Simulation of Viscosity Enhanced CO2 Nanofluid Alternating Gas in Light Oil Reservoirs

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Abstract

Thickened CO2 nanofluids are a mean to improve volumetric sweep efficiency and gas production in CO2 EOR projects in contrast CO2 flooding. Alternating injection of plain CO2 with thickened CO2 nanofluid is proposed as an economical alternative using the findings of CO2 viscosity enhancement through nanoparticles in current studies. This was achieved by using CMG GEM simulator and contrasting findings with other WAG and CO2 flooding simulations. The simulation was done on a light oil (40 °API) from a Neuquén Basin reservoir. A sensitivity analysis was done to contrast different type of injection schemes.

As CO2 nanofluids can be tailor made in order to adjust their viscosity (and other properties like asphaltene deposition control) diverse results were observed. Nanofluids improve the volumetric sweet efficiency, and even low viscosity increment increase the overall gas utilization and conformance compared to CO2 flooding. Since there is no face change, the use of CO2 based nanofluids can be a mean to control CO2 EOR projects avoiding injectivity loss problems. It was observed that injection of mere nanofluid (without alternating CO2) is not technically nor economically convenient as it decreases production rates and has an overall lower economic performance than both WAG and CO2 flooding. Nevertheless, alternating nanofluid with plain CO2 enables higher sweep efficiency while lowering the operational costs due to lower volumes of nanofluid utilized. Adding nanofluid to a WAG scheme also shows improvements in EOR performance.

Introduction

CO2 EOR is a major Enhanced Oil Recovery technology worldwide with high oil recovery capacity. In supercritical conditions, CO2 presents a similar density to light oils while having a gas-like viscosity. In the case of miscible floods, CO2 interacts with the oil to produce a miscible slug, which also has lower viscosity than the original reservoir oil. The significant viscosity disparity may lead to viscous fingering compromising the macroscopic sweep efficiency of the project.

Macroscopic sweep efficiency in miscible CO2 EOR is generally enhanced by the implementation of water alternating gas (WAG). Nevertheless, WAG has some limitations regarding the petrophysical properties of the reservoir and the fluid's characteristics. In strong water wet formations, water blocking can decrease the oil recovery considerably, especially at high water saturations^{1,2,3}. In these cases, oil in

smaller pores may not be contacted by the CO2 rich phase due to an insufficient capillary pressure creating a *capillary induced bypassing*⁴. Therefore, in water wet systems, reduced WAG ratios or continuous CO2 injection are recommended⁵.

Injectivity reduction has been observed in various CO2 EOR projects⁶. Both CO2 and water injectivity have shown to be reduced in WAG and simultaneous water-gas injection. This phenomenon can have severe effect on the technical feasibility of EOR projects. In the Grayburg Formation, water injectivity loss of up to 90% has been reported⁷. The loss of injectivity derives in a reservoir pressure drop making the displacement in-miscible. Additionally, gas liberation due to pressure drop adds a new phase to the system. Increasing the gas bank in WAG cycles (reducing WAG ratio) is suggested to decrease injectivity loss effects⁸. Furthermore, water availability or water quality issues can also be a concern in some regions. Corrosion problems due to water-CO2 interaction could be mitigated by the replacement or reduction of water usage.

CO2 polymer thickeners solutions

An affordable CO2 thickener solution has been recognized as a "game-changing technology," since it would have profound effects on oil recovery. A CO2 thickener solution, as a mobility control agent, has the benefit of adjusting the CO2-rich solution's viscosity by simply varying the thickener concentration and wouldn't depend on rock characteristics, oil and brine properties, or fluid saturations and flow rates. Viscosity enhancement additives have been achieved by the use of CO2 soluble surfactants and polymers (with and without co-solvents) and most recently with nanoparticles.

