LOW SALINITY WATER FLOODING IN CARBONATE ROCKS – DISSOLUTION EFFECT

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ABSTRACT

Low Salinity Water flooding in carbonate rocks has emerged recently as a new research trend and a promising method to increase oil recovery. Wettability alteration of mixed wet carbonates to more water-wet is thought to be the main mechanisms controlling the increase in oil recovery. There is very limited data available on dissolution effect during low salinity water flooding. This paper presents a simple experimental approach to investigate carbonate dissolution during single phase low salinity water injection.

We used a low permeability (0.5 mDarcy) limestone core from an oilfield located in Iraq. The core was fully saturated with seawater (TDS = 44,580 mg/l). We then injected seawater, 3 times diluted sea water, 6 times diluted seawater and deionized water. Pressure drop across the core was monitored and produced water samples were collected continuously. The results show increases in Ca⁺² ion concentration and in pH in the effluent which indicate limestone dissolution. The effluent pH increased up to 9 which can potentially increase oil recovery due to wettability alteration or alkaline effect. Scanning Electron Microscope (SEM) images of the inlet and outlet of the core indicate that dissolution can release carbonate fines which are then trapped near the core outlet. In spite of fines migration, we did not notice a significant change in core permeability and this can be attributed to the simultaneous effect of both dissolution and fines migration.

INTRODUCTION

A number of laboratory and field studies show the effectiveness of low salinity waterflooding to improve oil recovery [1-5]. Various mechanisms have been identified for low salinity flooding [6-8]. However, most of these mechanisms are associated with low salinity water flooding in sandstones. For carbonate rocks, wettability alteration is thought to be the major mechanism [6]. The wettability alteration mechanism is usually associated with ionic exchange associated with SO₄²⁻, Mg²⁺ and Ca²⁺ ions.

Yousef, Al-Saleh [1] achieved 19% total incremental oil by injecting seawater with sequentially reducing the salinity. They also observed a decrease in pressure drop across

the composite core. This change in pressure drop was attributed to change in pore geometry due to limestone rock dissolution which was enhanced the connectivity of micro-pores in the cores. Mahani, Keya [9] concluded that LSWF can exists without any dissolution and it is primarily driven by surface charge change by conducting zeta potential and contact angle measurements on limestone core.

Chandrasekhar and Mohanty [10] argued that Mg^{2+} and SO_4^{2-} are the main potential determining ions which change wettability. The sea water containing Ca^{2+} ion in the absence of Mg^{2+} and SO_4^{2-} was unable to change wettability of the rock. They concluded that dissolution and multi-ion exchange are the main mechanisms behind incremental oil recovery. In this paper we describe an innovative approach to investigate dissolution and dissolution induced fines migration. First, discuss the experimental facility and rock characterization. Then the results of a single phase experiments are presented. SEM images are used to show dissolution effect.

EXPERIMENTAL PROCEDURE

Rock and fluids systems

We used reservoir heterogeneous limestone core from an Iraqi oil field. From the XRD and XRF results, the core consists of 96.6% Limestone and 3.4% Dolomite with no clay. The SEM images of the cores did not show any fractures. The core initially has the dimensions of 65 mm length and 2.55 mm diameter. Due to sample length limitation of the Scanning Electron Microscope instrument, we cut the core to half. Scanning Electron Microscope (SEM) images were taken for the inlet and the outlet of the composite core. SEM images of before and after experiment flooding were taken for comparison purposes and to study the potential of dissolution on changing the rock geometry. We use synthetic sea water (SW) in the experiment (TDS = 44,580). Before the experiment the cores were fully saturated with the SW.

