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CLAY-SAND WETTABILITY EVALUATION FOR HEAVY CRUDE OIL MOBILITY

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Abstract. In this work, the effect of distilled water, a biodiesel viscosity reducer, and a commercial nonionic surfactant on the apparent permeability of clay-sand cores through the analysis of contact angle, linear swelling, and porous media fluid flow for a northern Mexico crude oil was evaluated. The results showed that the clay content influences the contact angle values having a lower wettability effect in the rocky medium. The addition of biodiesel produces a fluid movement similar to the addition of distilled water. Biodiesel-based flow enhancer not only reduces the crude oil viscosity but also improves the flowability through porous media. However, this behavior is only valid if the soil is not saturated with salty water.

Keywords: clay-sand wettability, fluid flow through porous media, contact angle, apparent permeability modification.

1. Introduction

Crude oil and crude oil derivatives still are essential factors in the global economy. In Mexico, petroleum production is one of the most significant activities for national development.[1,2] In the last decades, more than 50 % of crude oil of Mexican production corresponded to heavy and extra-heavy types,[3] which generate operational problems such as asphaltenes deposition on pipeline walls and high pumping power, increasing the probability of failure in the extraction systems.[4] Extracting these kinds of oils requires more energy, mainly due to their high viscosity and the physicochemical interactions between the fluid components and the rock reservoir.[5,6] Thus, the modification of viscosity through surfactants and bioreducers, and the change of fluid-rock interactions, has been a valuable option to improve production.[7-10]

Viscosity bio-reducers are dispersing agents that do not modify the oil fractions at different temperatures but interact with the components at the molecular level, avoiding particle aggregation to reduce the pressure drop. These chemicals can be obtained from vegetal oils[11-13] or extracted from plants over fermentation processes.[14-16] Another method to improve displacement efficiency is using a surfactant or alkaline solution, with concentrations up to 5 %, that changes the interfacial tension and generally produces oil-in-water emulsions that are less viscous fluids.[17-19]

However, the fluid-rock interactions that are present in the extraction processes have to be considered. Such interactions depend on the rock composition and the fluid ionic species that determine the oil/water surface wettability.[20-22] Wettability is an essential physico-chemical parameter that governs subsurface multiphase flow behavior and the distribution of fluids, directly affecting oil recovery.[23] The contact angle is a common characteristic of materials' wettability. It is sensitive not only to the fluid type but also to the solid composition, porosity, and surface rugosity.[23-26]

In this work, two chemicals applied in oil production systems on porous-media wettability are studied. These materials have been tested to reduce pressure drop in pipelines by decreasing the oil viscosity.[27-29] This work aims to contrast the theoretical results reported in previous work[11] and the experimental results concerning the efficiency of the materials to improve the fluid flow through porous media.

2. Experimental

For this research, crude oil from northern Mexico (viscosity at 298 K is 35000 mPa·s, API at 288 K is 10.2,

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SARA fractions (%) 39.6, 10.1, 23.5, and 26[11,27,30] was used. The solid phase was obtained from a mixture of sand (#20 mesh) and clay (5, 10, and 15 %) homogenized with deionized water (proportion 1:10 for clay content), compacted at 15000 psi (1 min). The probes obtained were 12.5 cm^3 cylinders representing the soil type of the reservoir and seal rocks of the Tampico-Misantla basin.[31,32] An outcrop sample from El Abra (San Luis Potosi, Mexico) was taken as a representative probe of the source rock for the same area, and this sample was employed only to compare contact angle results versus clay-sand samples. Probes were analyzed for Energy-Dispersive X-Ray Fluorescence (ED-XRF, P-Metrix, Xenemetrix Ltd.) at 50 kV/10W/400μA with Rh anode and Ti filter (300 counts per minute) to determine the main components of the soil materials. Triaxial tests (TRIAX Triaxial Press, Wykeham Farrance, model 28-WF4001) were performed to determine the compressive strength of the clay-sand probes and assess the maximum pressure of the material before the collapse. This test was developed under unconsolidated undrained conditions (UU), according to ASTM D2850.