Polymer thickener for CO2 has been developed by Bae and Irani with high molecular weight silicone oil with significant amounts of toluene. This formulation has proven to increment CO2 viscosity significantly up to 90-fold. A 6wt%, 4wt% and 2wt% polymer solution in CO2 increased its viscosity to 3.48cp, 1.2cp and 0.8cp respectively at reservoir conditions¹⁰. While this thickened CO2 has shown to improve oil recovery from cores and increase gas viscosity, the co-solvent (toluene) requirement made pilot-testing costs prohibitive.

Other formulations such as a fluorinated telechelic ionomer, a tri(semi-fluorinated alkyl) tin fluoride, a surfactant with two twin-tailed fluorinated tails, and a high molecular weight fluoroacrylate homopolymer have been proven8,11. Poly(fluoroacrylate-styrene) is a fluorinated compound which was able to increase CO2 viscosity by a 10-fold and 19-fold with under 1wt% and 1.5wt% additive concentration respectively11,12. Unfortunately fluorinated compounds are expensive and represent a health and environmental concern.

CO₂ nanofluid solutions

In the recent years, new thickeners were developed with the utilization of nanoparticles. Nanoparticles have been utilized to improve conformance control of water and also to form more stable CO2 foams. The novelty of these experiments was to disperse the nanoparticles directly in the gas.

- R. Shah developed a CO2 based nanofluid with CuO nanoparticles and PDMS as a co-solvent for heavy oils¹³. The formulation obtained had a 2.28cp viscosity at reservoir conditions and showed significant incremental oil recovery in core floods. He additionally developed a formulation with VRI.
- S.I. Hashemi et al. successfully dispersed NiO nanoparticles in CO2 using PDMS as a co solvent¹⁴. This formulation was aimed at miscible conditions with asphaltene deposition problems. NiO nanoparticles were able to destabilize asphaltene depositions in porous media, mitigating permeability reduction due to asphaltenes and achieving significant oil recovery factor improvement.
- S. Jafari et al. dispersed silica nanoparticles in CO2 using water as a co-solvent¹⁵. The use of water to disperse the nanoparticles in CO2 significantly reduced the cost of the project, although oil recovery factors increment were not as significant as in the other formulations. S. Jafari also conducted a WAG with nanoparticle saturated CO2 with positive results. It was observed that WAG with this nanofluids created oil in water emulsions.

Aside from increasing viscosity, polymer co-solvents as well as nanoparticles may have an effect in oil-CO2 interfacial tensions and rock wettability. These mechanisms were not included in this paper as they are highly dependent on the type of nanofluid formulation. Nevertheless, these factors should be taken into account while testing a specific design.

Experimental procedure

The simulation was done in CMG GEM compositional simulator. Consists of a 1/8th five spot patter with no inclination. To better understand the mechanisms of conformance control, the reservoir was represented by 25 layers with different petrophysical properties and an average permeability of 37md as shown in Fig. 1. The oil used to set the EOS parameters is a 40API oil with a minimum miscibility pressure (MMP) of 120bar, both determined by multiple mixing cells and slim tube at 50°C.

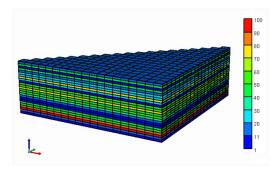


Figure 1—Model permeability distribution

The CO2 with enhanced viscosity was modeled maintaining all CO2 inherent properties with the exception of its viscosity. Both the surface tension variation and the wettability alterations of the rock were not taken into account as they are highly dependent on the type of formulation used. Five injection schemes were run in order to test the efficacy of nanofluids alternated with gas (Table 1).

Simulation 1	Continuous CO2 flooding
Simulation 2	Continuous CO2 nanofluid flooding
Simulation 3	CO2 alternated with nanofluid
Simulation 4	WAG
Simulation 5	WAG with nanofluid alternation

Table 1-injection schemes

Results and observations

Continuous nanofluid flooding

Continuous CO2 nanofluid or thickened CO2 injection is the most common scheme tested in core flooding experiments. Several authors have shown that such scheme are able to delay gas breakthrough and increase oil recovery factor significantly. Nevertheless, the cost of the additives and large volumes of thickened gas made the project cost prohibitive. For light oils, viscosity enhancement requirements are inferior to the ones pursued for medium or heavy oils. In fact, moderate viscosity increments are most beneficial as they are able to ensure high pressures throughout the reservoir maintaining miscibility. As miscible flooding is highly sensitive to pressure, 100-fold viscosity enhancement could be counterproductive, especially in reservoirs with low permeability. It was observed that moderate ~5-fold viscosity increment was most beneficial in order to improve the EOR process while maintaining reservoir pressure above MMP.

