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Foam Stability Enhanced Technology For Mobility Control Of CO2 EOR

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Summary

The latest CO2 foam technology reviews were conducted to understand recent research trends in CO2 enhanced oil recovery (EOR). In general, it is expected to improve CO2 sweep efficiency resulting in better oil recovery and prevention of early breakthrough. From CCUS point of views, the delay of gas breakthrough has a significant advantage in underground storage of industry-originated CO2. The reviews highlighted that various types of nano-additives have been investigated to develop further advanced foam technology. Key points to be focused on are how achieving more robust foam stability. Even a conventional CO2 foam generated with surfactant agents might be deteriorated in short period, those additives can extend foam half-life time. As additives, the recent researches have paid attention to nano-particles, polymer, viscoelastic surfactant, etc. The investigation measured half-life, viscosity, and differential pressure in core flood as key performance indicators. In addition, "high temperature (HT)" and "high salinity (HS)" are keywords in their researches. Namely, screening criteria of experimental conditions are aiming to more harsh conditions. However, the reviewed reports have not covered up to our target conditions in typical Middle East region. Thus, we have been concentrating to develop nano-additive enhancing CO2 foam technology in HTHS.

Introduction

Carbon dioxide (CO_2) has been used for a promising enhanced oil recovery (EOR) because of expecting miscible displacement whereby single phase oil is achieved by lowering minimum miscibility pressure (MMP). Even immiscible displacement, many advantages are still expected such as oil swelling, oil viscosity reduction, etc. The injection of CO_2 into reservoir is not only EOR but also a type of CO_2 sequestration. In other word, a series of EOR using CO_2 emissions from fossil fuel combustion in various industries: manufacturing and power plant, in particular, is Carbon Capture, Utilization and Storage (CCUS). However, a typical CO_2 EOR problem such as poor sweep efficiency makes more recycled CO_2 which are originated from carbon capture process, injected into reservoir and produced due to early gas breakthrough. This deteriorates CO_2 sequestration efficiency. The unexpected early gas breakthrough is often caused in heterogeneous reservoir consisting of high permeability layers and/or even in thick homogeneous reservoir allowing gravity segregation. To tackle with the technical challenges for improving sweep efficiency, a mobility control technology of injected CO_2 has been developed. The CO_2 foam technology has gathered interests as a high potential option. More homogeneous gas front can be created by increasing CO_2 viscosity in high permeable zone (see **Figure 1**).

