Journal of Petroleum Science and Engineering 108 (2013) 14–21

Contents lists available at SciVerse ScienceDirect

Journal of Petroleum Science and Engineering

journal homepage: www.elsevier.com/locate/petrol

Mapping oil saturation distribution in a limestone plug with low-field magnetic resonance

J. Mitchell [a,b], J. Staniland [b], R. Chassagne [b], K. Mogensen [c], S. Frank [c], E.J. Fordham [b,*]

[a] Department of Chemical Engineering and Biotechnology, University of Cambridge, Pembroke Street, Cambridge CB2 3RA, UK
[b] Schlumberger Gould Research, High Cross, Madingley Road, Cambridge CB3 0EL, UK
[c] Maersk Oil Research and Technology Centre, TECH 2 Building, Level 1, Unit 107, Al Gharrafa Street, Al Rayyan, Education City, PO Box 22050 Doha, Qatar

ARTICLE INFO

Article history:
Received 18 September 2012
Accepted 26 April 2013
Available online 9 May 2013

Keywords:
MRI
oil recovery
T_2 distribution
limestone
paramagnetic manganese doping

ABSTRACT

Magnetic resonance imaging (MRI) is used to quantify *in situ* the recovery of crude oil from a strongly oil-wet microporous limestone core-plug. We demonstrate the capability of low-field MRI to continuously monitor oil saturation distribution by obtaining a series of spatially resolved transverse relaxation time (T_2) distributions using the robust spin echo single point image (SESPI) profiling method to obtain T_2 maps with a temporal resolution of 45 min. These T_2 maps are shown to provide comparable data to nuclear magnetic resonance (NMR) well-logs. The low injection rate of 1.4×10^{-3} cm^3 s^{-1} (equivalent to an interstitial velocity of 1 ft day^{-1} in the formation) allowed a large number of T_2 maps to be acquired during the flood. Fluid-phase discrimination is achieved here in the T_2 dimension; the brine relaxation time is reduced by addition of paramagnetic manganese. Some manganese is lost through adsorption on the limestone surface, but sufficient relaxation contrast is obtained to position an unambiguous oil/brine T_2 cut-off. The spatial distributions of both the brine and oil are therefore determined simultaneously and independently. Capillary end effects are observed in the short core-plug due to the difference in wettability and permeability between the plug faces and the core-holder end-caps. The inclusion of the spatial dimension in the experiment allows a region of the plug, unaffected by end effects, to be considered representative of behavior in the reservoir. Overall, we highlight the importance of spatial resolution in laboratory-scale core analysis and demonstrate the capability of low-field MRI spectrometers to continuously monitor oil recovery experiments.

1. Introduction

Nuclear magnetic resonance (NMR) is an expedient well-logging tool, capable of providing information on porosity and final oil saturation in the vicinity of a well bore (Kenyon, 1997). In order to fully interpret the data obtained in the field, it is desirable to complement well-logs with laboratory-scale measurements. For example, Kantzas and coworkers use low-field NMR measurements in studies of heavy oil and bitumen (Allsopp et al., 2001; Bryan et al., 2006a,b; Goodarzi et al., 2005). Laboratory core floods are desirable when screening new enhanced oil recovery (EOR) chemicals such as polymers and surfactants (Mitchell et al., 2012b,c,d), prior to pilot or field-scale trials (Arora et al., 2010). Under ideal conditions, fluid-phase behavior would be quantified in long core-plugs or composite plug stacks (total length > 30 cm) so end effects due to geometry or capillarity are minimized. However, the sample volume that can be accommodated readily in commercial, low-field, bench-top NMR spectrometers is limited, often to a plug length of a few centimeters. Therefore, it is critical in core floods conducted on short plugs to obtain spatial information so that end effects can be discounted from the interpretation of oil recovery. It is prudent, then, to incorporate the principles of magnetic resonance imaging (MRI) into core analysis and oil recovery monitoring (Mitchell et al., 2012c).