0.5 cp (reservoir conditions) gas continuous injection was modelled and contrasted with regular CO2 flooding with 0.08cp supercritical gas. As expected, gas breakthrough was delayed and gas production rates were reduced. Fig. 2 shows that gas utilization was improved significantly, although recovery rates as a function of time were delayed. While it represents clear technical advantages at moderate viscosity augmentation, the oil production delay and the large volumes of thickened CO2 employed may not maximize economic performance.

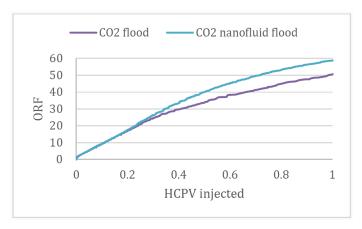


Figure 2—Oil Recovery Factor (%) vs HCPV injected

Nanofluid Alternating Gas (NAG)

Alternating pure CO2 with thickened gas is suggested as a technically and economically beneficial alternative for injection schemes. By alternating the injected gas with nanofluid, less volume of thickened gas is required reducing operational costs. Both 0.3 and 0.5cp gas viscosities were tested with pure CO2 injection alternation of 300 days each. As expected, viscous gas will first penetrate more permeable layers inducing plain CO2 penetration of lower permeability areas. Fig. 3 displays how gas further penetrates low permeability layers during alternating injection scheme. Nanofluid alternating gas even has a higher low-permeability-area gas penetration than continuous thickened CO2 with significantly less thickened CO2 volume used. Gas retention increment, as shown in Fig. 4, further confirms that conformance control in NAG scheme is improved. Not only both CO2 and thickened CO2 retention in general was higher in NAG than in CO2 flooding, but nanofluid retention has shown to be higher than pure CO2 in the NAG scheme.

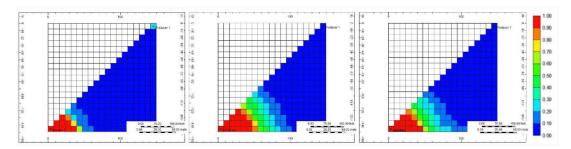


Figure 3—CO2 mole fraction in low permeability layer with CO2, thickened CO2 (0.5cp) and nanofluid alternating gas (0.5cp) at 0.5 HCPV injected

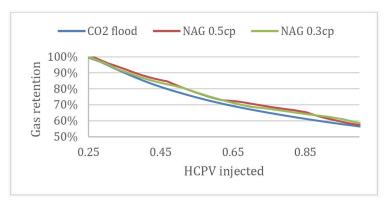


Figure 4—CO2 retention vs HCPV injected

It was observed that higher gas viscosities led to pressure loss in the reservoir, which can be problematic if it dropped below MMP. In this case, a modest increment of thickened CO2 injection pressure was sufficient to guarantee miscibility and gas liberation control.

CO2 utilization rates were also improved with nanofluid alternation as shown in Fig. 5. While still lower than continuous thickened CO2 utilization, an optimized economic performance can be adapted by adjusting NAG ratios. NAG not only has lower operational costs than continuous thickened gas injection, but also has a faster oil recovery as a function of time.

