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Study of wettability of calcite surfaces using oil–brine–enzyme systems for enhanced oil recovery applications

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ABSTRACT

Enzymes have recently been considered as possible agents for enhanced oil recovery (EOR) acting at the liquid–solid interface. One way to assess this is via measuring the wettability of calcite surfaces, important for EOR methods in carbonaceous reservoirs. In the present work, we have experimentally investigated the effect of enzymes on the wettability of calcite mineral surfaces with oil–brine systems. The action of various enzymes, including esterases/lipases, carbohydrases, proteases and oxidoreductases (along with two commercial mixtures) was studied by contact angle measurements and adhesion behaviour tests. Comparative studies with a surfactant, protein, purified enzyme, enzyme stabiliser using *n*-decane (as a model for the oil) have also been carried out in order to verify experimental results. The enzymes that have the highest effect on the wettability have been identified. Those enzymes, which were found the most promising from a practical perspective, have shown the ability to fully detach oil from the surface, even at very low enzyme concentrations. For example, esterases/lipases were found to strongly affect the wettability and to remove adhesion at concentrations as low as 0.1% of the enzyme product (corresponding to 0.002–0.005% protein). Likewise, proteases could also improve wettability, although the effect was not consistent and was dependent on impurities. Other enzymes had no effect on the wettability of calcite at the concentration studied. The main mechanism of enzymatic action has been found to be replacement of oil at the solid surface by the enzyme. Other mechanisms (modification of the surface tension or catalytic modification of hydrocarbons resulting in reducing the oil viscosity) have shown to be much less pronounced from the measurements reported here.

1. Introduction

Today, application of enhanced oil recovery (EOR) to carbonaceous reservoirs is becoming increasingly important, given the growing oil demand. Indeed, the recovery of oil from such reservoirs is usually considerably lower than that from sandstone reservoirs. Recently reported methods for EOR are mostly based on the application of biological agents such as enzymes (Feng et al., 2007; Nasiri et al., 2009; He and Zhonghong, 2011; Ott et al., 2011). Enzymes may be particularly advantageous as EOR agents, since they are biologically produced, environmentally friendly, surface-active substances, which usually act at extremely low concentrations. Several initial field trials in China, Indonesia, Venezuela and USA have demonstrated quite promising results (Feng et al., 2007; Moon, 2008; He and Zhonghong, 2011; Ott et al., 2011). Meanwhile, the mechanism of enzyme action and their efficiency have not been thoroughly investigated, especially, with respect to carbonaceous reservoirs. Consequently, there is currently no method for the selection of suitable enzymes and co-solvents, or their concentrations to apply to EOR.

Based on laboratory experiments, three potential mechanisms have been proposed to explain the positive effect of enzymes on oil extraction from the reservoir rocks (Feng et al., 2007; Moon, 2008; Nasiri et al., 2009; He and Zhonghong, 2011; Ott et al., 2011): (1) breaking the connections between oil and internal porous surface; (2) decreasing the interfacial tension (IFT) and creation of emulsions; and (3) decreasing the oil viscosity.

In all cases the mechanistic explanations result in an increase of oil mobility and, as a result, increased oil production.

The primary mechanism responsible for the successful action of enzymes is claimed to be their activity on the rock surface, breaking the oil–rock bonds (Feng et al., 2007). Some authors (Moon, 2008; Ott et al., 2011) have also reported a change of oil properties due to application of enzymes. For example, breakage of carbon bonds and

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a decrease of wax content with a consequent decrease of oil viscosity were previously reported for Apollo GreenZyme™ commercial product (Moon, 2008).

Most of the published scientific reports have used enzymes in the form of commercial mixtures. In such mixtures, enzymes are usually present in combination with stabilisers and surfactants (see for example, Apollo GreenZyme™ Material Safety Data Sheet; Feng et al., 2007). This makes it difficult to assign observed effects to a particular component of the mixture, meaning that experimental work with these commercial products may lead to misinterpretations. Further research is needed in order to identify the working mechanisms of pure enzymes and the relevant concentrations that can be applied in the field.

In general, data on specific classes of enzymes that might be effective for EOR application is very restricted. Indeed, to the best of our knowledge, only lipases have been applied as pure enzymes in previous reports (Nasiri, 2011).

In this study we have carried out a systematic screening of the four most promising groups of enzymes (esterases/lipases, carbohydrases, proteases and oxidoreductases) with respect to their ability to alter the wettability of the calcite surface, characteristic of the chalk reservoir rock and, ultimately, to detach oil from the surface.

