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**A Discussion On Chemical/Physical Understanding of Ionically Modified Water EOR
Method In Carbonate Reservoirs**

Hossein Ali Akhlaghi Amiri

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A Discussion On Chemical/Physical Understanding of Ionically Modified Water EOR Method In Carbonate Reservoirs

Hossein Ali Akhlaghi Amiri^{1,*} Mohammad Reza Rokhfrouz²

¹ Chemical Engineering Department, Faculty of Engineering, Ferdowsi University of Mashhad, Mashhad, Iran

² Department of Chemical and Petroleum Engineering, Sharif University of Technology, Tehran, Iran

*Corresponding Author's E-mail: ha.akhlaghi@um.ac.ir

Abstract

Water flooding has been the most frequent secondary method in enhancing oil recovery. During the last three decades, however, it has been discovered that injected water can be improved by modifying ionic composition and strength to cause oil recovery increment in fractured carbonate reservoirs by wettability alteration. Wettability alteration (toward water wet) enhances spontaneous imbibition from fractures into matrix. But the chemistry/physics behind this process is still under debate. The key to improve understanding about the real mechanism is to sum up the experimental studies done on crude oil-brine-rock interactions, being validated by field observations. This work evaluated different suggested chemical/physical theories. From chemical point of view, SO_4^{2-} in ionically modified water reduces the positive charge of carbonate surface, while Ca^{2+} (Mg^{2+}) releases carboxylic group of the oil from surface. However, from physical point of view, expansion or compression of electrical double layer of counter ions on mineral surface in presence of ionically modified water is the cause of wettability alteration.

Introduction

Almost all conventional onshore and offshore reservoirs go through water flooding after natural depletion, to recover the remaining oil. Water injection maintain reservoir pressure and displace oil by viscous force. However, even after a waterflood, a considerable amount of oil remains in porous media, especially in carbonate reservoirs.

The majority (almost 90%) of Iranian oil reservoirs are carbonate (limestone, dolomite or chalk). These type of reservoirs are normally highly fractured, mixed to oil wet and have low matrix permeability. Oil recovery, after waterflooding, is less than 30% in these reservoirs. The remaining oil is trapped in part because of interfacial and surface forces in pores.

Since 1980's it has been discovered that water flooding with different ion composition compared to formation water may cause incremental oil recovery; especially after exceptional experience of seawater flooding in Ekofisk chalk oil field in North Sea. Since then, the industry attention was drawn by the concept of this advanced water flooding and numerous experimental works were done to find the mechanism. The majority of the observed mechanisms were attributed to wettability alteration of the rock surface in presence of brine with different composition. Alteration of matrix rock wettability toward water wet results in positive capillary pressure; hence enhancing spontaneous imbibition of water from fracture into matrix pores.

Despite all the attempts, the detailed mechanism and the chemical/physical background of this process is not yet fully understood. Austad and his coworkers [1,2,3] reported numerous laboratory works, including core flooding and spontaneous imbibition tests, as a function of brine composition and temperature and emphasized on chemically based

interactions resulted by smart (ionically modified) water flooding. They attributed the wettability alteration to the chemical reaction of potential determining ions (PDI) with calcite mineral surface, which is positively charged in the pH range of formation brine. However, the influence of water salinity (multivalent ions of brine) on surface charge density and electrical double layer thickness were mentioned by some researchers [4,5] in this field as the main mechanism during advanced water flooding. The aim of this work is to sum up the proposed mechanism to conclude a realistic principle behind the wettability alteration during ionically modified water injection.

Result & discussion

Chemical understanding

The wetting condition of carbonates is dictated by pH of the equilibrium brine, reservoir temperature, crude oil properties including acid and base number and brine composition including divalent determining ions. Due to high buffer capacity of $CaCO_3$, the pH in carbonate reservoirs is almost constant, in the range of 7-8. In this range of pH, calcite surface charge is positive. Dissociation of surface reactive acidic components (carboxylic acid) in heavy fractions of oil, e.g., asphaltene and resin, causes negative charge in oil-brine interface. Under this condition, carboxylic group chemically adsorbs strongly onto the calcite surface and hence the carbonate becomes oil wet (Figure 1a).