The fluids employed were seawater (Gulf of Mexico coast, Ciudad Madero, Tamaulipas), distilled water (Sigma-Aldrich, conductivity at 25 °C ≤ 2 μohm/cm), biodiesel-based viscosity reducer from soybean, and lauryl glucoside derivative non-ionic surfactant. Six fluids were established for the experimental development: seawater (SW), seawater-crude oil (SW-CO, 1:1), distilled water-crude oil (DW-CO, 1:1), seawater-crude oil (1:1) with viscosity reducer at 5000 ppm (CO-B), and seawater-crude oil (1:1) with nonionic surfactant at 5000 ppm (CO-S). Crude oil alone (CO) was used as an experimental reference.

The rheological behavior of the mixtures was determined through a RheolabQC Anton Paar rheometer for different temperatures (318–333 K) and shear rates (160–320 L/s). Linear swelling tests were made (dynamic linear swell meter, OFITE) to determine the volume changes in the soil at 318 K using 60 mL of each mixture after an imbibition period (24 h). Contact angle determination was performed at 318 K with a digital microscope (Jiusion 40 to 1000x Magnification Endoscope) placed perpendicularly to the probe surface. All probes were lapped to reduce surface roughness, and the experiment was carried out for both dry and imbibed surfaces (seawater, 24 h) with drops standardized with a microsyringe, taking 40 μL of each fluid. Apparent permeability tests were performed with the system shown in Fig. 1, which consisted of a compressor, a paddle mixer, and a 0.0001–0.001 m^3 core holder. The core (0.0001 m^3) was flooded vertically and aged until saturation for 72 h at 318 K. The liquid effluent was collected and measured as the displaced fluid volume assuming the compressibility of zero. In this case, the work pressure was determined from the triaxial tests for each clay-sand ratio.

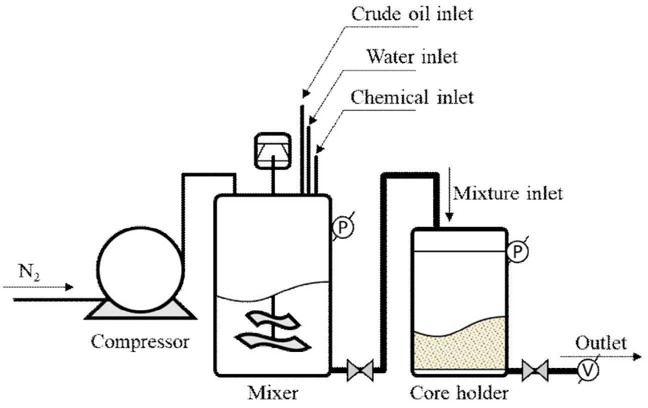


Fig. 1. Experimental rack schematic for permeability tests

3. Results and Discussion

Fig. 2 shows an example of the ED-XRF patterns obtained for clay, sand, and carbonate rock. The results show that clay and sand have in their structures some elements such as Al and Si, which are part of aluminosilicates (Al_2O_3-SiO_2). Other elements found were Fe, K, and Ca, and in a lesser relative content, Mn and S. For the carbonate rock El Abra, the presence of Ca and Mg ($CaCO_3$ and $CaMg(CO_3)_2$), as well as other elements such as V and Ti in a smaller proportion, was confirmed.[31,33] These results indicate that fluid-rock interactions cause an ionic change on the solid surface. In this sense, the correct salinity of the aqueous phase could alter the fluid affinity of the rock. Therefore, the activity of surfactants or flow enhancers must be oriented to enhance such alteration and promote a more effective water affinity on the rock surface.[20-26]

The triaxial test determined the pressure needed for core failure to occur subjected to compression. The core reaches a maximum resistance and then goes through a load drop generated by the fracture. For all probes, 200 kPa constant pressure was applied until fracture after 7 min, wherein the maximum loads for probes at 5, 10, and 15 % were 4901.2 kPa (2,986 mm displacement), 5020.1 kPa (2,836 mm displacement), and 5181.3 kPa (2,795 mm displacement), respectively.

