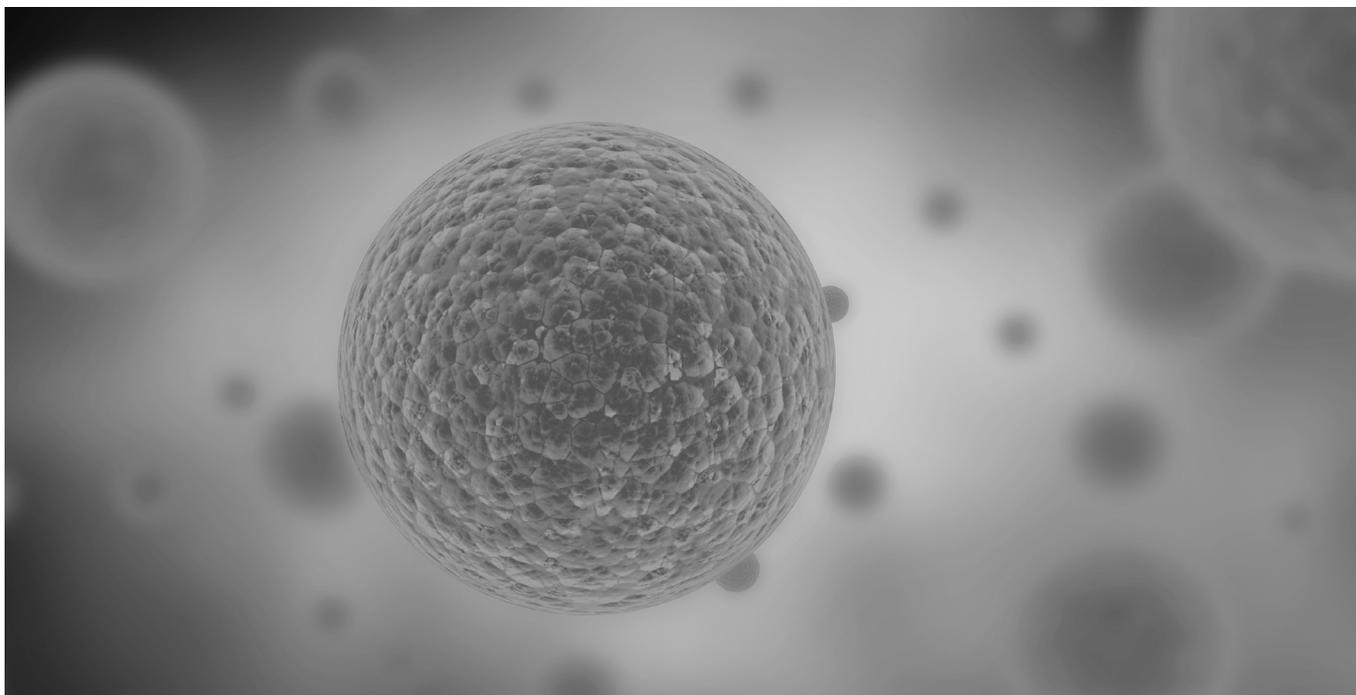


Enhanced Oil Recovery using Nanoparticles

Wettability Alteration and IFT Reduction using Attension Theta High Pressure



Abstract

Nanoparticles (NPs) have recently gained great attention as effective agents for enhanced oil recovery (EOR) applications. Herein, we are synthesizing, characterizing, and designing naturally-derived silicate-based nanopyroxene, and evaluating their potential as nanofluids for EOR. The proposed in-house NPs offer opportunities for scalability for field applications with no environmental footprints at a low cost. Techniques, such as SEM, FTIR, XRD, TGA, DLS, and Z-potential were conducted for the produced NPs to confirm their surface identity, functionality, stability, and morphology. In comparison with brine, nanofluids were generated from the synthesized NPs to test their performance toward EOR using sandstone cores. The EOR performance was investigated by interfacial tension (IFT), contact angle, spontaneous imbibition and displacement tests. The results showed that the nanofluids have the ability to improve oil recovery after water flooding. Contact angle in the presence of brine and nanofluids were measured as $74 \pm 2^\circ$ and $40.5 \pm 2^\circ$ respectively, confirming wettability alteration from oil-wet to water-wet. Interfacial tension was also noticeably reduced with the produced nanofluids at all temperatures, showing their great potential for oil displacement. To prove that, core flooding experiments were performed, confirming the capability of nanofluids as effective EOR agents in hydrocarbon reservoirs by recovering an additional 11 % after brine flooding.

Introduction

Conventional oil recovery methods (i.e., primary and secondary) typically extract approximately one-third of the original oil-in-place in the reservoir. [1] Estimated reserves worldwide range up to 1.5 trillion barrels. Using the figure of one-third of 1.5 trillion barrels, it is estimated that the remaining oil after conventional recovery would be approximately 1.0 trillion barrels. [2,3] Several enhanced oil recovery (EOR) techniques, generally grouped together as tertiary production schemes such as thermal recovery, chemical flooding or gas flooding, have targeted these huge unexploited reserves. [2,4] However, finding an economical, environmentally friendly and efficient method to extract the remaining residual oil after primary and secondary recovery still remains a challenge. Besides that, current tertiary practices depend on crude oil prices. [5,6] Hence, further studies are needed to introduce sustainable, affordable, cost-effective, efficient, and environmentally friendly techniques. Moreover, oil companies are relentlessly under pressure, continuously looking for novel techniques to recover the trapped oil which has taken up a huge portion of the total cost during oil recovery.

