

## EFFECTS OF OIL VISCOSITY AND INTERFACIAL REACTION ON THE DISPLACEMENT OF OIL FROM POROUS MEDIA

Vladimir HORNOF<sup>1,\*</sup>, Graham H. NEALE<sup>2</sup> and Alex YU

*Department of Chemical Engineering, University of Ottawa, K1N 6N5 Ottawa, Ontario, Canada;*  
*e-mail: <sup>1</sup> hornof@eng.uottawa.ca, <sup>2</sup> neale@eng.uottawa.ca*

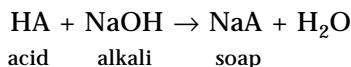
Received January 30, 2001

Accepted May 21, 2001

Displacement of oil from unconsolidated porous media was investigated. Waterflooding and alkaline flooding tests were conducted in model porous media consisting of fine glass beads wet-packed into a cylindrical holder. Mixtures of light and heavy paraffin oil of viscosity ranging from 20 to 70 mPa s were used as the oil phase. Acidic oil was simulated by dissolving 10 mmol/l of linoleic acid in the oil. As expected, recovery of neutral oil by waterflooding decreased as oil viscosity increased. Addition of acid to the oil reduced the waterflooding recovery by more than 20% for all oils. Alkaline flooding of after-waterflood residual oil produced incremental recovery only in the case of the least viscous oil (20 mPa s). The incremental recovery increased with the concentration of alkali only up to 25 mmol/l and remained constant thereafter.

**Keywords:** Alkaline flooding; Waterflooding; Oil recovery; Porous materials; Interfacial reaction.

Alkaline (caustic) flooding is a method of enhanced oil recovery. It has been employed in the field to improve the recovery of crude oil from partially depleted reservoirs. The method is based on an interfacial reaction between an injected alkaline solution and naturally occurring acids in crude oil. The interfacial reaction results in *in situ* formation of interfacially active compounds (soaps) which become adsorbed at the oil-water interface and reduce the interfacial tension between the resident oil phase and the injected water phase:



Low interfacial tension conditions are desirable in order to facilitate the displacement of oil droplets and ganglia from the interstitial spaces of the porous medium. First patented by Atkinson<sup>1</sup>, the alkaline flooding tech-

nique has now become one of the more promising enhanced oil recovery methods<sup>2</sup>.

The fundamental phenomena associated with the interaction between resident acidic oil and injected alkaline solutions have been studied in this laboratory for some time. Both naturally occurring acidic crude oils<sup>3,4</sup> and model acidified oils<sup>5,6</sup> have been used. A study published by the present authors<sup>7</sup> dealt with the effect of the flooding sequence on the displacement of acidic oil by alkaline solutions in unconsolidated sand packs. It was found that an injection of sodium hydroxide solution after the porous medium has been first flooded with pure water (*i.e.*, after the waterflood) produced more oil than continued waterflooding without alkali. An injection of alkali not preceded by a waterflood, on the other hand, generally resulted in lower oil recoveries as well as other problems, including the formation of hard-to-break emulsions. Importantly, it was also found that an addition of an oil-soluble acid (such as linoleic acid) to the originally acid-free paraffin oil brought about a large decrease in oil recovery.

The aforementioned investigations<sup>7</sup> were conducted using a light paraffin oil (viscosity 20 mPa s) as the oil phase. Real heavy oils, however, may possess a much higher viscosity; for example, the Western Canadian (Lloydminster) heavy crude oil used by Hornof and Bernard<sup>8</sup> had a viscosity of nearly 500 mPa s at 20 °C. In the present study, the effect of oil viscosity on oil recovery is investigated in both the presence and absence of interfacial reaction.

## EXPERIMENTAL

Details of the flooding equipment have been given in previous publications<sup>7,9</sup>. A wet-packing procedure similar to that described by Polikar *et al.*<sup>10</sup> was employed to pack glass particles into cylindrical holders in a uniform and homogeneous fashion. Glass beads ranging from 53 to 180  $\mu\text{m}$  in diameter were employed. The resulting bead packs had permeability to water of about 1.2  $\mu\text{m}^2$  at a porosity of 28–29%. The water-saturated packs produced by wet packing were first flooded with oil until no more water could be displaced from the porous medium (*i.e.*, until the irreducible water saturation was reached). Following this procedure the porous medium possessed an initial oil saturation of about 98–99%, with the rest of the porous space being filled by the residual water. All displacement experiments were carried out at the laboratory temperature of  $24 \pm 1$  °C.