Fig. 3 shows the results obtained from the rheological analysis of the fluids CO, CO-B, and CO-S. Three fluids show a constant behavior at 318 K between 150 and 1000 mPa·s. Below this temperature, biodiesel performs a significant reduction in comparison with the surfactant molecule, and at 303 K, crude oil viscosity reaches a 30 % reduction. The working temperature of 318 K was selected from this experiment to develop linear swelling, contact angle, and apparent permeability experiments since it represents the lower thermal energy necessary to decrease the viscosity and enhance fluid flow. All the values of shear rate *versus* viscosity present a Newtonian behavior, with similar results for the range of 100–200 s^{-1}.

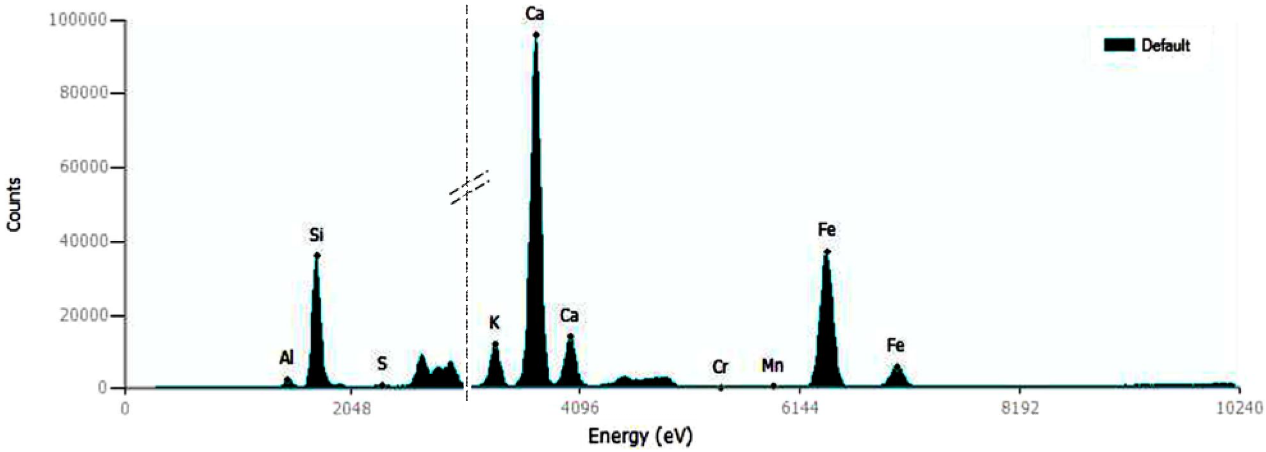


Fig. 2. ED-XRF diffraction pattern

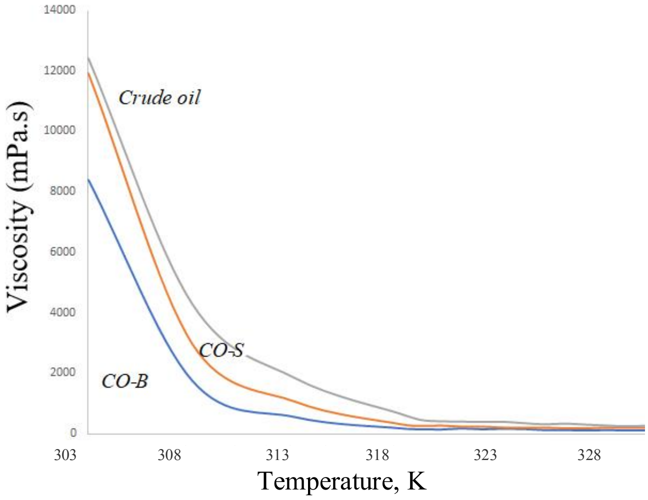


Fig. 3. Viscosity behavior *vs*. temperature

Table 1 shows the results of the linear swelling test that were applied only for the clay-sand 5 % probe as an emulating kind of soil in old reservoirs. It can be observed that the addition of the products positively influences the material swelling rate. The reduction of swelling affects the diameter of the extraction well by stabilizing it. For the cases of water addition being salty or distilled, a high increment of this property is observed, which is related to the formation of W/O emulsions considering the 1:1 ratio for water/crude oil. This test demonstrates water injection capability as an EOR technic; due to higher water content, the emulsion formed is O/W, which is less viscous and easy to extract from porous media.[33-35]

