines and core were evacuated up to a stable negative pressure. The CoreFlood system was placed in an oven and temperature was set to 50°C, such as reservoir. At this temperature, the viscosity of oil is 30 cP. Absolute and effective permeabilities of fluids were calculated with Darcy's equation:

$$\boldsymbol{Q = \frac{k\,A}{\mu\,L}\Delta P} \qquad \text{Equation 1}$$

where Q is the fluid's flow (m^3/s), L the sample's length (m), k is the permeability coefficient (m^2), A the sample's transversal area (m^2), μ the fluid's viscosity (kg/m s) and ΔP the differential pressure (kg/m s2).(Klinkenberg 1941, Darcy 1856).

The core was first saturated with brine and absolute permeability was obtained. Core was then saturated with medium oil, displacing brine, and obtaining irreducible water condition (*Swi*). Relative permeability to oil was calculated as:

$$Kro@Swi = \frac{Ko}{Kabs} \qquad \text{Equation 2}$$

Where *Ko* is the effective permeability of oil. Brine was then injected to displace oil up to a residual oil saturation (*Sor*). Relative permeability to brine was calculated as:

$$Krw@Sor = \frac{Kw}{Kabs} \qquad \text{Equation 3}$$

Where Kw is the effective permeability of brine.

Corey method was utilized to construct permeability curves plot. The equations for *Kro* and *Krw* are:

$$Kro = (Kro@Swi)\left(\frac{1-Sw-Sor}{1-Sor-Swi}\right)^{no}$$ Equation 4

$$Krw = (Krw@Sor)\left(\frac{Sw-Swi}{1-Sor-Swi}\right)^{nw}$$ Equation 5

Where *no* and *nw* are Corey exponents for relative permeability which depend on humecta-bility.

Results and discussion

Contact angles

Two slices were cut from core X1 and two slices from core X2. First two slices from each core SX1 and SX2 were used to measure contact angles with brine and with oil on their dry surface. The other two slices from each rock SXN1 and SXN2 were submerged for 24 hours in nickel nanofluid and allowed to dry. After this time, contact angles with brine and with oil on their dry surface were also measured. The results are shown in **Table 3**.

Contact Angle					
	Brine	Oil		**Brine**	**Oil**
SX1	36.67°	7.05°	**SXN1**	11.41°	13.60°
SX2	26.21°	11.56°	**SXN2**	8.39°	13.26°

Table 3. Average contact angle of brine and oil on the surface of dried rock slices (SX) and on the surface of rock slices impregnated with Nanofluid of Nickel (SXN).

It can be observed that both plugs (X1 and X2) are more related to oil than to water because contact angles for oil are lower than for brine. However, after impregnating the slices with nanofluid, contact angle with brine decreased more than a half. By the other side, the contact angle with oil increased after impregnating the slices with nanofluid. So, an improvement towards water-wetting was obtained when adding nanoparticles. This result is favorable for EOR, because oil is the fluid that needs to be removed from rock. As the rock is preferably oil wet, *no* and *nw* from Equations 4 and 5 were used in this work equal to 5 and 3 respec-tively.

Core X1 was used for coreflooding tests. Core X2 was used for repeatability. The clean core was placed into the coreholder, evacuated, and then saturated with brine. Absolute permea-bility was obtained. Medium oil was then injected, and after no more water was flowing outside the core, water irreducible saturation, *Swi*, was calculated as well as oil relative per-meability. Brine was used to recover oil until no more oil was flowing outside the core, re-sidual oil saturation, *Sor,* was obtained as well as brine relative permeability. All the param-eters mentioned above are shown in **Table 4**. Average oil recovery achieved with brine was 31.5%.

Property	X1	X2
Absolut permeability, mD	0.039	0.043
Swi	0.180	0.199
Sor	0.690	0.678
Krw@Sor	0.257	0.445
Kro@Swi	0.176	0.574
Oil Recovery, %	31	32

Table 4. Oil recovery with Brine @50°C.

Permeability curves for both tests are presented in **Figure 2**. As observed, there is a rock preference for oil. The intersection of curves is around 25% water saturation.