In recent years, nanotechnology as an alternative in the form of nanoparticles (NPs) alone or integrated with the already mentioned conventional enhanced recovery processes have shown promising performance in improving oil recovery. [7-9] Nanoparticles (diameter size between 1 and 100 nm) can drastically improve oil recovery by changing the geomechanics of the reservoir and modifying the reservoir properties, like altering the reservoir wettability and reducing the interfacial tension between oil and flooding fluid. [10] Based on their adsorption capability, they can be used in overcoming production problems such as inhibiting asphaltene and wax deposition. [11-13] The proposed nano-EOR mechanism includes interfacial tension reduction, wettability alteration, oil viscosity reduction, enhancing thermal recovery, improving the fluid rheology, and structural disjoining pressure. [14-16] However, most of these studies have been conducted under ambient conditions and using costly prepared precious nanomaterials. Moreover, the recovery mechanism using NPs still requires further investigation especially by using environmentally friendly and cost-effective NPs at reservoir conditions.

Purpose of the Study

The objective of this study was to synthesize, characterize, and design naturally-derived silicate-based nanopyroxene, and evaluating their potential application as nanofluids for EOR. The formulated nanofluids were evaluated for their potential to recover residual oil by performing interfacial tension, contact angle measurements, and spontaneous imbibition in comparison with commonly used brine. The optimum nanofluids from the imbibition experiments are selected for the core flooding experiments.

Materials

The oil sample used was a real dead oil provided by a local oil company here in Canada. The crude oil had a viscosity of 9.5 ± 0.02 cP at 60 °C, density 0.87 g/cm³ at 25 °C, an approximate content of 5.09 wt % of asphaltenes, and an acid number < 0.1. For testing the oil recovery, sandstone cores, with 20-22% porosity and permeability of 78 mD, were prepared at Kocurek Industries Inc., Caldwell, TX. The core characterization was conducted by EDX and SEM analysis and showed that the sandstone cores consisted of mainly quartz. Synthetic brine, representing formation brine, was prepared from sodium chloride (NaCl) at 20,000 ppm and deionized water. The details of the nanoparticle synthesis and nanofluid preparation can be found in our detailed study as reported elsewhere. [11]