Table 1. Volume linear changes at 318 K

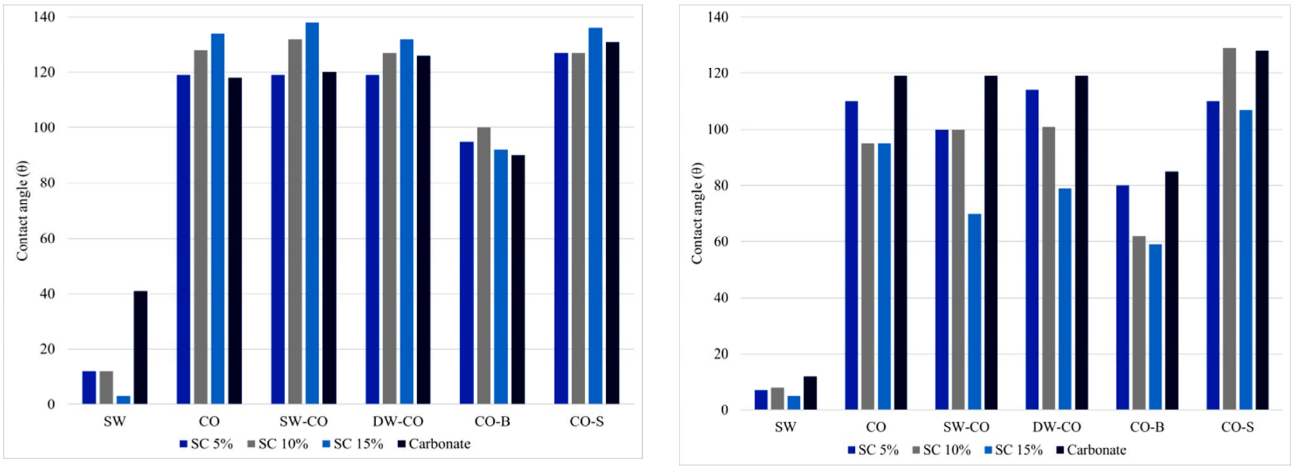
Sample	Linear swelling, %v/v ±0.021
CO	0.520
CO-B	0.418
CO-S	0.453
SW-CO	0.808
DW-CO	1.219

Fig. 4 shows some micrographs examples of the materials and the drop test. Fig. 5 shows the contact angle results. A similar behavior between CO, SW-CO, DW-CO, and CO-S for the dry system is observed, and the addition of biodiesel promotes contact angle values around 90°. There are significant differences when the core is imbibed. In this case, the increase in clay content reduces the contact angle values except for the mixture CO-S, which indicates that the nonionic surfactant maintains a better cohesion work in the sine of fluid even in the presence of salinity.[24,25] There is no apparent effect of the mixtures studied for the carbonate rock, and the contact angle values remain in the same tendency.[26]

Table 2 shows the apparent permeability results for the clay-sand samples performed under the maximum pressures obtained in the triaxial test for each probe. The addition of biodiesel seems to produce a fluid movement similar to the addition of distilled water. This behavior supports the idea that low salinity water enhances the recovery of crude oil from wells and that biodiesel reduces the crude oil viscosity and improves the flowability through porous media. However, this behavior is only valid if the soil is not saturated with salty water, demonstrating the contact angle values for the CO-B mixture shown in Fig. 3b.