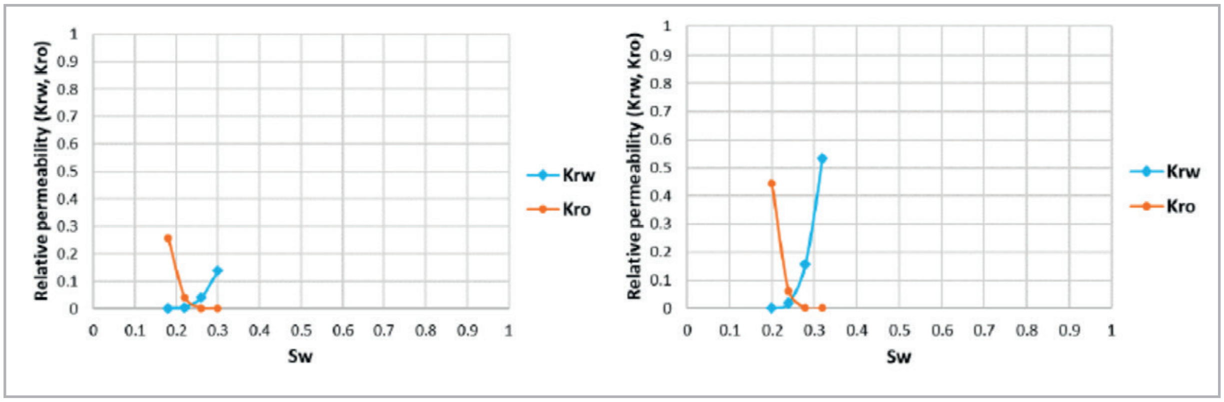


Figure 2. Relative permeability curves obtained with Corey method for EOR with brine@50°C.
Core X1 (left) and Core X2 (right).

The tests continued in series because of shortage of rock samples. After brine recovery, nanofluid consisting in 2500 ppm nickel nanoparticles in 36,000 ppm brine was injected to the core. The oil recovery with nanofluid was added to the previous recovery with brine. Results are shown in **Table 5**. Average of total oil recovery achieved with brine and nanofluid was 58%.

Property	X1	X2
Absolut permeability, mD	0.039	0.043
Swi	0.180	0.199
Sor	0.440	0.395
Krw@Sor	0.514	0.585
Kro@Swi	0.176	0.574
Oil Recovery, %	56	60

Table 5. Oil recovery with nanofluid (2500 ppm nickel nanoparticles in 36,000 ppm brine) after brine recovery, @50ºC.

Permeability curves for the last tests are presented in **Figure 3**. It can be noted that intersection between curves was displaced to the right (more than 35% water saturation) when injecting nanofluid, being favorable for oil recovery. It indicates that the rock can change its wettability.

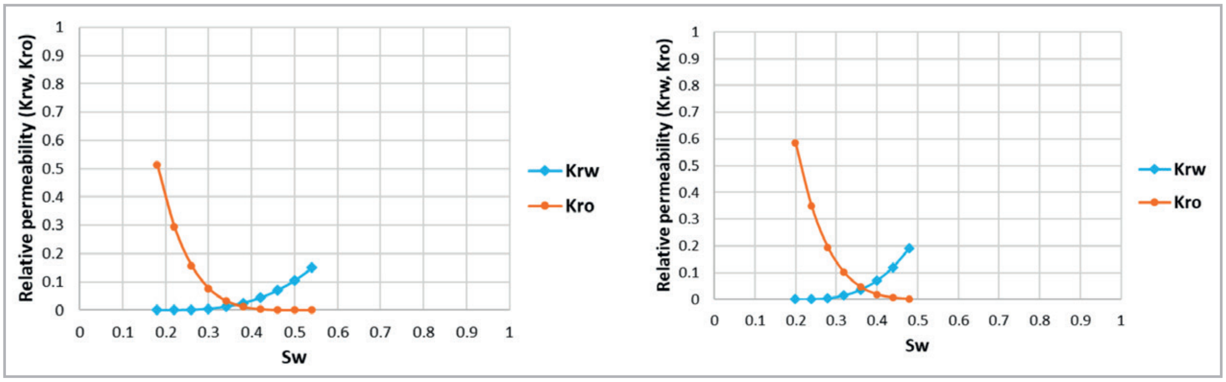


Figure 3. Relative permeability curves obtained with Corey method for EOR with nanofluid (2500 ppm nickel nanoparticles in 36,000 ppm brine), after brine recovery, @50°C. Core X1 (left) and Core X2 (right).