MRI has experienced an intermittent history in core analysis spanning the last three decades (Edelstein et al., 1988; Gummerson et al., 1979; Rothwell and Vinegar, 1985). Many of these spatially resolved measurements were conducted on intermediate field strength magnets designed for clinical studies or biomedical imaging of rodent anatomy (Baldwin and Yamanashi, 1989; Doughty and Maerefat, 1989; Edelstein et al., 1988; Fordham et al., 1993; Gleeson and Woessner, 1993; Nørgaard et al., 1995). These large, superconducting magnets are of sufficient size to accommodate core-plugs or even whole cores (Brown, 1988). However, there are two significant drawbacks to these MRI systems: (1) magnetic susceptibility induced field heterogeneities, that scale with magnetic field strength, prevent quantitative determination of fluid volumes (Mitchell et al., 2010; Straley et al., 1994), and (2) data obtained at intermediate magnetic field

* Corresponding author. Tel.: +44 1223 325263.
E-mail addresses: jm600@cam.ac.uk, jmitchell16@slb.com (J. Mitchell), fordham1@slb.com (E.J. Fordham).

0920-4105/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.petrol.2013.04.008

strengths (B_0~1–3 T) are not directly comparable to those from well-logging tools which operate at very low magnet field strengths ($B_0 < 50$ mT). High-field magnets are preferred in clinical MRI as the signal-to-noise ratio (SNR) generally improves with increasing magnetic field strength. In medical imaging, good SNR allows high resolution images to be obtained rapidly by virtue of providing sufficient signal per voxel for meaningful interpretation of the images. Unfortunately, the aforementioned magnetic susceptibility contrast limits the practical spatial resolution in porous media studies, so the assumption that a stronger magnet automatically provides better images is not valid in core analysis. Pore-scale image resolution is impractical at any magnetic field strength, and so the advantages of low-field magnets in core analysis outweigh the inherent reduction in achievable spatial resolution. One-dimensional (1D) spatial resolution obtainable at $B_0 \approx 50$ mT within a reasonable experimental time (say, less than 1 h) is sufficient to observe non-uniformities in liquid saturation on the millimeter scale. The full history of MRI applications in core analysis is given in a recent review (Mitchell et al., 2013).

Numerous imaging techniques are available in clinical MRI (Haacke et al., 1999), and these have a variety of advantages and disadvantages depending on the precise combination of magnet and sample. The single point imaging (SPI) (Emid and Creyghton, 1985) method is favored for porous media and solids as it provides quantitative images that are insensitive to the relaxation time weighting inherent in conventional spin-echo imaging techniques (Callaghan, 1991). Each datum in a SPI experiment is acquired at a fixed encoding time, so any relaxation time weighting is consistent across the image. As such, SPI is well suited to the determination of quantitative saturation states in reservoir rocks. The SPI pulse sequence has been improved in the form of SPRITE (Balcom et al., 1996) which uses small angle radio frequency (rf) spin excitation pulses to acquire a complete profile or image in a single scan. SPRITE is useful for determining the distribution of porosity in a sample (Marica et al., 2006). However, the use of small tip angle rf pulses (leading to poor SNR per scan) is not ideal for very low-field spectrometers. A modification to the SPI methodology that is well suited to low-field instruments is the spin echo single point imaging (SESPI) technique (Beyea et al., 2000; Li et al., 2009; Petrov et al., 2011).

Spatial resolution is achieved in MRI by encoding nuclear spins with a frequency shift that is proportional to the Fourier inverse of their physical location. As such, MRI data are acquired in the time domain, or k-space, being the Fourier reciprocal of real (image) space. Spatial encoding is provided by the application of a magnetic field gradient. In most imaging modalities, such as spin-warp imaging (Edelstein et al., 1980) or SPI, the data are acquired concurrently with the application of this gradient. Acquiring signal in the presence of a magnetic field gradient has a notable limitation: the data must be sampled with a digital filter bandwidth sufficient to encompass the necessary range of wave-numbers in k-space (typically Δk~100 kHz) or the image will be distorted by the filter function. A wide band filter offers no advantage in noise reduction, and so the data have low SNR. Dynamic filtering can be used to improve the SNR for SPI-based acquisitions, although the implementation is complicated (García-Naranjo et al., 2010). The filter bandwidth limitation is waived when using the SESPI technique as the data are not acquired in the presence of a gradient. Instead, only the natural line width of the sample/magnet (typically, $\Delta k \ll 1$ kHz) needs to be encompassed by the filter. A well designed narrow band digital filter is advantageous, particularly for very low-field experiments, by virtue of enhancing the SNR (wide band noise suppression) and eliminating contamination from fluorine (^{19}F) commonly found in NMR-compatible core holders.

