THE EFFECTS OF NANOPARTICLE TYPES ON CARBON DIOXIDE FOAM FLOODING IN ENHANCED OIL RECOVERY

MOHAMMED JAMAL ALHAJ ESMAIL

UNIVERSITI TEKNOLOGI MALAYSIA

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MOHAMMED JAMAL ALHAJ ESMAIL

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To my beloved The Almighty, Allah S.W.T.,

To my beloved Prophet Muhammad S.A.W.,

To whole Muslim Umma.,

To my beloved family and friends.

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ABSTRACT

Carbon dioxide (CO_2) flooding is a well-established and extensively used enhanced oil recovery technique. However, the mobility of the CO_2 in the reservoir is higher than the mobility of crude oil which viscous fingering and gravity segregation problems always occur during CO_2 injection. To overcome these problems, foams has been used to improve displacement efficiency because foam has high viscosity and low mobility. Although surfactants are good foaming agents, there are several weaknesses on surfactant-stabilized foam which are high surfactant retention in porous media, relatively low foam stability and degradation of surfactant at high reservoir pressure and temperature. However, nanoparticles (NPs) properties such as being solid, able to withstand high temperatures and very small size can be utilized to improve foam stability. The main objective of this project was to investigate CO_2 foam performance at various concentrations of different types of nanoparticles ((Silicon Dioxide, Aluminium Oxide, Titanium Dioxide and Copper Oxide in the presence of fixed concentration of surfactant (0.5 wt% of AOS) and salinity (2 wt% of NaCl). In this study, experiments were divided into two parts. The first part was to investigate foam stability at various nanoparticle concentrations (0.1 wt%, 0.3 wt%, 0.5 wt% and 1 wt%), whereas, the second part was the displacement test for determining oil recovery at the optimum concentrations for each nanoparticle. The results revealed that all nanoparticle types used were able to improve the stability of CO_2 foam at certain concentrations. However, the optimum concentration was found at 0.1 wt%. It was clearly observed that the introduction of higher nanoparticle concentrations decrease the foam stability for all nanoparticle types. Furthermore, the oil recoveries were 14% by Al_2O_3 NPs, and 11% by SiO_2 NPs. Meanwhile, both TiO_2 and CuO NPs recovered about 5%. The recovery results matched with the stability results for all types of nanoparticles used.

ABSTRAK

Banjiran karbon dioksida (CO_2) ialah teknik yang meluas digunakan dalam perolehan minyak tertingkat. Bagaimanapun, mobiliti CO_2 dalam reservoir adalah lebih tinggi daripada mobiliti minyak yang menyebabkan masalah jejarian pengasingan graviti berlaku semasa suntikan CO_2. Untuk mengatasi masalah ini busa telah digunakan untuk meningkatkan kecekapan sesaran kerana ia berkelikatan lebih tinggi dan mobility yang lebih rendah. Walaupun surfaktan ialah agen pembusa yang baik, terdapat beberapa kelemahan pada kestabilan busa surfakatan iaitu surfakatan yang tinggi di media berliang, kestabilan busa agak rendah dan degradasi surfakatan pada tekanan takungan dan suhu tinggi. Bagaimanapun, ciri-ciri utama partikal nano seperti merupakan pepejal, berupaya bertahan pada suhu tinggi dan saiznya yang sangat kecil boleh digunakan untuk meningkatkan kestabilan busa. Objektif utama projek ini adalah untuk menentukan ciri-ciri khas busa CO_2 dengan menggunakan pelbagai jenis partikal nano (silikon dioksida, alluminium oksida, titanium dioksida dan kuprum oksida) pada pelbagai kepekatan dengan kepekatan surfakatan yang tetap (0.5 wt% AOS) dan kemasinan air (2 wt% NaCl) yang tetap. Dalam kajian ini, eksperimen dibahagikan kepada dua ujian. Ujian pertama dijalankan untuk menyiasat kestabilan busa pada pelbagai kepekatan (0.1 wt%, 0.3 wt%, 0.5 wt% dan 1 wt%). Manakala, ujian kedua ialah ujian sesaran untuk penentuan perolehan minyak pada kepekatan optimum yang ditemui dalam ujian kestabilan untuk setiap partikal nano. Keputusan mendedahkan bahawa semua empat jenis partikal nano yang digunakan mampu memperbaiki kestabilan busa CO_2 pada kepekatan tertentu. Bagaimanapun, kepekatan optimum didapati ialah 0.1 wt% dan dengan kepekatan partikal nano yang lebih tinggi akan mengurangkan kestabilan busa untuk semua jenis partikal nano yang digunakan. Selanjutnya pula, perolehan minyak optimum ialah 14% oleh Al_2O_3, diikuti 11% oleh SiO_2. Sementara itu, kedua-dua TiO_2 and CuO menghasilkan perolehan 5%. Keputusan perolehan minyak adalah sepadan dengan keputusan busa bagi partikal nano yang terlibat.

