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Enhanced oil recovery from fractured carbonate reservoir using membrane technology

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ABSTRACT

Membrane technology has been investigated experimentally for enhanced oil recovery (EOR) in fractured rocks in this paper. Two membrane-forming material fluids, copper sulfate solution and potassium hexacyanoferrate solution, are sequentially injected into a fractured rock which was pre-saturated with mineral oil and irreducible water using a high solute fluid, to form a semi-permeable membrane over the surface of fractured rock. Then a low solute concentration fluid is injected into the rock to establish a chemical potential gradient across the membrane. As a result, water can enter the matrix across the membrane to increase the pore pressure and to displace additional oil from the matrix. Factors which influence osmotic pressure have been examined for their effect on oil recovery. It was found that the rate of oil recovery increases with increasing concentrations of membrane-forming materials, increasing temperature, and increasing solute concentration ratio between matrix water and injection solution, as well as decreasing permeability of the matrix rocks. Such correlation is attributed to the spontaneously occurrence of osmosis, leading to water entering the matrix and oil being displaced. The results are indicating that the membrane technology may be an effective EOR method for a fractured carbonate reservoir.

1. Introduction

Oil recovery in naturally fractured reservoirs is typically quite low. In medium-permeability to high-permeability naturally fractured carbonate reservoirs, in particular, oil recovery is often less than 15% of the oil-in-place. In such cases, it is generally difficult to recover the oil from the matrix due to fingering, where the injected flooding solution bypass through easy paths available in the natural fractures. Water flooding is often used to displace oil from the carbonate reservoir but generally it is only effective in the presence of the higher permeability natural fractures.

As many carbonate oil reservoirs are mixed or oil-wet, spontaneous imbibition of water from the water flood was too low to improve recovery from bypassing through natural fractures and matrix portion of the reservoir. One of the basic problems in carbonate EOR lies in increasing the sweep efficiency of water flooding. Injected water breakthrough too early in the production wells due to the fingering of the water through the highly permeable natural fractures, leaving behind oil in the matrix without being mobilized. Even in cases where the imbibition or water flooding is successful, the process is very slow and/or water production or cycling is very high.

Technologies are advancing for enhancing the oil recovery from fractured reservoir. An experimental study of supercritical CO_2, CO_2-foam, and N_2-foam injections in fractured Edwards limestone core samples was reported (Haugen et al., 2014). The results showed that mobility control by foam improved both the recovery rate and ultimate oil recovery in fractured, limestone core plugs compared with injections without mobility control. Improvement by foam was the most prominent at oil-wet conditions. Foam injections under miscible conditions had significantly higher recovery rates than for immiscible conditions.

Oil can be recovered from fractured, initially oil-wet carbonate reservoirs by wettability alteration with dilute surfactant and electrolyte solutions. The idea of injecting surfactant solution to improve imbibition recovery was proposed later for fractured North Sea chalk (Austad and Milter, 1997). Wettability alteration increased the oil recovery rate from initially oil-wet Texas Cordova Cream limestone cores by imbibition (Gupta and Mohanty, 2011). In fractured reservoirs, an effective matrix-fracture mass transfer is required for oil recovery. Surfactants have long been considered for oil recovery enhancement, mainly in terms of their ability to reduce oil–water interfacial tension. Surfactants are effective when

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the fractured formations are water-wet, where capillary imbibition of surfactants from the fracture into the matrix contributes to oil recovery. However, another beneficial aspect of surfactants, namely their ability to alter wettability, remains to be explored and exploited. Surfactants are capable of altering wettability especially in oil-wet fractured formations, where the surfactant in the fracture diffuses into the matrix and alters the wettability, enabling imbibition of even more surfactant into the matrix. This sequential process of initial diffusion followed by imbibition continues well into the matrix yielding significant enhancements in oil recovery (Ayirala et al., 2006). The effect of fractures on oil recovery and in-situ saturation development in fractured chalk has been determined at near neutral wettability conditions (Aspenes et al., 2007).

Capillary imbibition is one of the major recovery mechanisms in naturally fractured reservoirs where most of the oil is stored in tight matrix blocks (Qasem et al., 2008). For naturally fractured reservoirs which typically have low primary recovery with water injection or aquifer drive, the subsequent recovery of oil from the rock matrix is mainly dependent on the process referred to as spontaneous imbibition of water (Morrow and Mason, 2001). In this process, water is sucked into the oil containing matrix blocks from the fractures by capillary forces and then oil is expelled. Two main types of spontaneous imbibition (also known as free imbibition or capillary imbibition) are recognized: counter-current spontaneous imbibition, in which the displacing wetting fluid flows in the opposite direction to the produced non-wetting fluid, and co-current spontaneous imbibition, in which wetting phase and non-wetting phase flow in the same direction.