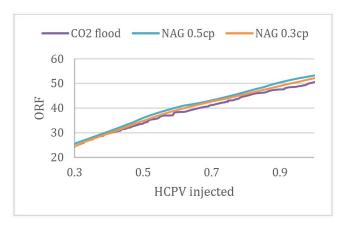


Figure 5—Oil Recovery Factor (%) vs HCPV injected

Gas production, which is a major economic issue in CO2 EOR projects, was also mitigated by the alternation of nanofluids and gas. Treatment plants for gas are a significant capital cost expenditure in CO2 EOR developments. Gas production as a function of HCPV injected was cut by half with nanofluid alternating gas in comparison to a continuous gas flood, as shown in Fig. 6. Another major advantage is the CO2 breakthrough delay.

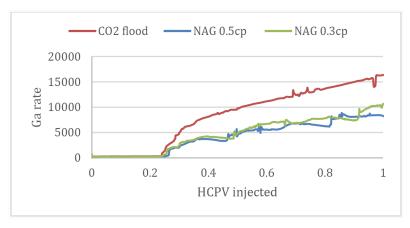


Figure 6—Gas Production Rate (m3/day) vs HCPV injected

WAG and Nanofluid-Alternating-Gas

Water Alternating Gas is the most commonly used scheme in CO2 EOR as it is capable of enhancing volumetric sweep efficiency and controlling gas production. Nonetheless, it has encounter operational problems regarding oil trapping, injectivity loss, relative-permeability-hysteresis mobility loss and pressure drop leading to loss of miscibility conditions. Depending on the petrophysical and fluid characteristics of the reservoir, larger gas slugs and lower WAG rates have the potential to remedy many issues encountered in these type of schemes, but may require further control regarding production gas rates and CO2 utilization. By injecting moderate slugs CO2 nanofluid within a WAG scheme (Fig. 7) we observed that overall outcomes were improved. Nanofluid introduced in WAG (nWAG) are able to increase CO2 utilization (Fig. 8) while controlling gas production rate and delaying gas breakthrough (Fig. 9).

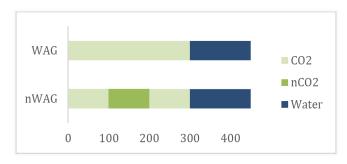


Figure 7—Fluid injection schemes in days

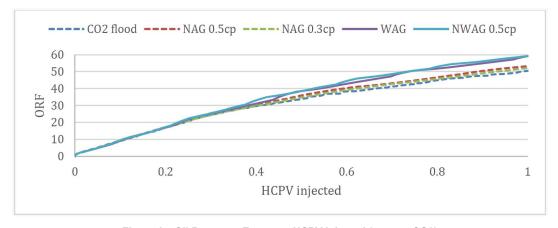


Figure 8—Oil Recovery Factor vs HCPV injected (water + CO2)

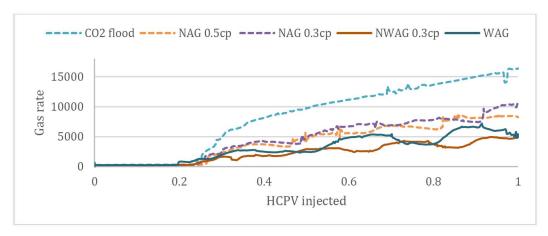


Figure 9—Gas Production Rate (m3/day) vs HCPV injected (water + CO2)

Higher oil recovery at breakthrough and greater gas retention (Fig. 10) suggests improved volumetric sweep efficiency with the utilization of nanofluid in nWAG schemes.

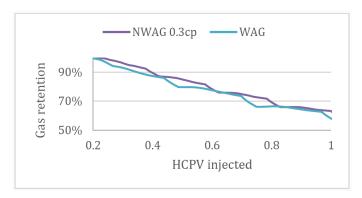


Figure 10—Gas retention vs HCPV injected (water + CO2)

Furthermore, loss of water mobility and injectivity due to the consideration of relative permeability hysteresis must be taken into account since it derives in an average pressure decline across the reservoir. WAG modeling with hysteresis consideration displayed significant gas liberation in the reservoir, inmiscible displacement, increased gas production and a significant decline in oil recovery factor. Higher injection pressure can be considered, although viability may depend on rock fracturing pressure.