After no more oil was recovered with nanofluid, a 10% solution of weak acid diluted in brine was injected to the core, obtaining an average of total oil recovery of 74%. Results can be observed in **Table 6** and **Figure 4**.

Property	X1	X2
Absolut permeability, mD	0.039	0.043
Swi	0.180	0.199
Sor	0.228	0.285
Krw@Sor	0.771	0.656
Kro@Swi	0.176	0.574
Oil Recovery, %	77	71

Table 6. Oil recovery with weak acid (10% diluted in 36,000 ppm brine) after nanofluid and brine recovery, @50°C.

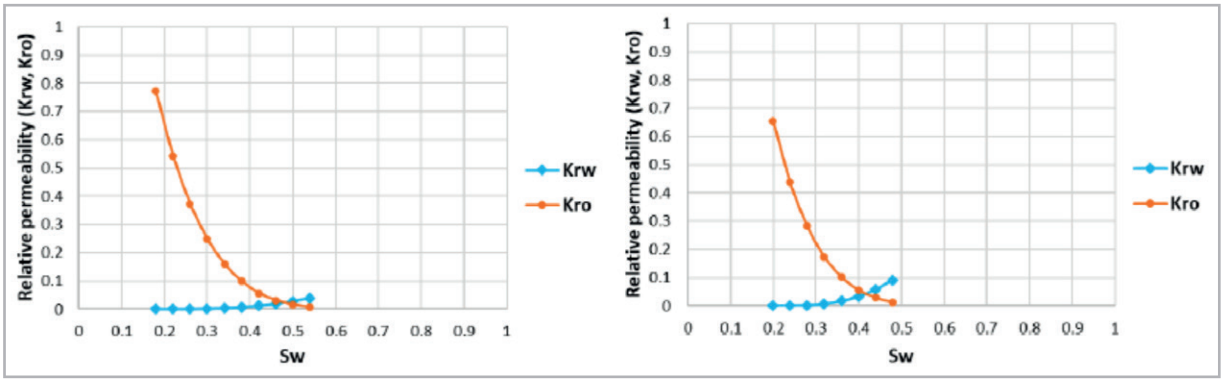


Figure 4. Relative permeability curves obtained with Corey method for EOR with weak acid (10% diluted in 36,000 ppm brine) after nanofluid and brine recovery, @50°C. Core X1 (left) and Core X2 (right).

Intersection between curves was displaced more to the right (between 40 and 50% water saturation) when injecting weak acid. It indicates that the rock is changing its wettability again, but there is an extra factor. Weak acid induces damage in permeability. That is a reason why the recovery factor increased even more after nanofluid injection.

Conclusions

In this work, two similar tests were carried out for recovery of medium oil from siliciclastic rock. Brine injection recovered 31.5% oil, which is in the range of results reported for oil recovery with brine. (Yildiz, Valat, and Morrow 1999, Bagci, Kok, and Turksoy 2001). After brine, nanofluid consisting in nickel nanoparticles diluted in brine was injected, obtaining an accumulated recovery factor of 58%, which corresponds to 26% more than with only brine. This percentage is in the range of other papers working with nanoparticles. (Onyekonwu and Ogolo 2010, Sun et al. 2017) When adding weak acid, the recovery factor increased even more, up to 74% because of permeability damage. There were no results found in literature for enhanced oil recovery with weak acid.

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Semblanza de la autora

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Más de 10 años de experiencia en la caracterización fisico-química, reológica, PVT composicional, destilación simulada y SARA de aceites pesados y extra-pesados. Así como el modelamiento de estas propiedades y simulación con química computacional. Laborado en 4 proyectos de CONACYT SENER Hidrocarburos y arrancado dos laboratorios de hidrocarburos (IIM-UNAM e IPICYT).

Experiencia en análisis petrofísicos y recuperación mejorada del Petróleo en CoreFlood por métodos térmicos y químicos a través de roca siliciclástica, arenisca y carbonatada. Referente a los métodos químicos, enfocada en la recuperación mejorada de petróleo con nanopartículas de nickel y sílica.