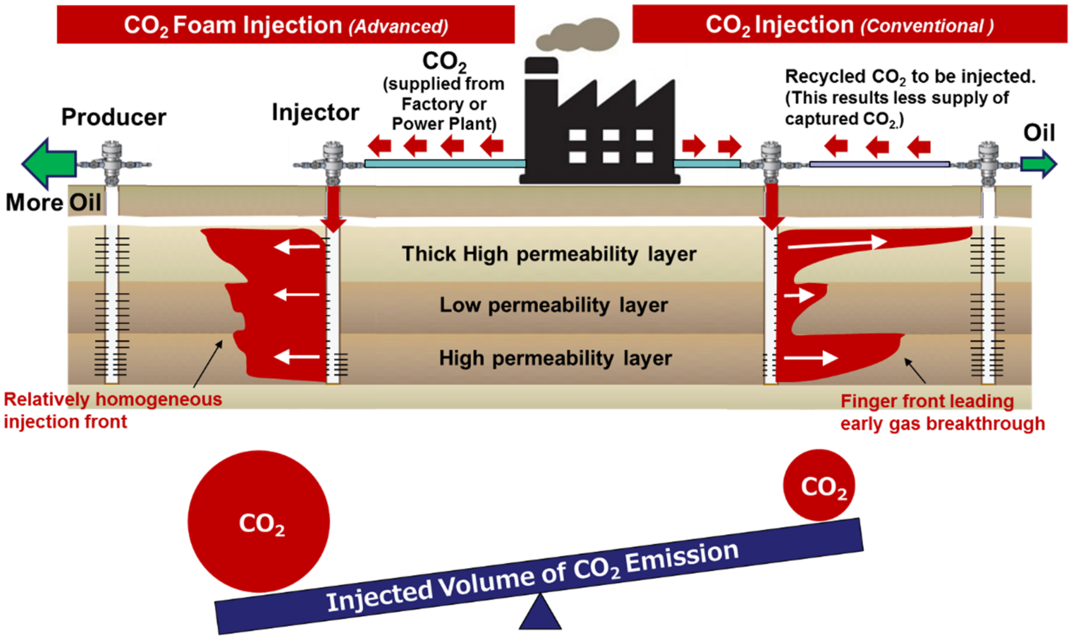

Figure 1 *Comparison of CO_2 EOR versus CO_2 Foam EOR from a viewpoint of storing CO_2 Emission.*

Recent Research Review

The CO_2 foam technology was initially patented and suggested in 1950's (Bond and Holbrook, 1958) and has long research history. This paper reviewed the recent advanced concept. A technical challenge of CO_2 foam is to improve foam stability in harsh reservoir condition: higher salinity and temperature because foam is thermodynamically and kinetically unstable in general. The expansion of CO_2 foam application criteria can contribute more CO_2 sequestration. From a viewpoint of enhancing foam stability, various additives have been evaluated in recent years.

- nanoparticles
- polymer
- viscoelastic surfactant (VES)

Nanoparticles have been investigated to stabilize foam by many researchers (Emrani *et al*. 2017; Emrani and Nasr-El-Din. 2017; Ibrahim *et al*. 2017; San *et al*. 2017; Nazari *et al*. 2018; Razali *et al*. 2018; Rognmo *et al*. 2018).

Emrani and Nasr-El-Din (2017) used two types of nanoparticles such as SiO_2 (two sizes: 100 and 140nm) and Fe_2O_3 (less than 50nm). They evaluated foam stability in the presence of nanoparticles as sensitivity analyses of pressure ranged from 300 to 800 psi, temperature ranged from 24 to 82°C, and NaCl concentration ranged from 1 to 5wt%. In their work, nanoparticles improved foam half-life at the milder conditions such as 24°C, NaCl 0.1wt%, or 300-400 psi. Ermani *et al* (2017) conducted another work using silica nanoparticle (140nm) that was not for EOR purpose but hydraulic fracturing utilization to improve mobility control of fracturing fluid. In this case, the performance of nanoparticle-stabilized CO_2 was investigated under the condition of 5wt% NaCl, and temperature of 25 and 121°C. As a result, foam stability could be improved by adding nanoparticle even at high temperature.

Four types of nanoparticles such as hydrophilic/hydrophobic types of SiO_2 (7-12nm), ZnO (less than 100nm), and TiO_2 (less than 25nm) were evaluated by Razali *et al* (2018) for comparing nitrogen foam half-life time at 110°C. As a result, three types of nanoparticles (two types of SiO_2 and TiO_2) revealed enhancing foam half-life time compared with that of surfactant foam alone. Hydrophilic type of SiO_2 was remarkable, in particular, because its addition showed only increase of half-life time at existence of oil (45°API). They proposed a mechanism of surfactant molecules attaching on the surface of SiO_2 nanoparticles to increase foam stability. The interface between SiO_2 and surfactant formed a steric layer at the lamella structure which could avoid foam shrinkage or expansion (see **Figure 2**).

In the study by Ibrahim *et al* (2017), both of SiO_2 nanoparticles and VES were utilized to stabilize CO_2 foam. The foam stability was evaluated through coreflood tests at 65°C and 5wt% NaCl. Addition of nanoparticles increased 6.5 % recovery factor from the baseline of CO_2 foam injection. Both addition of nanoparticles and VES revealed further increase of 7.7 % from the nanoparticles adding case (i.e. 14.2% increase from the baseline).

