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EDTA chelating agent/seawater solution as enhanced oil recovery fluid for sandstone reservoirs

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ABSTRACT

Experimental investigations and field applications showed noticeable increase in the oil recovery when low salinity water flooding is used. The mechanisms leading to the increase in oil recovery by low salinity water injection are debatable. Furthermore, low salinity water injection requires relatively huge amount of fresh water to dilute seawater which is not available in many areas around the world especially in the Arabian Gulf region. Using low salinity water as an enhanced oil recovery fluid is a costly process because it requires a lot of fresh water to dilute the seawater.

In this paper we introduced EDTA (Ethylene Diamine Tetra Aceticacid)/seawater system for enhanced oil recovery in sandstone reservoirs. This fluid can be used in the secondary or tertiary flooding modes. EDTA/seawater enhanced oil recovery fluid utilizes high pH chelating agents at low concentrations prepared in seawater. Coreflooding experiments were performed using Berea sandstone cores at 100 °C to investigate the effectiveness of EDTA/seawater EOR fluid system. In addition, Zeta potential measurements were performed for the EDTA/seawater and crushed Berea sandstone cores to examine the effect of EDTA/seawater on the rock surface charge. Also the effects of the chelating agent on the surface and interfacial tension (IFT) and oil recovery were evaluated. The effect of iron content on the sandstone rock charge was investigated using high iron content sandstone (Scioto sandstone). The effects of EDTA concentration and pH on oil recovery were also investigated. Also the effects of EDTA salt and chelating agent type on the oil recovery were investigated.

The results of the coreflooding experiments showed that the EDTA/seawater fluid system was able to recover additional oil recovery up to 30% from the initial oil in place after seawater flooding when injected in the tertiary mode. The results of zeta potential revealed more negative values for the EDTA/seawater system more than the seawater and low salinity water, confirming that the rock wettability was altered towards a more water-wet condition due to the high negativity of the rock surface. The EDTA/seawater yielded low interfacial tension values with the crude oil used in the flooding experiments. Inductively coupled plasma (ICP) analysis for the coreflooding effluent samples showed increase in various cations concentration. The increase in cations concentrations confirmed the rock dissolution during the flooding process. EDTA chelating agent eliminated the iron effect on the surface charge in high iron content Scioto sandstone. Coreflooding experiments showed that EDTA should be used at concentrations higher than 5 wt% to yield high oil recovery. Also EDTA should be used at pH higher than 12 to obtain high oil recovery. Sodium salt EDTA performed better than the ammonium salt EDTA in the oil recovery experiments. EDTA chelating agent was better than the HEDTA chelating agent in terms of oil recovery.

Based on the experimental results, the possible recovery mechanisms when using EDTA/seawater system at pH 12.2 could be: IFT reduction, rock dissolution, and wettability alteration.

1. Introduction

Waterflooding is applied in oil fields to maintain the reservoir pressure during the primary stage of recovery and to some extent to improve the oil recovery. Recently, the quality of the injected water was given more attention and the composition of the injected brines was found to play an important role in changing rock wettability to a more water-wet condition. The salinity of the injected brine also was found to be an important factor for preventing inorganic salts precipitation but not for improving oil recovery (Chie Kozaki, 2012). Later, several work reported that the water composition can affect oil recovery (Bernard, 1967; Tang and Morrow, 1999; Lager et al., 2007; Austad, 2010;

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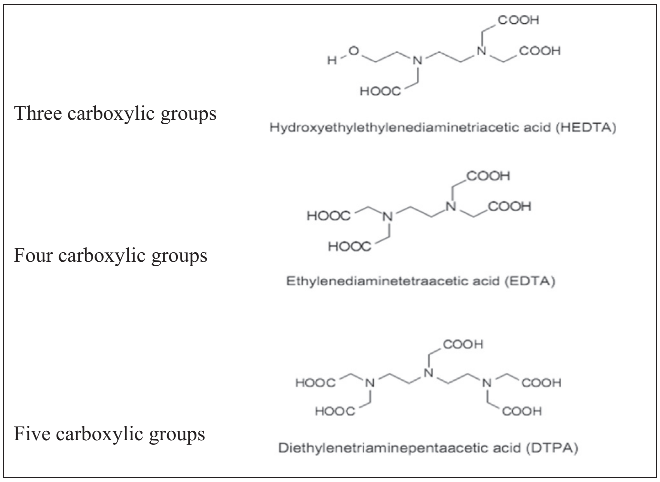

Fig. 1. Chelating agent used in the oil industry (Mahmoud et al., 2015).

Nasralla et al., 2011; Al-Yousef et al., 2011). The general consensus among those is that injecting low salinity brine somehow creates a wetting state of the rock that is more favorable to oil recovery.