Among different techniques, adhesion tests of oil drops on mineral surfaces, in the presence of known enzyme solutions, are the most suitable for wettability screening as they keep the balance between accuracy, timing and simplicity which is very important in the case of a large number of samples. Measurement of the contact angles in conjunction with adhesion tests gives an even better indication of wettability (Buckley and Morrow, 1990). This method was used in the present work. In order to distinguish the specific effect of the enzymes, comparative studies were conducted with a surfactant, a protein and an oil model (mimic). The obtained results should enable direct assessment of the enzyme as a working biological component and correlation of the enzyme class with respect to its potential for EOR. Adsorption of enzymes at interfaces and/or formation of surface-active compounds were proposed to be key mechanisms underlying changes introduced into a crude oil–brine–calcite system.

The experimental program is proposed as the first step in the study of the applicability of enzymes for enhanced oil recovery. Further studies will be necessary, including dynamic adsorption experiments, flow-through experiments, flooding tests and pilot reservoir tests. However, the present study is independent of the subsequent steps and provides a thorough description of the wettability alteration mechanisms as well as reasonable screening criteria for enzyme selection and working concentrations of enzymes.

The paper is organized as follows. First, we give an overview of materials and methods applied (Section 2). Section 3 describes results of the assessment of wettability of crude oil–sea water and enzyme–calcite systems. The reference experiments and comparative studies for similar systems are discussed in Section 4. In Section 5, we discuss significance of our findings for enzymatic EOR. Finally, the key results of the work are summarized in Section 6.

2. Materials and methods

2.1. Materials

2.1.1. Fluids

All the tests were performed using light dead oil recovered from a chalk reservoir in the Danish sector of the North Sea. None of the enzymes utilised in this study interact with small hydrocarbon molecules, so that the difference between the live and dead oils was unimportant for the purpose of the experiment.

In the reference experiment *n*-decane (Sigma-Aldrich, purity ≥ 99%) was used as the model oil phase.

Table 1
Composition of synthetic North Sea water used for adhesion behaviour and contact angle tests.

Salt	Concentration (g/l)
NaCl	18.01
$NaHCO_3$	0.17
KCl	0.74
$MgCl_2 \cdot 6H_2O$	9.15
$CaCl_2 \cdot 2H_2O$	1.91
Na_2SO_4	3.41
Total dissolved solids	33.39

The aqueous phase was synthetic North Sea water (pH = 7.78; composition as given in Table 1). Chemicals for brine preparation were purchased from Fluka (purity ≥ 99.5%) and were not subjected to further purification.

2.1.2. Enzyme, protein and surfactant samples

Fifteen enzyme products kindly provided by Novozymes A/S, and two enzyme-based commercial mixtures (Apollo GreenZyme™ and EOR-ZYMAX™) were investigated in the study (Table 2). Each of the Novozymes enzyme products belonged to one of four classes (esterases/lipases, carbohydrases, proteases, oxidoreductases). Three solutions (0.1%, 0.5%, and 1% (weight/weight)) were prepared for each enzyme sample by dilution of the enzyme products in the sea water (SW). The actual content of protein is much lower, typically in the range of 2–5% of the enzyme products. This is further discussed in Section 4.1.

Two oxidoreductases were applied (peroxidase and laccase) that required the presence of hydrogen peroxide (1–3 mM) and oxygen, respectively. Hydrogen peroxide (Sigma-Aldrich) was added during preparation of the peroxidase solution, while no additional amount of oxygen was supplied during application of laccase, since the amount of dissolved oxygen was considered to be sufficient.

Bovine serum albumin protein (BSA, 98% purity) and sodium dodecyl sulphate surfactant (SDS, 99% purity) were purchased from Sigma-Aldrich. Concentrations of BSA (0.001%, 0.005%, 0.01%, 0.05%, 0.1% and 1% w/w) and SDS (0.003%, 0.05%, 0.5% w/w) were chosen so that they were correlated with the amount of enzyme used in experiments. The BSA and SDS solutions in synthetic brine were prepared in an identical way to the enzyme solutions.

Other chemicals used were propylene glycol (Sigma-Aldrich, purity ≥ 99.5%), and a purified version of the enzyme (lipase) sample NS 44034 (Novozymes A/S) (without stabilisers).

2.1.3. Calcite minerals

In laboratory experiments it is usual practice to use various minerals to mimic specific reservoir rocks. Calcite minerals were used in this work to represent a chalk reservoir. Three calcite crystals (white, yellow and grey) with crystal faces were kindly provided by the Geological Museum of Copenhagen, Denmark. A further calcite sample with the surface created after cleavage of a larger mineral was kindly supplied by Center for Arctic Technology, Technical University of Denmark (Lyngby, Denmark). One of the crystal face samples was transparent. One of the samples with the crystal face and freshly cleaved samples were transparent and opaque calcites with no additives, correspondingly. Two other samples were yellow and grey minerals, where the colour was due to the presence of colour-changing additives. Application of these particular samples allowed assessment of the effect of different additives and effect of origin of the mineral surface.

In order to approach realistic roughness of the natural surfaces (such as pore walls), the calcite surfaces were not subjected to any