To provide a common physics of measurement with NMR well-logging, it is necessary to use low-field magnets in laboratory-scale core analysis. Also, NMR logs are typically composed of T_2 relaxation time distributions acquired as a function of reservoir depth. Accordingly, we are interested in methods of obtaining spatially resolved T_2 distributions in core-plugs. Laboratory-scale T_2 maps are directly comparable to well-logs except that the vertical resolution Δy is on the order of millimeters rather than tens of centimeters (Mitchell et al., 2012c). In this manuscript, we use SESPI T_2 maps to monitor recovery of light Middle East crude oil from a microporous limestone plug during a brine flood. The crude oil and limestone plugs were obtained from a reservoir in Qatar.

When monitoring oil recovery, it is necessary to obtain a separation of the NMR signal from the oil and brine present in the core-plug. Both fluid-phases contain protonated species (i.e., molecules with ^{1}H nuclei) and so they both contribute a detectable signal in the NMR experiment. The total liquid signal is a measure of porosity. Various techniques exist for determining spatially resolved oil and brine saturations, such as paramagnetic doping (Baldwin and Yamanashi, 1988, 1989), chemical selective imaging (Borgia et al., 1994; Doughty and Tomutsa, 1996; Edelstein et al., 1988; Enwere and Archer, 1992; Nørgaard et al., 1995), or complete suppression of the brine signal using heavy water (D_2O) substitution (Brautaset et al., 2008; Green and Dick, 2008; Maddinelli and Brancolini, 1996; Mahmood et al., 1990; Saraf and Fatt, 1967). Here, we opt to achieve oil and brine discrimination by doping the aqueous fluid-phase with paramagnetic manganese to reduce the relaxation time below that of the oil. Manganese provides a large reduction in both T_1 and T_2 relaxation times at low-field, even at modest concentrations, and is therefore preferable to other available doping agents. Paramagnetic doping agents have been used occasionally in NMR well-logging to provide contrast between oil and aqueous (brine, drilling mud) fluid-phases. It is recommended that manganese be chelated with ethylene diamine tetra-acetic acid (EDTA) for use in clay-based drilling muds or sandstones where ion exchange is a possibility (Kleinberg and Vinegar, 1996). Chelation is not appropriate in limestones as the EDTA binds the calcium in the carbonate, eroding the pore structure even under alkaline conditions (Mahmoud et al., 2011). Unchelated manganese is used in carbonate formations, as demonstrated in a heavily dolomitized reservoir (Horkowitz et al., 1997), and the bare metal ion has the advantages of a weaker temperature dependence (change in relaxation properties with temperature) and reduced economic cost compared to the chelate. However, unchelated manganese will adsorb on the pore surface, leading to a loss in fluid-phase sensitivity (Mitchell et al., submitted for publication). Notwithstanding, we use unchelated manganese here, which provides sufficient T_2 relaxation enhancement to allow an unambiguous T_2 cut-off to be defined between the oil and brine signal components.

In related work we have considered the application of frequency encoded T_2 mapping to core flood monitoring (Mitchell et al., 2012b,c). Under ideal conditions, the multi-echo profiling sequence of Majors et al. (1997) provides improved temporal resolution. However, we note that the implementation of SESPI is more robust and reliable; phase encoding enables quantitative profiling in macroscopically heterogeneous materials (Marica et al., 2006). Furthermore, a modified SESPI sequence (Petrov et al., 2011) offers the opportunity to spatially resolve short T_2 samples, enabling studies of oil recovery from unconventional reservoir material. Our present work differs from previous publications in several significant details.

(1) In previous work we used frequency encoded T_2 mapping. Here we demonstrate the more robust phase-encoded T_2 mapping for the continuous monitoring of forced displacement of oil, see Section 3.2.