General comparison

The utilization of CO2 nanofluid, both alternated with CO2 flooding and WAG injection, has substantial technical benefits. Gas utilization factors are improved by both the implementation of nanofluids and water. The combination of WAG scheme with thickened CO2 accounts for fluid efficiencies similar to continuous thickened CO2 injection (Fig. 11), with considerable operational costs reduction. For equivalent recovery factors, gas production is reduced by both the use of CO2 based nanofluid and water. The nWAG combination shows to have excellent gas control capacities, similar to continuous thickened CO2 injection (Fig. 12) although with significantly lower costs.

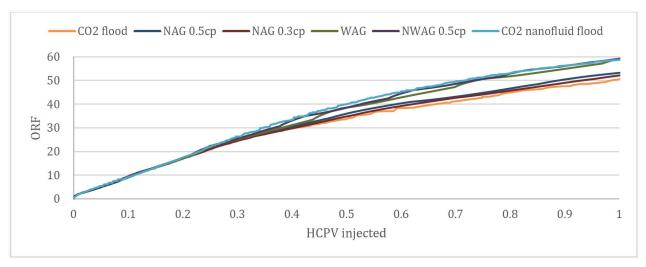


Figure 11—Oil Recovery Factor vs HCPV injected (water + CO2)

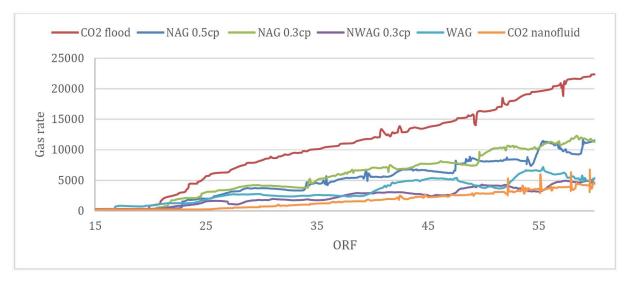


Figure 12—Gas Production Rate (m3/day) vs Oil Recovery Factor (%)

The rate, as a function of time, in which oil is produced is determinant of the NVP analysis and overall economic performance of a technology. While thickened CO2 has excellent technical performance indicators, high OPEX and slower recovery performance (Fig. 13) makes these projects economically challenging. In contrast, pure CO2 has the highest oil production rates at the cost of poor gas utilization and high gas production expenses. Nanofluid alternating gas, WAG and nWAG appear to be the best compromise solutions to ensure maximum economic and technical performance. In addition, the flexibility of this technology regarding nanofluid viscosity and slug size allows each individual project to tailor design their own injection schemes.

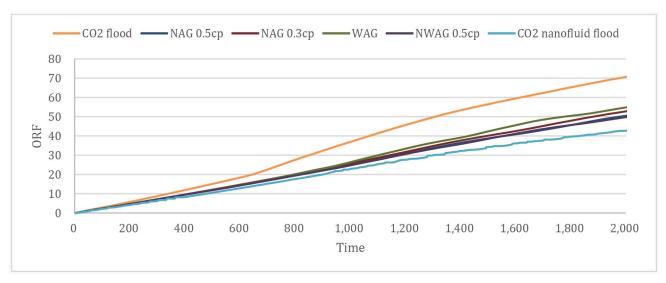


Figure 13—Oil Recovery Factor vs Time (days)

Conclusions

- Thickened CO2 injected both continuously and alternated with pure CO2 improve conformance and gas utilization in CO2 EOR projects
- Light oil requires moderate gas viscosity augmentation in order to improve sweep efficiency and guarantee miscibility, having reduced OPEX in comparison to heavy oil solutions
- Nanofluid-Alternating-Gas enhances conformance and gas utilization, with substantial cost savings with comparison to continuous thickened CO2 injection
- NAG can be alternated with water injection (nWAG) in order to improve conformance and gas production control
- nWAG allows the use larger gas slug sizes and decreasing WAG ratios where needed
- The flexibility of this technology regarding CO2 viscosity, thickened gas slug size and water alternation allows optimum technical and economic design of injection schemes
- Additionally nanofluids have a potential of having further positive impacts over other parameters such as asphaltene deposition or rock wettability alterations

