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The influence of NaOH on the stability of paraffinic crude oil emulsion

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Abstract

The alkaline–surfactant–polymer flooding using sodium hydroxide as the alkali component to enhance oil recovery at the on shore oil fields at Daqing in China has brought new problems for the oil industry. Even though, the reservoir contained paraffinic crude oil, the alkali added formed stable water-in-crude oil emulsion and de-emulsification process was necessary to separate oil and water.

The problems related in the enhanced oil recovery process using the alkaline–surfactant–polymer flooding technique in the Daqing oil field have been investigated in the laboratory using fractions of Daqing crude oil. The oil was separated into asphaltene and aliphatic fractions and then used in an additive free jet oil to form model oils. The emulsion stability of each of the water-in-model oil emulsions formed between water or 0.6% sodium hydroxide solution and model oil was investigated. The interfacial properties such as interfacial tension and interfacial pressure of the systems were also measured. These in combination with the chemical nature of the fractions were used to get insight into the problem related to the ASP flooding technique using sodium hydroxide as the alkaline component.

The study reveals that the sodium hydroxide solution reacts with fatty acids in the aliphatic fraction of the crude oil and/or with the fatty acids formed from the slow oxidation of long chain hydrocarbons, and form soap like interfacially active components. These accumulate at the crude oil–water interface and contribute to the stability of the oil/water emulsion.

Keywords: Asphaltene; ASP flooding; Interfacial tension; Interfacial pressure; Water-in-crude oil emulsion

1. Introduction

Recovery of crude oil from the oil bearing reservoirs from the on shore oil fields in China has been improved over the past few years. Apart from the primary recovery phase and the traditional water flooding secondary recovery phase, China is experimenting to improve the tertiary recovery phase using the alkaline–surfactant–polymer flooding (ASP) technique. Several different alkaline components have been experimented as the alkaline component in the ASP technique. The results have shown that the ASP technique enhances the oil recovery, but some of the components in ASP form stable water-in-oil emulsions. This is seen as a serious problem for the petroleum industry because the separation of oil and water from the emulsion seems a challenging and costly process.

The alkaline–surfactant–polymer flooding technique has been tested in the same manner at the on shore oil field at Shengli during the past few years using partially hydrolysed polyacrylamide (HPAM) as the polymer, petroleum sulphonate (WPS) as the surfactant and sodium carbonate as the alkaline component. The results indicated that the tertiary recovery has been improved, but the oil recovered from these fields contained stable water-in-crude oil emulsions. It was found that the alkali added reacts with the acidic components (and resins and asphaltenes) in crude oil during the residence in the reservoir and form interfacially active components that accumulate at the oil–water interface and facilitates the formation of water-in-crude oil emulsion [1]. The stability of this

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emulsion depends on the concentration of the reservoir formed alkali–oil surfactant components at the interface. This again depends on the concentration of the potential acidic components from crude oil that form interfacially active soap components [1].

The same technique with sodium carbonate as the alkaline component was tested in the Daqing oil field. The recovery was not enhanced significantly. According to the data from Table 1 [2,3], this seems reasonable because the acidity of the Daqing crude oil is significantly lower and the oil contained very little asphaltenes (paraffinic crude oil). However, when the alkaline component was replaced by sodium hydroxide, to our surprise, the recovery was enhanced and the oil recovered contained water-in-crude oil emulsion. Some of the works on the study of the stability of water-in-crude oil emulsions have shown that the surfactant (ORS-41) and the polymer (HPAM) are not responsible for the stability of water-in-oil emulsion. HPAM enhances only the stability of oil-in-water emulsions and makes the water treatment difficult. Furthermore, our investigations revealed that the resin, asphaltene and aliphatic fraction of Daqing crude oil reacted with sodium hydroxide for 1 or 2 days were unable to form stable emulsions. The anamalous behavior of the paraffinic crude oil in enhancing the stability of water-in-crude oil emulsion in the presence of sodium hydroxide in the oil field led us to carry out a laboratory study regarding the chemical nature of the problem.

Johan Sjøblom and his co-workers have published a series of articles related to water-in-crude oil emulsions based on the North Sea crude oils [4–16]. Different aspects of the emulsion such as stability, destabilisation, and separation of interfacially active components, dielectric properties and the design of adequate model systems were investigated. Furthermore, chemical modifications of the interfacially active components, both artificial and natural ageing have been carried out to understand the effect of molecular properties on the stability of water-in-crude oil emulsions. All these studies have given us insight into the problems relating to stability of water-in-crude oil emulsions. Our focus in this paper is to study the long time effect of NaOH with the aliphatic fraction of paraffinic crude oil from the Daqing oil field to understand the stability of oil-in-water emulsions in the oil field. In order to do this, the aliphatic fraction of Daqing crude oil was separated first and model oil containing the aliphatic fraction was prepared in additive free jet oil. The interfacial tension and interfacial shear viscosity between the aliphatic model oil and sodium hydroxide in Daqing formation water were followed for 2 months. The stability of the emulsion formed between the two also was measured during this period.

Table 1
The composition of Gudong and Daqing crude oils

	Gudong crude oil [2]	Daqing crude oil [3]
Saturate (%w/w)	41.62	18.6 (Paraffin)
Aromatic (%w/w)	26.76	
Resins (%w/w)	14.42	12.1
Asphaltenes (%w/w)	11.72	0.1
Acid number	3.217	0.183

The nature and the problems related to the emulsion stability in the enhanced oil recovery phase have not been so far reported in the literature. The present study would give some insight and information regarding the chemistry involved in the stability of the water-in-oil emulsion formed during the oil production.

2. Experimental

2.1. Separation of crude oil fractions

The aliphatic fraction used in the experiment was separated from Daqing crude oil. As shown in Fig. 1, the separation of asphaltene fraction from the crude oil was carried out by pentane precipitation. Hundred grams of crude oil was agitated with 3000 ml of pentane at room temperature for 30 min. The mixture was then left to stand for 24 h. The precipitated asphaltene fraction was filtered and washed with smaller portion of pentane and dried. The filtrate from the above was then poured in a column containing silica. The aliphatic fraction was extracted by 1800 ml pentane, and then the pentane was evaporated to separate the fraction.

A jet fuel from a refinery without any additives was used as dispersion media for the model oil. The jet fuel was purified by silica adsorption before the experiments were carried out. The model oils were prepared as 1–5% aliphatic fraction (w/w) in the jet fuel. The water used in the experiments was synthetic Daqing formation water, the composition of which is given in Table 2.

The interfacial tension was measured in the following way. A mixture of 150 ml of 5% aliphatic model oil and 150 ml of 0.6% NaOH solution was placed in a 500 ml conical flask and thermostated in a water bath at 45 °C. The mixture in the conical flask was shaken by hand 50 times and placed back in the water bath. The conical flask was corked tightly to prevent the evaporation of the model oil components. The shaking was carried out three times every day. After three times shaking, the mixture was allowed to stand for a while. Portions of 5 ml of the model oil and 5 ml

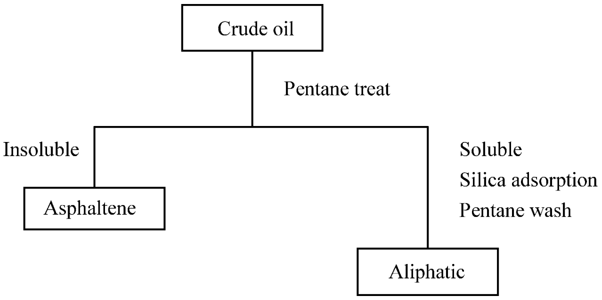

Fig. 1. Separation of crude oil fractions.