a) b) c)

Fig. 4. Micrographs of sand (a), carbonate (b), and contact angle drop test (c)



a) b)

Fig. 3. Contact angles values (±1°) for samples on the dry core (a) and core after imbibition (b)

It is common to have salty water as part of the fluids during production that affects the fluid mobility through porous media. In some cases, water injection (smart water) is one of the EOR methods applied to recover crude oil.[20,22,23,36] The crude recovered percentages from CO-B and CO-S mixtures in the permeability test are between the values obtained for SW-CO and DW-CO mixtures. This behavior could be related to the efficiency of the biodiesel and surfactant to improve crude oil recovery.

Table 2. Time for 4 ml outlet volume and crude oil recovered from the apparent permeability test at 318 K

Sample	Time, h:min:s	Crude recovered, % v/v ±1
CO	1:55:12	100
DW-CO	1:11:15	78
SW-CO	1:32:10	65
CO-B	1:12:00	76
CO-S	1:20:15	73

It is necessary to extend the study to other pressures; however, similar results would be expected provided that there is no associated gas due to the low effect of pressure on the composition of liquids. Therefore, experiments would include the study of multiphasic systems gas-liquid-solid.

4. Conclusions

In this work, the permeability effect of biodiesel and a surfactant molecule on clay-sand cores with different concentrations of clay for the fluid of Mexican crude oil was studied. The fluids analyzed were crude oil, crude oil with biodiesel, crude oil with a surfactant, and crude oil within distilled and seawater. Contact angles results show values equal and higher than 90° for all cases in the dry surface. When the core was imbibed with salty water, the increase in clay content reduces the contact angle values except for the mixture crude oil-surfactant, which indicates that the nonionic surfactant maintains a better cohesion work in the fluid sine. A carbonate rock was analyzed as a comparison for clay-sand cores. In this case, there is no apparent effect of the mixtures studied, and the contact angle values remain in the same tendency.

It is remarkable that, although the contact angle is around 90° (meaning that surface can be wet by oil or water), in the analysis for permeability, results show an enhance in mobility. Distilled water (smart water) shows the best results with a higher percentage of clay in the composition than surfactant dosage. Nevertheless, for this case, it is not easy to reach a low-salinity concentration in actual reservoir practical cases. The surfactant improves apparent permeability and contact angle. Although the surfactant mixture helps for both the sandy medium and the carbonated medium, possibly by forming an interface between the solid and the liquid, it is necessary to water composition in a reservoir that requires a more in-depth future analysis. The combination with biodiesel may help for the water-free cases, as crude oil separated from the gas in pipelines or low water content in the case of carbonate reservoirs.

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ОЦІНКА ЗМОЧУВАНОСТІ ПІЩАНОЇ ГЛИНИ ДЛЯ РУХЛИВОСТІ ВАЖКИХ НАФТ

Анотація. *Для встановлення впливу дистильованої води, знижувача в'язкості біодизельного палива та комерційного нейоногенного ПАР на ефективну проникність піщаної глини визначено кут змочування, лінійне набухання та рух рідини через пористе середовище на прикладі північно-мексиканської нафти. Показано, що кількість глини суттєво впливає на значення кута змочування, з меншою величиною змочуваності в каменистому середовищі. Додавання біодизеля викликає рух рідини, подібний до додавання дистильованої води. Підсилювач потоку на основі біодизеля не тільки зменшує в'язкість сирої нафти, але також покращує текучість крізь пористі середовища. Однак така поведінка справедлива лише в тому випадку, якщо ґрунт не насичений солоною водою.*

Ключові слова*: змочуваність піщаної глини, рух рідини через пористе середовище, кут змочування, модифікація ефективної проникності.*