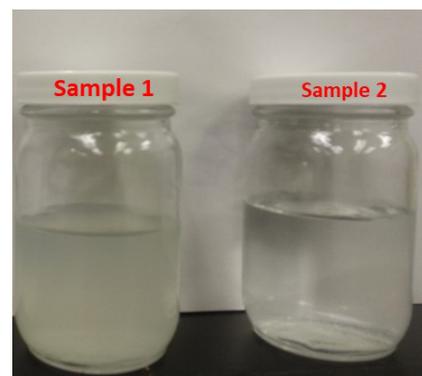
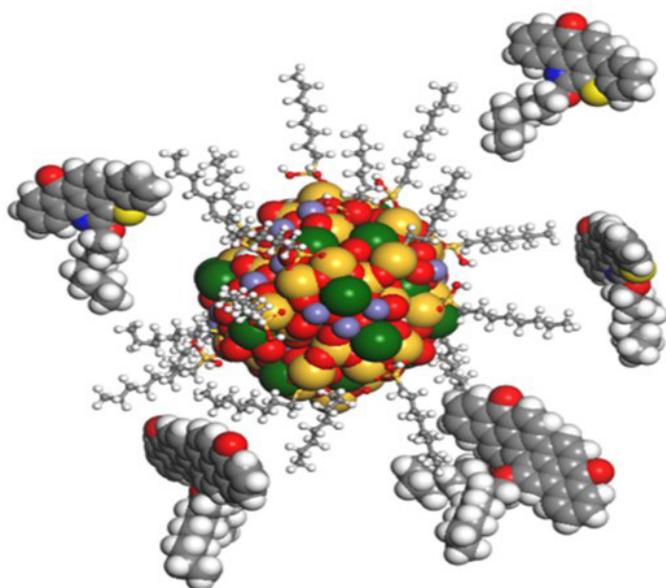


Figure 1 Prepared silicate-based nanopyroxene nanoparticles and nanofluid samples 1 and 2 of different concentrations.

IFT Reduction

Interfacial tension measurements (IFT) were performed for the prepared nanofluid to evaluate their role in reducing the IFT between oil and brine at ambient pressure and temperatures between 25 and 60 °C. The measurements were carried out by a system inside the high-pressure chamber that is manufactured by Biolin Scientific, Finland. The system consists of a stainless steel (EN 1.4401) chamber that enables surface and interfacial tension measurements at high pressure and various temperatures, using the pendant drop technique. For sealing, an O-ring is equipped with the standard system according to the used fluids. At the top of the chamber, there are three connection ports for the temperature probe, sampling, and bulk fluid introduction. For each IFT measurement, brine or one of the nanofluids is introduced

inside the chamber. Then, an oil droplet was created through a needle at the interface between the needle and the liquid phase using the pendant technique, IFT was then determined for a given time interval. All measurements were repeated in triplicates, and the mean \pm standard error of the mean was reported.

Contact Angle Measurements

To determine the tendency of the nanofluids to alter the rock wettability, a quantitative assessment of the wettability of the core plugs before and after the treatment with nanofluids was performed. Polished sandstone substrates were cut and aged in oil for about 2 weeks to alter their initial wettability at 70 °C and atmospheric pressure and later dried in an oven for 6 h at 60 °C. Oil aged substrates were then submerged into the prepared nanofluids for 48 h at 60 °C.

After that, each substrate was dried in an oven at 55 °C for 2 h. Contact angle measurements between sandstone substrate and brine or nanofluid and oil drop system of the substrates treated with either brine or different nanofluids were performed with an accuracy of $\pm 3^\circ$ at 60 °C. The angles were then analyzed to quantify the effect of the nanofluid on wettability alteration.



Figure 2 Attension Theta High Pressure from Biolin Scientific.