Mixing light paraffin oil (20 mPa s) and heavy paraffin oil (134 mPa s) provided oils of different viscosity. BDH Inc. supplied both oils. The density and viscosity of mixed oils, measured at 25 °C, are shown in Fig. 1 as a function of the heavy oil content.

Oils having the viscosities of 20, 31, 55 and 70 mPa s were prepared and stored in glass containers before use. The surface tension and the interfacial tension (IFT) against pure water were measured using a Fisher Autotensiomat instrument. Both parameters were essentially independent of oil composition at 28 and 50.5 mN/m, respectively. Simulated acidic

oils were prepared by dissolving 10 mmol/l of linoleic acid (Fisher Scientific) in each stock oil. Pendant drop measurements<sup>11</sup> have shown the acidified oil to exhibit transient (time-dependent) IFT which stabilized after about 20 min at approximately 50% of the value observed for pure oil. Contacting acidic oil with alkaline solutions resulted in a much more drastic IFT reduction. A typical IFT vs time curve measured with the help of a University of Texas model 300 spinning drop tensiometer is shown in Fig. 2.

The displacing phase injected into the porous medium was either distilled water or NaOH solutions with concentrations ranging from 2.5 to 250 mmol/l. The sodium hydroxide was of Fisher Certified Grade.

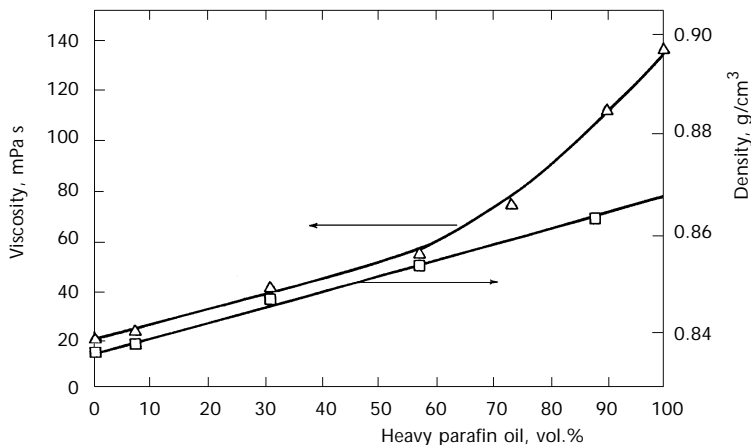


FIG. 1

Density and viscosity of paraffin oil mixtures at 25 °C

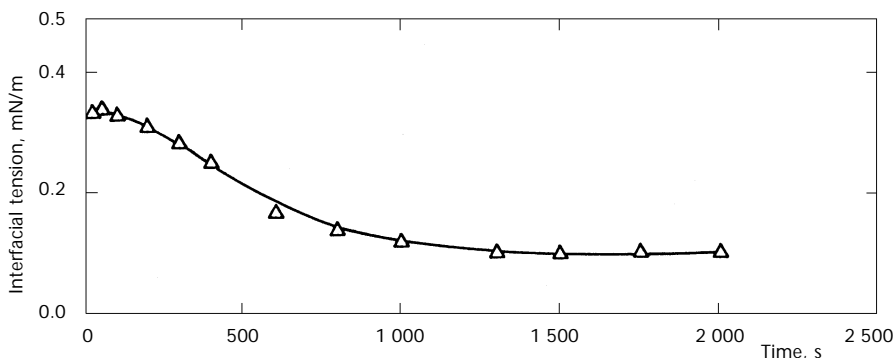


FIG. 2

Typical transient interfacial tension vs time curve for acidified oil against alkaline solution (acid concentration 10 mmol/l, NaOH concentration 25 mmol/l, oil viscosity 20 mPa s)

## RESULTS AND DISCUSSION

### *Effect of Oil Acidity*

Previous research has shown<sup>7</sup> that the addition of 10 mmol/l of linoleic acid to light (*i.e.*, 20 mPa s) paraffin oil caused the waterflood recovery to drop from over 80% of the oil originally present in the case of pure oil to just about 55% in the case of acidified oil. It was thus of interest to see whether analogous behavior would be observed when using oils of higher viscosity.