The composite cores were mounted in the coreholder at 50 deg C. We used filter paper at the inlet and outlet to make sure no fines comes out of the core in the effluent. So, any incremental ions concentration in the effluent only represents dissolution. An injection rate of 0.1 cc/min was maintained during the experiment. Initially sea water was injected followed by 3x diluted, 6x diluted and deionized water. For each of the four injection concentration, at least 15 pore volumes (PV) were injected. Pressure drop across the composite cores was recorded continuously. The produced brine samples were collected at the outlet and pH was measured immediately to minimise interaction with atmospheric CO₂. Then ionic chromatography was run on all of the effluent samples to quantify produced anions and cations concentrations. After the flow experiment SEM images were taken again for the inlet and outlet of the core plugs.

RESULTS

Permeability and Ionic Concentrations

Figure 1 shows the measured permeability results. There is no significant change in permeability during the experiment. However, during the de-ionized water injection, the permeability changes slightly from 0.55 mD to 0.60 mD. This could be attributed to pores enlargement due to dissolution of carbonate in de-ionized water. To further confirm dissolution we conducted ion chromatography and inductively coupled plasma optical emission spectrometry (ICP-OES) analysis on the produced water samples. All the cations' and anions' concentrations were measured with an uncertainty of 0.1 mg/l and 1.0 mg/l, respectively. The concentration of Ca^{2+} is given in Figure 2. Figure 3 shows the total dissolved solids (TDS) concentration. There is no significant difference between the injected and produced TDS profile except the deionized water injection. During the deionized water injection, TDS produced is 20-30 mg/l compared to 0 mg/l injected. During this phase, Ca^{2+} show increased concentration further supporting the dissolution of calcite. The equation of the dissolution is:

$$CaCO_3 + H_2O \leftrightarrow Ca^{+2} + HCO_3^- + OH^-$$
(1)

Equations-1 shows that the dissolution should increase the pH of the produced solution. pH measurements of the produced water samples (Figure 4) show an increase of pH to 9.5 during de-ionized water injection. Such high pH values can cause alkaline effect which may increase oil recovery during two-phase displacements. For higher salinity injection phases SW, 3x diluted and 6x diluted; pH values increase up to 8.

SEM images and Fines migration

We imaged 40 subsections of the injection and production faces of the composite core. These subsections included one or multiple pores. All of the images show fines migration. The suggested mechanism of these fines migration is dissolution. The dissolution effect breaks the bond between the grain and the rock surface which leads to fines mobilization and subsequent blockage. Fines migration in sandstones have been studied in a number of previous studies [5, 11-14]. Fines migration can improve volumetric sweep efficiency and hence oil recovery by partially or fully blocking the high permeability channels. Our SEM images show that such mechanism can exist in carbonate rocks Figure 5. Unlike previous sandstone studies[5, 6], we did not observe any permeability drop during the flow experiment (Figure 1). This is probably due to the coexistence of dissolution and fines migration. Fines migration and subsequent blockage causes permeability to drop but dissolution causes permeability to increase.



Figure 1: Laboratory measurements of permeability



Figure 2: Ca²⁺ concentration of produced water samples



Figure 3: Total concentration of produced water samples



Figure 4: pH of produced water samples



Figure 5: SEM images of the core before and after injection – pore enlargement and fines migration

4. Conclusions

We present a single phase experiment to investigate dissolution and fines migration mechanisms in carbonate rocks. An integrated core and fines characterization approached was adopted to investigate dissolution and fines migration effects.

- Increase in the produced Ca⁺² ions concentration show dissolution effects.
- SEM images of the rock showed considerable fines migration which is most likely induced by dissolution. The dissolution and dissolution induced fines migration can result in pore enlargement or partial or complete pore blockage.
- Despite fines blockage, no significant change in the pressure drop was observed. The increase in pressure drop due to fines migration and the decrease in pressure drop due to dissolution can compensate each other.
- An increase in pH was observed which further supports dissolution of carbonate. During de-ionized water injection pH increased to 9.5. Such a high pH increase can affect oil recovery due to alkaline effect or wettability alteration. Rock dissolution, pH change and fines migration may significantly affect oil recovery from carbonate rocks.

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Text for Acknowledgements in Times New Roman 12 Point (margins justified), single space.

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