Results

Nanofluids in EOR methods depending on the type of oil and reservoir properties usually results in an intermediate IFT. Using the high-pressure chamber, nanofluids could reduce the IFT at different temperatures compared to brine as shown in figure 3b. Also, figure 3 (a), shows that the nanofluids can reduce IFT with time compared with brine.

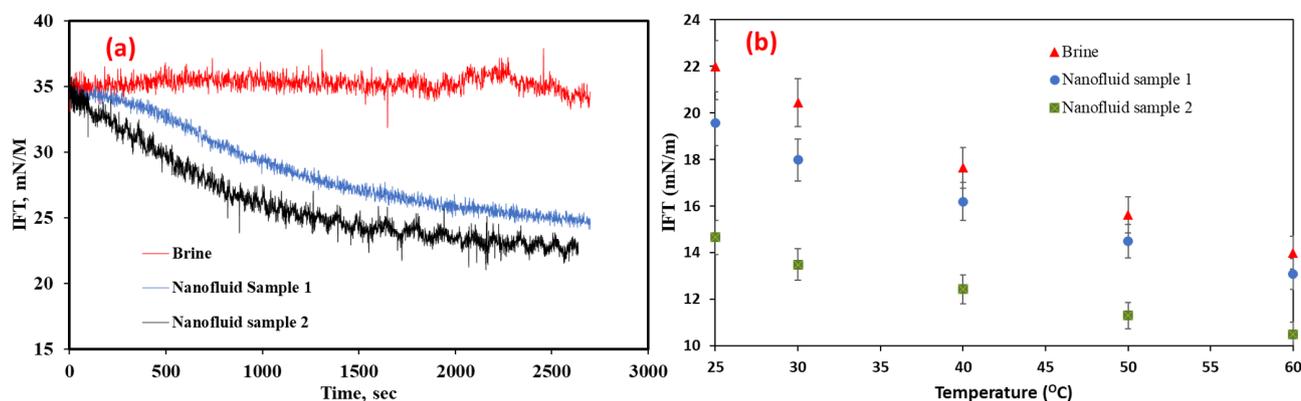


Figure 3 IFT measurements in the presence of nanofluids as a function of time and with different temperatures.

Contact angle measurements were performed before and after aging the sandstone substrates in oil. The original core wettability was strongly water-wet, and after aging in oil, contact angle increased towards oil-wet state due to partial adsorption of polar components in crude oil on the sandstone substrate. After aging with oil, the water drop contact angle was more than 90° indicating oil wetness. As for the aged core, the core surface became strongly hydrophobic and could weakly interact with water. These results confirmed converting the core surface from water-wet to oil-wet by the aging process. Figure 4(a) shows an oil drop contact angle in the presence of brine and the oil aged substrate, which is $77^\circ \pm 2$ indicating an oil-wet state. The shape of the oil drop in the presence of pyroxene nanofluids can also be seen in panels of Figure 4(b and c), in comparison to that of brine. A contact angle can be measured with a water drop or oil drop. The varia-

tion in contact angle measurements was additionally obtained for the oil drop in the presence of the brine and different nanofluids. Figure 4 shows the oil drop contact angle measurements that were obtained in the presence of (a) brine and (b) and (c) pyroxene nanofluid with different concentrations. The estimated contact angles were around 77 , 106.3 and 139.5° , respectively. These contact angle values can be explained by the approach reported by Anderson et al, [17] according to his approach, using (heavier phase) the range of contact angles measured are defined as follow; between 0 - 75° , the system is water-wet. When the contact angle is in the ranges of 75 - 105° , and 105 - 180° , the system corresponds to intermediate-wet, and oil-wet, respectively. Worthily mentioning here that contact angles were measured in the presence of oil droplet and contact angle for the denser phase can be estimated by subtracting the measured values from 180° .