Oil recovery results obtained with 31, 55 and 70 mPa s oil are shown in Figs 3a, 3b and 3c, respectively. It is evident that the behavior is essentially identical in all three cases, and that the oil recovery is always strongly reduced in the case of acidified oil. On the contrary, the influence of oil viscosity on recovery is relatively weak. The results shown in Fig. 4 represent cumulative waterflood recoveries after 7 pore volumes of water have been injected for all four oils in the absence and in the presence of acid. It is seen that for pure oil, recovery decreases from about 85% in the case of the 20 mPa s oil to just under 80% in the case of the 70 mPa s oil. A similar decrease is observed in the case of the acidified oils, although the absolute recovery percentages are always about 25% lower than in the case of pure oils.

Touhami *et al.*<sup>11</sup> have shown that linoleic acid acts as a mild surfactant when acidified oil is put in contact with water. As a result, an approximately 50% reduction in IFT (from 50 mN/m for the pure oil–water system to about 25 mN/m for the acidified oil–water system) has been observed. This translates into a 50% decrease in the capillary number and, as a consequence, one might expect improved oil mobilization and an increase in oil recovery when conducting the displacement tests. That this does not happen is an indication that another mechanism is at play.

The clean glass beads used to make the porous pack are strongly water-wet, as evidenced by rapid spontaneous imbibition of water into the porous medium when a dry bead pack is contacted with water. When a water-saturated wet pack is subsequently flooded with pure oil, the solid particles continue to be covered with a thin film of water and consequently remain water-wet. Pure paraffin oil is immiscible with water and does not contain any components that could partition into water and become adsorbed on the solid surface. Linoleic acid, however, albeit sparsely soluble in water, can diffuse into the aqueous phase and dissociate therein. Adsorption of the amphipathic acid anion or undissociated acid on the surface of

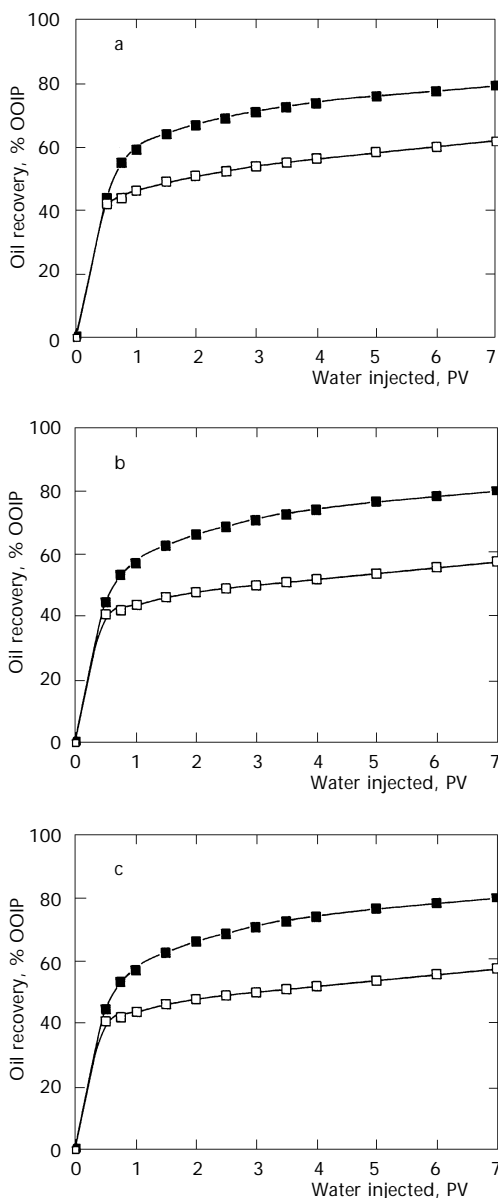


FIG. 3

Comparison of waterflooding neutral and acidified oil (■ no acid in oil, □ 10 mm acid in oil). Oil viscosity (in mPa s): 31 (a), 55 (b) and 70 (c). (OOIP, oil originally in place, *i.e.*, the oil present in the interstitial volume of the bead pack at the start of a displacement experiment; PV, pore volume, *i.e.*, the interstitial volume of the bead pack)

the beads is expected to make the originally water-wet surface less hydrophilic and more compatible with oil (oil-wet).