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LIST OF ABBREVIATION

AOS	Alpha Olefin Sulfonate
CMC	Critical Micelle Concentration
CO_2	Carbon Dioxide
EOR	Enhanced Oil Recovery
ROS	Residual Oil Saturation
WAG	Water Alternation Gas

LIST OF SYMBOLS

P_A	-	Liquid pressure at centre lamella
P_B	-	Liquid pressure at Plateau border
P_{CA}	-	Capillary pressure at centre lamella
P_{CB}	-	Capillary pressure at Plateau border
P_G	-	Pressure in gas- phase
R	-	Radius of curvature
R_{1A}	-	radius of curvature at the lamella centre
R_{1B}	-	radius of curvature at the plateau border
V_g	-	Gas foam volume
V_L	-	Liquid solution volume
wt%	-	weight percent

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CHAPTER 1

INTRODUCTION

1.1 Background

A fast growth of worldwide oil demand and the subsequent surge in oil prices is intensifying the efforts to increase oil production. These efforts are classified in three categories: finding new oil reserves, developing proven reserves and improving the efficiency of oil production. The rate of new oilfield discoveries is in steady decline and most of the producing oilfields are in late stages of production which makes it most unlikely to have any breakthrough in the first two categories. But taking into account the fact that about two third of reservoir oil cannot be recovered by conventional production methods, the importance of improving oil production efficiency by enhanced oil recovery (EOR) techniques can be acknowledged.

Therefore, EOR methods are the key techniques applied to increase the oil recovery from the existing oil reservoirs, and to increase the oil field production life cycle by mobilizing the remaining trapped oil. EOR involves the injection of fluids that are not present in the underground reservoir to mobilize the immobile remaining oil (Lake, 1989).There are several common types of EOR techniques that are chemical flooding, thermal recovery processes, gas flooding, microbial enhanced oil recovery and vibro-seismic technology.

Gas flooding is one of the most widely applied EOR methods in field applications. Gas flooding is normally applied on the reservoir that has been water flooded. The type of gas injected in this method can be hydrocarbon (light natural gas) and non-hydrocarbon. The non-hydrocarbon gas can be nitrogen, carbon dioxide, flue gas, hydrogen sulphide, and others. The fundamental mechanism of gas flooding method is to increase microscopic sweep efficiency of the oil displacement and reduce the residual oil saturation (ROS) (Lake, 1989).

The viscous fingering and gravity segregation are the main issues of displacing gas due to frontal instability in gas flooding. To mitigate these problems, water alternating gas injection (WAG) has been used in several field applications (Dicharry *et al.*, 1973; HR, 1977). One of the drawbacks is that the contact between the resident oil (displaced fluid) and injected gas (displacing fluid) is blocked by the large quantity of injected water leading to a larger ROS. This water-blocking phenomenon is more detrimental in water-wet reservoir or the reservoir that has been water-flooded previously as secondary recovery technique (Stalkup, 1970). Some of the injected gas (such as CO_2) has high solubility in water and it increases the consumption of that gas making the project less economically feasible, but injecting some harmful gases (such as CO_2) into the subsurface can have a potential impact on altering both oil recovery and/or sequestration (and storage) which has good effect from the environmental view.

Concept of applying gas foam for mobility control was first proposed by Bond and Helbrook (Holbrook, 1958). To alleviate the challenges of gas flooding and WAG process, foam flooding using the injected gas can be the potential solution (Du *et al.*, 2007; Farajzadeh *et al.*, 2009a; Fried, 1960; Rossen, 1996). Applying foams in EOR techniques is very useful to improve displacement efficiency because of its high viscosity and low mobility during the displacement across a porous medium (Green and Willhite, 1998). Extensive experimental studies were performed on using surfactant as the foam generation agent to stabilize the foam to reduce the gas mobility in gas flooding (Kim *et al.*, 2004). The Snorre CO_2 flood was one of the most successful demonstrations of foam mobility control (Tore *et al.*, 2002). Foam also was used as mobility control for surfactant aquifer remediation at Hill Air Force

Base in Utah (Hiraski, 1989). Other than that, foam was used as mobility control for alkaline surfactant flooding in China (Demin *et al.*, 2001; Yunxiang *et al.*, 2000). However, there are several weaknesses of surfactant-stabilized foam and these are high surfactant retention in porous media, relatively low foam stability, and degradation of surfactant at reservoir conditions (Kim *et al.*, 2004; Ransohoff and Radke; 1988, Wang, 1984).

Nanotechnology has been developed in various fields in the past few decades. In the petroleum industry, applications of nanoparticles contribute to the exploration, formation evaluation, well drilling, production, enhanced oil recovery, etc. (Shen et al., 2006). Potential applications of nanotechnologies in oil industry include: injection of nanoparticles (nano sensors) into tight oil-bearing sandstones for data collection/characterisation of reservoirs; drilling fluid mixed with nanoparticles for wettability alteration and drag reduction; effect of nanoparticle size exclusion on the efficiency of EOR. This new technology developed in Nano-science has provided an alternative for the generation of stable CO_2 foam.