Due to the complexity of oil/brine/rock interactions, the mechanisms leading to the additional recovery by low salinity is not clearly identified. Moreover, the process of treating seawater to overcome sulfate precipitation and other problems is costly. Another important point is that low salinity water in creating locations needs huge amount of fresh water for dilution and fresh water in not readily available in many places such as the Arabian Gulf countries. All of these factors will have an impact on the selection of low salinity waterflooding as a mean for EOR. The objective of this paper is to introduce an alternative EOR fluid system utilizing high pH chelating agents prepared using seawater.

Chelating agents are chemical compounds which chelate metal ions such as calcium, magnesium, and iron and form complex compounds. There are many types of chelating agents. Fig. 1 shows some types of chelating agents that are used in the oil industry. Table 1 shows the stability constant for the most commonly used chelating agents with calcium, iron, and magnesium. Stability constant describes the bond strength between the chelate and the metal ion (cation), the higher the value the more stable the compound. Also high stability constant means high affinity of the chelating agent to this cation. For example for all chelating agent the stability constant is the highest with the iron, this means a chelating agent first will sequester iron if it is existing in the rock or solution, then it will look for other cations such as calcium and at last magnesium.

Fredd and Fogler (1998) were the first to use Chelating agents as stimulating fluids. Previously, chelating agents were used to remove calcium sulfate anhydrite scale (Moore et al., 1972; Jamialahmadi et al., 1991) and to remove sulfate and carbonate minerals from clay assemblages (Bodine et al., 1973).

In this study, chelating agents were found to be having very favorable properties such as good cations chelation, wettability alteration of reservoir rocks to more water-wet conditions, mobility control agent due to the increase in the viscosity as a result of cations chelation, in addition to the improvement of rock permeability that also will increase the bond number and in turn reduce the residual oil saturation. No scale inhibitors are required when using chelating agent in the EOR projects because chelating agents will capture all metal ions and prevent scale precipitation.

Table 1
Stability constant for different chelating agents with different cations (LePage et al., 2011).

Chelating Agent	Log (stability constant)		
	Ca^{2+}	Fe^{3+}	Mg^{2+}
DTPA	10.9	28.0	9.30
EDTA	10.7	25	8.83
HEDTA	8.4	19.8	7

1.1. Properties of chelating agents

The use of chelating agents for EOR applications depends on capturing cations from the injected water and formation brine which will force the rock surface to release more cations to achieve equilibrium. In addition, capturing cations from the connate water and the rock will change the surface of the rock to more water- wet conditions through the promotion of ion exchange. The amount of chelated cations depends on the pH value of the fluid (Mahmoud et al., 2011b). As the pH value increases the amount of chelated cations from the rock increases. The rock dissolution process will force the rock to release some oil that is attached to the rock surfaces resulting in an increase of oil recovery. In this study for the EOR process only high pH chelants will be used.

Al-Al-Rossies et al. (2010) reported that the pH value of the solution and the oil composition alter the wettability of sand grains to be oil-wet or water-wet. Mahmoud et al. (2011b) reported that chelating agents chelates cations from the rock and consequently increase in the density and viscosity causing an increase in the pressure drop with time until no more chelation of cations. The chelant will complex metal ions from seawater, formation water, and rock surfaces forming complex structure with high density and viscosity. The increase in the injected fluid viscosity will improve the displacement efficiency and will improve the mobility of the oil phase.

Mahmoud et al. (2011b) studied the change in permeability during the stimulation process of Berea sandstone cores with chelating agents and they concluded that an improvement in the permeability of Berea sandstone by a factor of 1.2 with EDTA, 1.14 with HEDTA, and 1.16 with GLDA compared to the original permeability after the stimulation process with high chemical concentration.

The effluent concentration of the chelating agents during the coreflooding experiments was measured by Mahmoud et al. (2011a). They found that the outlet concentration was the same as the inlet concentration for the high pH chelating agents. They tested the concentrations of HEDTA, EDTA, and GLDA chelating agents at pH values greater than 11. At high pH chelating agents reacts with the rock by chelation and they will bind the ions to their structure, therefore, they will not lose their strength as low pH ones. They reported zero adsorption of chelating agents at high for both carbonate and sandstone rocks.

In this study for enhanced oil recovery purpose, chelating agents will be used at low concentrations (maximum 5 wt%), therefore the improvement in permeability will not be as in the case of the stimulation but at least it will not cause formation damage and keep the permeability at a constant value or slightly improved.

1.2. Sandstone rock charge and wettability alteration

Sandstone rocks and clays tend to have negative charges with brines at pH greater than 2 (Menezes et al., 1989; Hussain et al., 1996). At low pH values the oil tends to have positive charge. The charge of oil changes from positive to negative as pH increases. This behavior was confirmed with all oils.

The zero charge point (isoelectric) of oil occurred in the range from 2 to 6 pH depending on the oil composition (Takamura and Chow, 1985; Buckley et al.,1989). The thickness of the double layer and the charge at the oil-brine surface and the charge at the mineral-brine surface determine the magnitude of important parameter which gives indications about the charge of the rock with the different fluids. This parameter is called Zeta Potential. Zeta potential is the potential at the