Displacement visualization studies carried out by Hornof and Morrow<sup>12</sup> have shown that porous medium wettability has a strong effect on the stability and general nature of the displacement fronts. Displacement of non-wetting phase by wetting phase (which, in the system investigated here, reflects the displacement of pure oil by water) is governed by imbibition provided the IFT is not too low. Imbibition of the wetting phase (water) into smaller pores takes place thus producing a smooth displacement front and high recovery of the non-wetting phase originally in place (oil). In the opposite case, *i.e.* when a non-wetting fluid is displacing a resident wetting fluid, the displacements take place in the drainage mode. The displacement fronts are ragged and much of the flow occurs through larger pores and through zones having the highest permeability. This type of behavior, which probably describes what is happening in the present work when acidic oil is the fluid originally in place, generally results in a lower oil recovery. The effects of crude oil-induced wettability changes on oil recovery have been thoroughly investigated by Morrow and coworkers<sup>13</sup>. Recent work published by Zhou *et al.*<sup>14</sup> shows conclusively that rock surface wettability alteration towards a more oil-wet state, caused by adsorption of amphipathic, crude oil components, resulted in reduced imbibition rates, ultimately causing a decrease in oil recovery.

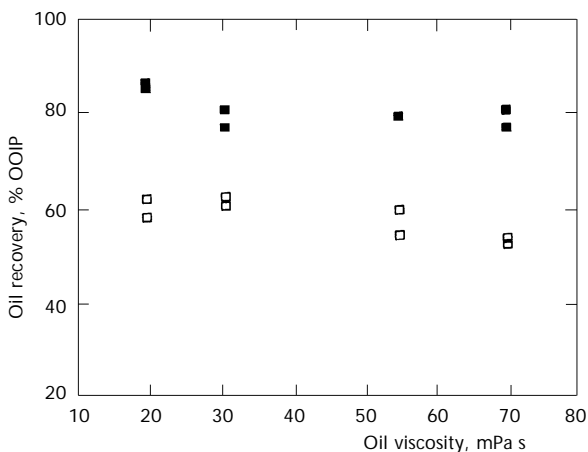


FIG. 4

Cumulative waterflood recoveries after injection of 7 pore volumes of water into bead packs saturated with neutral and acidic oils (■ no acid in oil, □ 10 mM acid in oil)

*Effect of Oil Viscosity and Alkali Concentration*

In the experiments described below, acidified paraffin oil was first flooded with one pore volume of water, immediately followed by continuous flooding with an alkaline solution. This flooding scheme was in accordance with the Strategy A flooding experiments reported by Hornof *et al.*<sup>7</sup>. Strategy B, in which alkaline solutions were injected immediately without being preceded by a waterflood, was not employed in this work. Oil recovery results obtained at four oil viscosities and with alkaline concentration ranging from 2.5 to 250 mM NaOH are shown in Fig. 5. Each point on the graphs represents one displacement experiment and shows the respective incremental recovery as a function of the concentration of sodium hydroxide in the injected solution. The incremental recovery is defined as the difference between the oil recovery observed when one pore volume of water followed by five pore volumes of alkaline solution were injected, minus the recovery obtained after injecting just six pore volumes of water. It is observed that only in the case of the least viscous oil (20 mPa s) are there significant incremental recoveries observed. From about 5% at 2.5 mM NaOH, the incremental recovery rises to about 15% at 25 mM NaOH and then stabilizes. The incremental recovery values observed with the three more viscous oils appear to be almost randomly distributed around the zero mark and the small observed differences are not statistically significant in view of the ex-

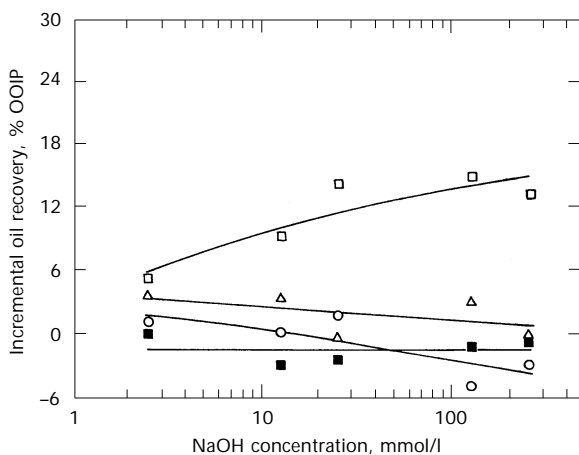


FIG. 5

Effect of oil viscosity on incremental oil recovery obtained with alkaline flooding. Oil viscosity (in mPa s):  $\square$  20,  $\circ$  31,  $\blacksquare$  55 and  $\triangle$  70

perimental error which has been estimated to be  $\pm 4\%$  absolute for these flooding experiments.