Membrane technology is widely applied in petroleum industry (Charles and Harry, 1978). Application of thin film composite membranes with forward osmosis technology has been reported for the separation of emulsified oil–water (Bader, 2006; Duong and Chung, 2014). It showed that osmotic pressure can be treated as a hydraulic potential that drives water into or out of shale formations (Chen et al., 2003). The first suggestion of semi-permeable membranes to create osmotic pressure for oilfield application had been previously described in a United States patent (Hinkel and England, 2000). The patent described the use of a chemical potential gradient or osmotic pressure gradient to remove fracturing fluid from an artificially created fracture and thereby increasing the effective length of the created fracture. A technical review of osmotic pressure with regards to its application in petroleum industry as well as in other areas is presented in the next section.

The first step of EOR based on membrane osmosis is to determine the in-situ properties of the fluids naturally present in the fractured reservoir, so as to help designing the fluid formulation. The next step is to pump a fluid containing a membrane-forming material into the injecting wellbore. The injection volume is determined with the knowledge of the swept volume between the injecting well and the producing wells. The membrane will provide a barrier between the water swept in the higher permeability natural fractures and that present in the matrix of the reservoir immediately adjacent to the natural fractures. The next fluid to be pumped is a fluid with a low solute concentration (compared to the formation water in the matrix) to displace the water in the natural fracture leaving the membrane in place. As the low solute fluid is injected, the natural process of osmosis will take place due to the chemical potential gradient.

Preferred membranes should possess the following characteristics, such as water-wet, easy and cost-effective to establish, and be capable to achieve acceptable capillary pressures. The ideal membrane should be freely permeable to water, impermeable to all solutes, and even more preferably permeable to oil in a reverse direction to the water. The key is to lock solute in the matrix to attract water, hence displace oil by increasing the hydrostatic pressure. Materials suitable to establish the membrane include polyhydroxy compounds (Moawed and El-Shahat, 2013), galactomannans crosslinked with boric acid (Ratcliffe et al., 2013), and cellulose acetate (commonly used in dialysis) (Senna et al., 2014). The membrane can also be prepared with inorganic materials. In this study, for example, a semi-permeable membrane of copper hexacyanoferrate was formed with a membrane-forming fluid containing copper sulfate and potassium hexacyanoferrate trihydrate. Copper sulfate and potassium ferrocyanide can contact and react to form a copper hexacyanoferrate membrane.

2. Technical background

Osmotic pressure is the hydrostatic pressure produced by a solution in a space divided by a semipermeable membrane due to a differential in the concentrations of solute. Osmotic potential is the opposite of water potential with the former measuring the degree to which a solvent (usually water) tends to stay in a liquid.

When a difference in solute is present on the two sides of a membrane water flows across the membrane into the side with more concentrated solute, causing the particular side to expand due to osmotic pressure. The osmotic pressure π of a dilute solution can be calculated using the formula

$$\pi = iMRT \tag{1}$$

where

i is the van't Hoff factor,

M is the molarity,

R is the gas constant, where $R = 0.08206\ \mathrm{L\ atm\ mol^{-1}\ K^{-1}}$,

T is the thermodynamic temperature (formerly called absolute temperature).

Note the similarity of the above formula to the ideal gas law and also that osmotic pressure is not dependent on particle charge.

Osmotic pressure is the basis of reverse osmosis, and the process commonly used to purify water (Khorami et al., 2013). The water to be purified is placed in a chamber and put under an amount of pressure greater than the osmotic pressure exerted by the water and the solutes dissolved in it. Part of the chamber opens to a differentially permeable membrane that lets water molecules go through, but the solute particles could not. The osmotic pressure of ocean water is about 27 atm. While the pressure used by reverse osmosis desalinators to produce fresh water from ocean salt water is around 50 atm.

Osmotic pressure is necessary for many plant functions. It is the resulting turgor pressure on the cell wall that allows herbaceous plants to stand upright, and to regulate the aperture of their stomata. As to animal cells which lack cell walls however, excessive osmotic pressure can result in cytolysis.

Zhang et al. (Zhang et al., 2014) investigated a hybrid forward osmosis membrane distillation (FO–MD) system for sustainable water recovery from oily wastewater by employing lab-fabricated FO and MD hollow fiber membranes. Pore pressure changes by various mechanisms such as capillary flow, viscous flow and osmosis flow (Zeynali, 2012). Osmosis flow driving force is due to the existing chemicals and ions with different compositions in pores and the outside solution.

This paper proposes the utilization of osmosis procedure to create an osmotic pressure gradient so that fluids will be forced to flow with the purpose of displacing unrecovered or previously unrecoverable oil.

As the fluid carrying the membrane-forming additives fills the fractures, a membrane can be formed on the exposed surface of the fractures, resulting in a film or skin-like substance that is semi-