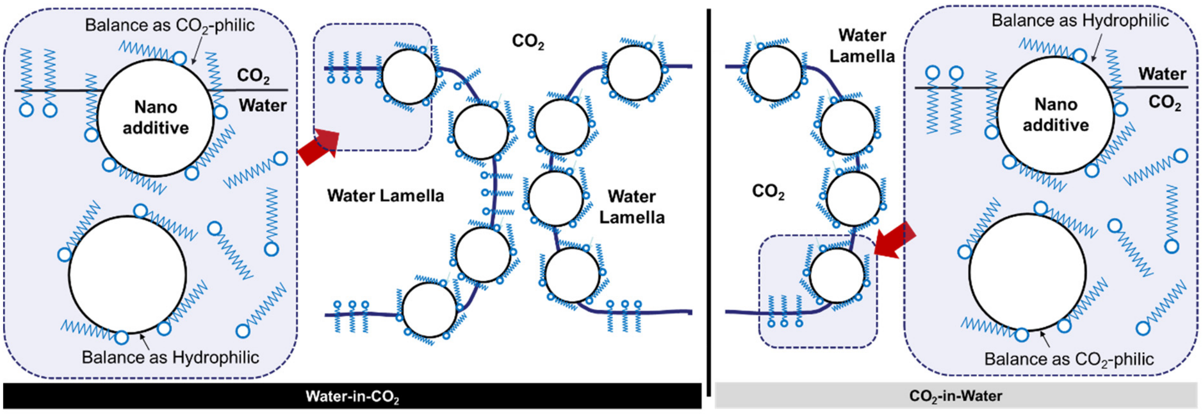

***Figure 2** Schematic Image of Nano-materials enhanced CO_2 Foam (CO_2-in-Water)/CO_2 Emulsion (Water-in-CO_2).*

A physics-based polymer enhanced foam flow model was established by Luo *et al* (2018). In their theoretical works, polymer additive improved foam stability by increasing viscosity in aqueous phase and disjoining pressure. Small sized polymers existing in foam film can boost foam stability because bonding between certain hydrophobic heads of polymers and surfactant molecules can increase surface elasticity.

Rognomo *et al* (2018) used silane modified colloidal SiO_2 nanoparticles (23nm) solution for CO_2 foaming purpose. The nanofluids were observed stable up to 25wt% TDS in the existence of mono- and divalent ions and up to 120°C through the static stability tests. The nanofluids revealed less retention compared with surfactant in coreflood tests using homogeneous and water-wet Bentheimer sandstone cores (1-3 darcy, 20-25% porosity).

Nazari *et al* (2018) focused on polyelectrolyte complex nanoparticles (PECNP). They mixed polymers and dextran sulfate sodium salt. The stability of mixture was confirmed in brine up to 200,000 ppm salinity. The core flooding using PECNP-added CO_2 foam showed the highest pressure drop in two brine concentrations of 34,000 and 67,000 ppm at 40°C.

The polymer enhanced CO_2 foam concept was also used by Ahmed *et al* (2017). They used a conventional polymer of hydrolysed polyacrylamide (HPAM) and associative polymer. This combination with the associative polymer revealed a significant viscosity enhancement. Their screening was performed by assuming a light crude (43°API), 3wt% NaCl and 80°C. The highest case of polymer-enhanced foam half-life extended twice of polymer free case.

Experiments

Currently, the foam technology has been attracting attention because of mobility control requirement in heterogeneous carbonate reservoirs. Therefore, a research target has been set to cover a typical harsh condition: high temperature (more than 99°C) and high salinity conditions (see **Table 1**) in Middle East region.

Table 1 *Typical Composition of Seawater and Arab D Formation Water. (Lindlof and Stoffer. 1983)*

	NaCl [ppm]	$CaCl_2$ [ppm]	$MgCl_2$ [ppm]	Na_2SO_4 [ppm]	Total [ppm]
Seawater	40,000	1,800	8,460	6,580	57,000
Arab D Formation Water	130,000	82,500	16,700	148	230,000