The poor results obtained with alkaline flooding may be attributed to the lack of mobility control. Shuler *et al.*<sup>15</sup> asserted that this imposed severe limitations on the oil recovery in their displacements of a 40 mPa s viscosity crude oil with an alkaline solution of 1 mPa s viscosity. When they adjusted the viscosity of the alkaline solution to 43 mPa s, the incremental recovery increased from 17 to 58%.

Foster<sup>16</sup> identified the mobility (viscosity) ratio as one of the most important parameters affecting recovery. Even when residual oil becomes mobilized by, for example, reducing interfacial tension, it will not be recovered from the porous medium unless the mobility ratio (*i.e.*, the ratio of the displacing phase viscosity to the displaced phase viscosity) is at least as high as a threshold value of about 0.05–0.1. In the displacements conducted in the present work, the viscosity ratios are 0.05, 0.03, 0.02 and 0.014 corresponding respectively to 20, 31, 55 and 70 mPa s oil. As a consequence, a small incremental recovery at best, of the order that was observed in the present experiments, would be expected in the case of the 20 mPa s oil. The three more viscous oils, however, would be expected to produce little or no incremental oil.

Parallel flow visualization experiments carried out in transparent porous media have shown that in alkaline flooding, the situation is further complicated by the depletion of the injected alkali<sup>17</sup>. This effect has been also confirmed by computer simulation<sup>18</sup>. Additional work is being carried out in order to further elucidate the mechanisms affecting oil mobilization and recovery.

## CONCLUSIONS

1. Addition of acid to paraffin oil resulted in an approximately 20% decrease in oil recovery. This decrease was observed for all four oils tested, ranging from 20 to 70 mPa s in viscosity.

2. When an alkaline flood was conducted after a waterflood, incremental oil recovery was only observed with the least viscous oil (20 mPa s) and none at all with the three more viscous oils.

3. The incremental recovery obtained with the 20 mPa s oil increased with NaOH concentration up to 25 mmol/l and remained constant when the NaOH concentration was increased further.



*The authors thank the Natural Sciences and Engineering Research Council of Canada for the continuing financial support of their work.*

## REFERENCES

1. Atkinson H.: U.S. 1 651 311 (1927); *Chem. Abstr.* **1928**, 22, 682.
2. Donaldson E. C., Chilingarian G. V., Yen T. F.: *Enhanced Oil Recovery, II, Processes and Operations*. Elsevier, Amsterdam 1989.
3. Chiwetelu C. I., Neale G. H., Hornof V., George A. E.: *J. Can. Petrol. Technol.* **1994**, 33, 7.
4. Khulbe K. C., Hornof V., Neale G. H.: *AOSTRA J. Res.* **1985**, 2, 95.
5. Nasr-El-Din H., Khulbe K. C., Hornof V., Neale G. H.: *Rev. Inst. Fr. Petrol.* **1990**, 45, 231.
6. Chiwetelu C. I., Hornof V., Neale G. H.: *Chem. Eng. Sci.* **1990**, 45, 627.
7. Hornof V., Neale G. H., Yu A.: *J. Petrol. Sci. Eng.* **1994**, 10, 291.
8. Hornof V., Bernard C.: *Exp. Fluids* **1992**, 12, 425.
9. Dormani N. A., Hornof V., Neale G. H.: *J. Petrol. Sci. Eng.* **1990**, 4, 189.
10. Polikar M., Puttagunta V. R., Ferracuti F., Farouk Ali S. M.: *J. Petrol. Sci. Tech.* **1988**, 1, 263.
11. Touhami Y., Hornof V., Neale G. H.: *J. Colloid Interface Sci.* **1994**, 166, 506.
12. Hornof V., Morrow N.: *SPE Reservoir Eng.* **1988**, 3, 251.
13. Morrow N. R., Lim H. T., Ward J. S.: *SPE Formation Eval.* **1986**, 1, 89.
14. Zhou X., Torsaeter O., Xina X., Morrow N. R.: *Presented at the 68th Annu. Tech. Conf. Exhibition of the SPE, SPE 26674, Houston (TX), October 3–6, 1993.*
15. Shuler P. J., Kuehne D. L., Lerner R. M.: *J. Petrol. Technol.* **1989**, 41, 80.
16. Foster W. R.: *J. Petrol. Technol.* **1973**, 25, 205.
17. Hornof V., Neale G. H., Gholam-Hosseini M.: *J. Colloid Interface Sci.* **2000**, 211, 196; and references therein.
18. Jahoda M., Hornof V.: *Powder Technol.* **2000**, 110, 253.