References

- 1. Tiffin, D. L., & Yellig, W. F. (1983, June 1). Effects of Mobile Water on Multiple-Contact Miscible Gas Displacements. *Society of Petroleum Engineers*. doi:10.2118/10687-PA
- 2. Lin, E. C., & Huang, E. T. S. (1990, May 1). The Effect of Rock Wettability on Water Blocking During Miscible Displacement. *Society of Petroleum Engineers*. doi:10.2118/17375-PA
- 3. Shyeh-Yung, J.-G. J. (1991, January 1). Mechanisms of Miscible Oil Recovery: Effects of Pressure on Miscible and Near-Miscible Displacements of Oil by Carbon Dioxide. *Society of Petroleum Engineers*. doi:10.2118/22651-MS
- 4. Stern, D. (1991, January 1). Mechanisms of Miscible Oil Recovery: Effects of Pore-Level Fluid Distribution. *Society of Petroleum Engineers*. doi:10.2118/22652-MS
- 5. Shelton, J. L., & Schneider, F. N. (1975, June 1). The Effects of Water Injection on Miscible Flooding Methods Using Hydrocarbons and Carbon Dioxide. *Society of Petroleum Engineers*. doi:10.2118/4580-PA
- 6. Rogers, J. D., & Grigg, R. B. (2000, January 1). A Literature Analysis of the WAG Injectivity Abnormalities in the CO2 Process. *Society of Petroleum Engineers*. doi:10.2118/59329-MS

- 7. P. M. Jarrell, C. Fox, M. Stein and S. Webb (2002). Practical aspects of CO2 flooding. *Society of Petroleum Engineers*. SPE Monograph Series Vol. **22**. Pg.
- 8. Rogers, J. D., & Grigg, R. B. (2000, January 1). A Literature Analysis of the WAG Injectivity Abnormalities in the CO2 Process. *Society of Petroleum Engineers*. doi:10.2118/59329-MS
- 9. R. M. Enick and D. K. Olsen. Mobility and Conformance Control for Carbon Dioxide Enhanced Oil Recovery (CO2-EOR) via Thickeners, Foams, and Gels A Detailed Literature Review of 40 Years of Research. DOE/NETL-2012/1540. Activity 4003.200.01
- 10. Bae, J.H.; Irani, C.A. (1990, September). A Laboratory Investigation of Viscosified CO2 Process. *SPE 20467. published as SPE Advanced Technology Series*, Vol. 1, No. 1, April 1993, pp.166–171
- 11. J. Xu and R.M. Enick (2001). Thickening Carbon Dioxide with the Fluoroacrylate-Styrene Copolymer. SPE 71497, presented at the 2001 SPE Annual Technical Conference and Exhibition, held in New Orleans, LA, September 30-October 3, 2001
- 12. Z. Huang, C. Shi, J. Xu, S. Kilic, R.M. Enick and E. Beckman (2000). Enhancement of the Viscosity of Carbon Dioxide Using Styrene/Fluoroacrylate Copolymers, *Macromolecules*, 2000, Vol. **33**, No.15, pp. 5437–5442.
- 13. Shah, R. D. (2009, January 1). Application of Nanoparticle Saturated Injectant Gases for EOR of Heavy Oils. Society of Petroleum Engineers. doi:10.2118/129539-STU
- 14. S.I. Hashemi, B. Fazelabdolabadi, S. Moradi. (2016) et al. On the application of NiO nanoparticles to mitigate in situ asphaltene deposition in carbonate porous matrix. *Appl Nanosci* (2016) **6**: 71. doi:10.1007/s13204-015-0410-1
- 15. S. Jafari, A. Khezrnejad et al. (2015, January) Experimental investigation of heavy oil recovery by continuous/WAG injection of CO2 saturated with silica nanoparticles. *International Journal of Oil, Gas and Coal Technology*. Jan 2015, Vol. 9, Issue 2, pp. 169–179