Therefore, in this study, higher contact angles will indicate water wetness and lower contact angles less than 90° will indicate oil wetness. Evidently, the nanofluids gave a high contact angle value compared with the brine, indicating that the core wettability was altered from oil-wetting to strongly water-wetting conditions, using nanoparticles of different concentrations. Details of the imbibition and core flooding experiment are not included in this case study, they can be found in our published article. [11]



Figure 4 Contact angle measurements with brine (a) and nanofluids (b) and (c) of different concentrations.

Conclusions

In this study, nanopyroxene nanoparticles were synthesized and nanofluids were formulated from the synthesized nanoparticles, then used as EOR agents in sandstone core plugs. Pyroxene-based nanofluids could noticeably reduce the IFT up to 14 %, respectively and this was measured as a function of time. Contact angle measurements in the presence of nanofluids with different concentration were measured as $73.7^\circ \pm 2^\circ$ and $40.5^\circ \pm 2^\circ$ confirming wettability alteration from oil-wet to strongly water wet, which is in line with the structural disjoining force mechanism reported in the literature. Moreover, the contact angle decreased as nanoparticle concentration increased.

Biography



PhD Farad Sagala

Farad Sagala is a PhD candidate in Chemical and Petroleum Engineering at the University of Calgary. Currently, he worked as teaching and research assistant in the department of Chemical and Petroleum Engineering. He teaches many graduate and undergraduate courses for Petroleum Engineering students such as Enhanced oil recovery, Thermodynamics, Production Engineering, Reservoir Engineering, water flooding, Oil and gas processing and fundamentals of fluid flow in the porous medium. In his PhD research, he is working on synthesis and performance evaluation of silicate-based nanoparticles

for enhanced oil recovery. He synthesizes and characterizes nanoparticles and use them as nanofluids for EOR application. By using both experimental techniques and modelling he studies the usage of these nanofluids for enhanced oil recovery together with existing inexpensive techniques such as smart water injections. He has published several peer reviewed journal papers and presented his research in various conferences. He is also an active member of Dr. Nassar group for Nanotechnology research at the University of Calgary and American chemical society (ACS).



PhD Afif Hethnawi

Afif Hethnawi is a PhD candidate in Chemical and Petroleum Engineering at the University of Calgary. Currently, he worked as teaching and research assistant in the department of Chemical and Petroleum Engineering. He teaches many graduate and undergraduate courses (Behavior of Liquids, Gases and Solids, fluid dynamics, heat transfer, natural gas processing, and wastewater issue for oil and gas industry). In his PhD research, he worked on oil spills cleaning up and treatment of silicate and total organic carbon from produced water coming from oil-sand industry in Alberta-Canada, using effective nanomaterials. He also worked on synthesis and characterization of environmentally safe and effective functionalized nanomaterials for enhancing of oil recovery (EOR) applications. In his MSc, he was an active member of Dr. Nassar group for nanotechnology research. He worked on treatment of dissolved organic matters from various industrial effluents with silicate-based nanomaterials. He integrated the environmentally safe, costly and effective nanoparticles on sand-bed filtration process to enhance the removal efficiency of many toxic compounds from different industrial wastewater. He has published plenty of research peer reviewed papers on synthesis and characterization of silicate and iron-based nanomaterials and their applications in oil spills removal, EOR and removal of heavy metals, pharmaceutical compounds, dyes, and total organic carbon from various industrial effluents. He attended many international conferences and symposiums inside and outside Canada.