Studies show that small solid particles can absorb at fluid/fluid interfaces to stabilize drops in bubbles in foams. These solid stabilized dispersions may remain stable for years in storage. Nanoparticle stabilized CO_2 foam has several advantages such as nanoparticle being solid; the nanoparticle stabilized foams have potential to withstand the high temperature reservoir conditions for extended periods. With their very small size, suitably surface-treated in this case by Triton X-100 nanoparticles can flow easily in the reservoir rock (Espinoza *et al.*, 2010).

This recent widely developed nanotechnology has provided an alternative in creating a more stabilized foam using nanoparticles without surfactant or in additional to surfactant. Dickson et al.,(2004) highlights that the higher adhesion energy of nanoparticles to the fluid interface stabilizes longer lasting foams than surfactant.

This study focuses on the effects of different types of nanoparticles with various concentrations on stabilized CO_2 foam for mobility control in immiscible flooding with fixed concentration of anionic surfactant (AOS) and brine.

1.2 Problem Statement

The critical weaknesses for CO_2 flooding are the poor volumetric sweep efficiency due to channeling of CO_2 because of low viscosity, and gravity segregation because of its low density. Both of these factors are important for improving mobility control.

The implication of foam in mobility control was first brought up by Bond and Helbrook (Holbrook, 1958). Foam is used at all stages in petroleum recovery and processing industry such as production, drilling, injection and process plants. In EOR, foams are used to reduce gas mobility, thus, improve the mobility ratio of oil and solution. Foam quality is one of the most controversial parameters affecting foam flow behavior.

By adding an additive in the foam aqueous phase we can enhance foam stability and apparent viscosity. Surfactant is one of the common foaming agents. There were many extensive research efforts carried out on surfactant-stabilized foams and they presented several weaknesses that are unstable foam properties, high surfactant retention in porous media and surfactant degradation at reservoir condition (Kim *et al.*, 2004; Ransohoff and Radke; 1988, Wang, 1984). Instead of using surfactant, polymer is added to foam as additive. Many research has been done to check foam stabilization after adding polymer and the results of the experiments show that polymer destabilize foam moderately. They conclude that there is no intrinsic stabilizing effect of polymer to foam in the presence of crude oil.

Nowadays, the development of nanotechnology provides many alternatives and potential opportunities to the oil and gas industry especially the applications of nanoparticles in EOR techniques (Zhang *et al.*, 2010; Zhang *et al.*, 2009). One of the applications is to create stable nanoparticle stabilized foam that is able to withstand the high temperature reservoir condition.

However, this study focuses on the effect of different types of nanoparticles Silicon Dioxide (SiO_2), Titanium Dioxide (TiO_2), Aluminum Oxide (Al_2O_3) and Cupper Oxide (CuO) on CO_2 foam properties performance. All nanoparticles used with various concentrations start from 0.1 wt% , 0.3 wt%, 0.5 wt% and 1 wt%, with fixed concentrations of salinity 2%wt (NaCl) and surface foaming agent (Alpha Olefin Sulfonate (AOS)).

1.3 Objective of Study

The objectives of this study are:

a) To determine the effectiveness of different nanoparticle types on CO_2 foam stability by using various concentrations of nanoparticles at fixed surfactant concentration (AOS) and dispersion salinity.

b) To determine oil recovery performance of each nanoparticle type and compare their results.

1.4 Scope of Study

In this study, parameters interested to enhance the performance of foam are nanoparticles types (Aluminum Oxide (Al_2O_3), Silicon Dioxide (SiO_2), Titanium Dioxide (TiO_2) and Copper Oxide (CuO)) and nanoparticles concentrations (0.1 wt%, 0.3 wt%, 0.5 wt% and 1 wt%) with fixed concentration of anionic surfactant (AOS) and water salinity.

For purpose of this study, sand pack models with 30.5 cm of length and 5.4 cm of diameter made from Acrylic (Perspex) were used and packed with granule sizes of sand in range between 250-355 μm. Porosity and permeability of sand packs were measured.

The stability test was prepared and modified based on ASTM-D 6082-62, D892-06 and D1881-97 (Borole and Caneba, 2013). In this study the stability of the aqueous foam was evaluated by the Ross-Miles method, using half-life measurements. The technique used in generation of foam is air expansion. This technique was used to evaluate the stability of foams in presence of nanoparticles, surfactant and brine.

Displacement tests were carried out by using five unconsolidated sand pack models. The sand packs were located in the horizontal position to consider that the effect of gravity force is negligible. Initial oil saturation was created by red dye paraffin oil which took a role as oil. Water flooding was applied for secondary recovery with 2PV, flow rate of 3ml/min and oil recovery after water flooding was calculated. Lastly, sand packs were subjected to foam flooding by injecting aqueous nanoparticles dispersion at 4 ml/min with co-injected CO_2 gases at 9 ml/min for additional oil recovery and for better volumetric sweep efficiency. All experiments were conducted at atmospheric pressure and room temperature.

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