In our CO_2 foam EOR research (Yonebayshi and Miyagawa. 2017), we are developing useful nano-additives to stabilize CO_2 foam under high temperature and high salinity (HTHS) condition. After foamability/stability screening tests, the screened materials are planned to evaluate its apparent viscosity increase through a slimtube test. The first screening process have already revealed certain enhancement of CO_2 foam stability at HTHS. A typical slimtube apparatus is shown in **Figure 3**. Sand- or carbonate grain-packed slimtube (inner diameter of 4.7mm and length of 12m) is prepared with a heat jacket. Prior to the slimtube, a small sandpack is set for mixing purpose to create foam from simultaneous injected CO_2 and foaming agent solution (FAS). The foaming situation can be observed through a sight cell between the slimtube and sandpack. To evaluate viscosity increase, differential pressure is monitored during injection. By comparing with baseline case (i.e. water flood and/or CO_2 single injection), a relative effect of CO_2 foam can be understood. Currently, the differential pressure (dP) can be monitored for a whole slimtube; however, the apparatus is being improved to monitor several dPs by section such as inlet-side, middle, and outlet-side. Preparatory slimtube tests are being conducted to optimize the apparatus design: clear variation between foam flood and other cases, nano-additive consumption due to adsorption, mesh size for packed material retention, etc. The preliminary work could increase 4-5 times of viscosity compared with the water flood case under ambient condition. This viscosity increase was estimated 50 times higher than CO_2 sole injection.

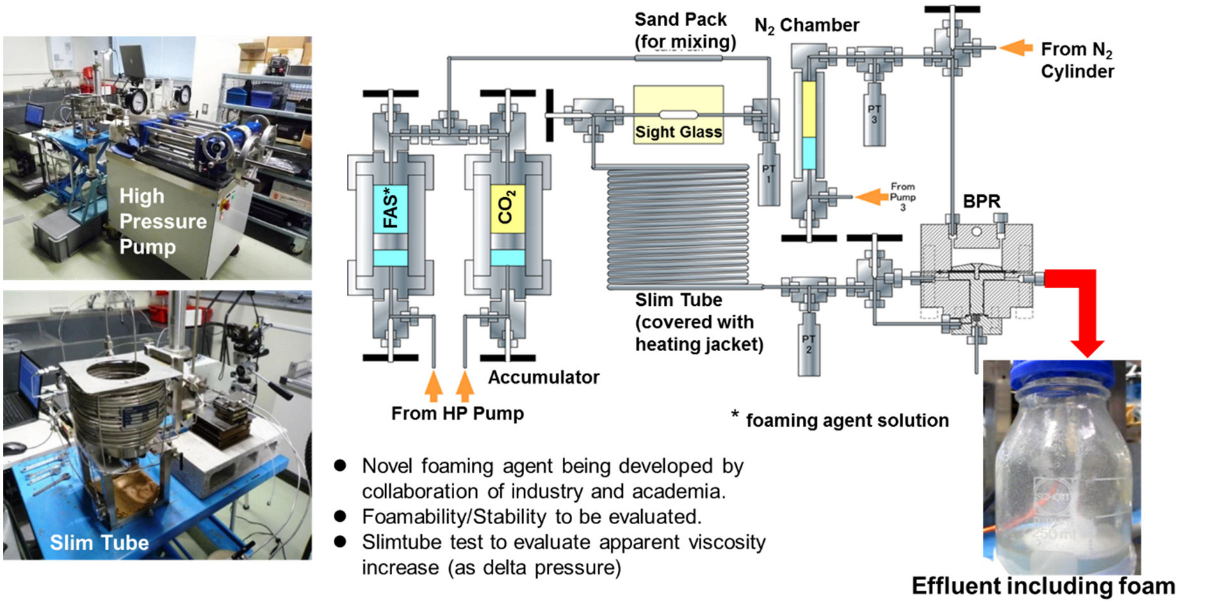

Figure 3 *Slim Tube Test Apparatus for Evaluating CO_2 Foam EOR from a Viewpoint of Differential Pressure Increase.*

Conclusions

- Various additives, such as nanoparticles and polymers, have been investigated to improve foam stability. The investigation were conducted from many perspectives of foam half-life time, viscosity increase, and differential pressure in flooding tests.
- Function of those additives are expected to work at harsh conditions: high temperature and high salinity. However, the recent researches have not been matchable to our target conditions in typical Middle East region yet.
- In our preliminary study, a potential of adding nano-additive was extracted through foamability tests at HPHT conditions and further investigation is necessary to estimate apparent viscosity increase in slimtube tests.

Acknowledgements

The authors would like to thank INPEX management for their permission to publish this paper. We gratefully acknowledge Nissan Chemical Corporation and Hirosaki University for the supply of nano-foaming agents.

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