Introducing smart water with modified divalent ion composition can change this chemical stability. SO_4^{2-} , which is one of the potential determining ions in smart (sea) water, will influence the charge density and sign of carbonate surface, even at low concentrations. So carbonate becomes less positively charged, hence adsorbed carboxylic material become loose and also Ca^{2+} (or Mg^{2+} at higher temperatures) of the brine approach the surface. Ca^{2+} (or Mg^{2+}) then bound with carboxylic group and release it from the surface, so wettability of the surface will be modified toward more water wet. The schematic of this process is depicted in Figure 1b and c.

Chemical theory of smart water can also explain observed enhancing oil recovery of low salinity water in some of carbonate rock samples [3]. Presence of anhydrite ($CaSO_4$) in structure of carbonate rocks, may support aqueous SO_4^{2-} of the injected brine.

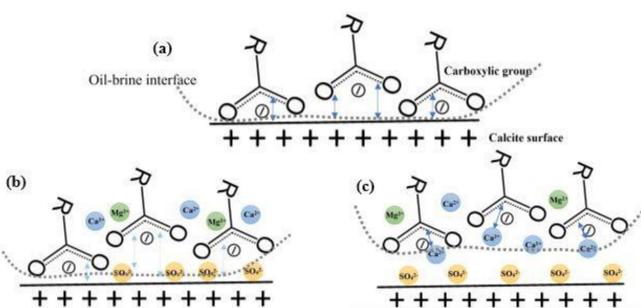


Fig.1. Schematic illustration of the oil-brine-rock chemical interactions a) oil wet surface before smart water injection, b) loosed oil-rock bonds due to SO_4^{2-} in injected brine, and c) bonding Ca^{2+} with carboxylic group and releasing it from surface

Physical understanding

Another explanation for ionically modified water EOR is based on stability of water film on mineral surface, affected by electrical double layer and zeta potential around surface surrounded by aqueous phase. Water film on the mineral surface can be described as bounded by an brine-oil interface on one side and brine-rock interface on the other side [4,5]. As the brine-oil and rock-oil interfaces have opposite charges, electrostatic attraction results in thin water film, as shown in Figure 2a; hence probably oil wet mineral surface. Conversely, when these two interfaces have similar charges, an electrostatic force of repulsion increases the disjoining pressure and results in thick water film (Figure 2b). This situation is more likely modify the surface wettability to more water wet situation. Electrical double layer around brine-rock interface depends on electric surface charge, which is a function of the injected brine salinity and pH.

Wettability of carbonates is dictated by the stability of water film between the rock surface and the oil phase which is related to zeta potential of oil-water-rock interfaces. It has been found that seawater depleted in Na^+ and Cl^- ions results in higher oil recovery. Less concentration of these ions in double layer provides easy access of divalent ions (SO_4^{2-} and Ca^{2+}) to reach mineral surface.

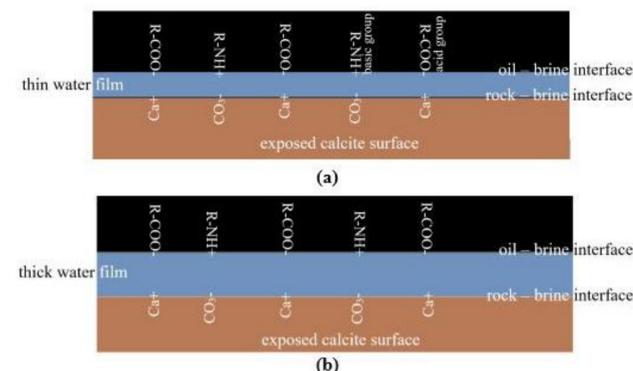


Fig.2. Schematic illustration of the water film around calcite mineral surface, a) original wetting condition of thin water film (more oil wet) a) decreased ionic strength of the injected brine and expansion of double layer (more water wet)

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