Prof. Nashaat N. Nassar

Dr. Nassar is a professor in the Department of Chemical and Petroleum Engineering at the University of Calgary. He is an internationally recognized leader within the fields of nanoparticle technology for energy and environmental applications. The main goal of his research is to improve oil quality, reduce gaseous emissions, improve natural gas transportation and advance water recyclability using innovative technologies. As such, he has made major contributions in several areas of research, including nanoparticle synthesis, enhanced oil upgrading and recovery, solid hydrocarbon waste utilization, industrial wastewater treatment, natural gas conditioning and process optimization. Dr. Nassar's work has been widely recognized through several awards including: The first place Global Research Initiative (GRI) Concept to Commercialization award (2019), Emerging Leader in Chemical Engineering National Award (2018), the Association of Professional Engineers and Geoscientists of Alberta (APEGA) Early Accomplishment Award (2018), Innovation, Development and Entrepreneurship first place Award (2018), Early Research Excellence Award from the Schulich School of Engineering (2016), and the Great Supervisor Award (2017) among many others. Dr. Nassar has contributed towards the development of many highly qualified professionals, as he supervised 6 postdoctoral fellows, 12 PhD students, and 30 Masters students as well as 36 undergraduate students (16 in summer work, and 20 in term research thesis projects).

Dr. Nassar's expertise has been sought by a large community of researchers and industrial partners. He has written more than 100 peer-reviewed journal papers published or in press, given more than 150 technical presentations, edited one book, and filed 6 patents. He has an h-index of 37 and his work has been cited more than 3813 times (google scholar). Dr. Nassar is a member of the editorial board of several journals like Journal of Natural Gas Science and Engineering (published by Elsevier), Fuels and Energies (published by MDIP) and has been an expert reviewer of more than 100 journals in a wide array of science and engineering. He is a professional examiner for the Petroleum Engineering Examination for Professional Engineers Ontario, professional educator for the Association of Professional Engineers and Geoscientists British Columbia, was an expert reviewer for US patents and many more. He also has excelled in teaching, designing two graduate and one final year undergraduate courses on natural gas processing and technologies and effluent treatment processes for energy industry that are highly-sought-after by industry professionals. He is an active member in many scientific organizations and learned society mainly in the role of an expert.

References

1. S. Farad, H. K. Nsamba, A. Al Hassan, W. Joseph and, I. Kabenge, Am. Assoc. Sci. Technol., 2016, 3, 47-52.
2. R. Bentley, S. Mannan and, S. Wheeler, Energy policy, 2007, 35, 6364-6382.
3. A. Katende and F. Sagala, Journal of Molecular Liquids, 2019.
4. D. Wang and J. Sun, Scientific reports, 2019, 9.
5. A. A. Olajire, Energy, 2014, 77, 963-982.
6. S. Farad, M. A. Manan, H. K. Nsamba, W. M. K. B. W. Jaafar, K. Isa, and W. Joseph, Technology, 2016, 3, 53-60.
7. A. Bera and H. Belhaj, Journal of Natural Gas Science and Engineering, 2016, 34, 1284-1309.
8. R. Nazari Moghaddam, A. Bahramian, Z. Fakhroueian, A. Karimi and S. Arya, Energy & Fuels, 2015, 29, 2111-2119.
9. M. Manan, S. Farad, A. Piroozian, and M. Esmail, Petroleum Science and Technology, 2015, 33, 1286-1294.
10. S. O. Olayiwola and M. Dejam, Fuel, 2019, 241, 1045-1057.
11. F. Sagala, T. Montoya, A. Hethnawi, G. Vitale and N. N. Nassar, Energy & fuels, 2019, 33, 877-890.
12. J. Norrman, A. Solberg, J. Sjoblom and K. Paso, Energy & Fuels, 2016, 30, 5108-5114.
13. C. A. Franco, N. N. Nassar, M. A. Ruiz, P. Pereira-Almao and F. B. Cortés, Energy & Fuels, 2013, 27, 2899-2907.
14. R. Hashemi, N. N. Nassar, and P. Pereira Almao, Energy & Fuels, 2013, 27, 2194-2201.
15. B. Hou, R. Jia, M. Fu, Y. Wang, C. Jiang, B. Yang, and Y. Huang, Journal of Molecular Liquids, 2019, 294, 111601.
16. H. Jang, W. Lee and J. Lee, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2018, 554, 261-271.
17. W. G. Anderson, Journal of petroleum technology, 1987, 39, 1,605-601,622.