
● Short Communication

**EVALUATION OF CHEMICALLY-INDUCED PORE SURFACE MODIFICATIONS
ON ROCK CORES**

G. MADDINELLI AND R. VITALI

Eniricerche S.p.A., San Donato, Milan, Italy

Chemical modification of pore surface properties due to active components of crude oils could significantly affect production processes. Specific chemical treatments can prevent surface alteration, protecting pores from deposition of heavy oils components. Both relaxation times analysis and nuclear magnetic resonance (NMR) imaging technique are a valuable method for nondestructive monitoring of solid/liquid interface alteration especially if applied to heterogeneous rock cores, which are impossible to study using conventional methods (e.g., Amott tests and dynamic angle contact). In our work, we examined carbonate core plugs subjected to aging treatments in crude oil. Relaxation times measurement, revealing modifications of fluid/surface interactions and imaging, was applied in characterise heterogeneous systems and reveal fluid distribution changes. Nuclear magnetic resonance results were compared with a special microscopy technique (Cryo-SEM) that allows observation of fluids at the pore level, providing a better understanding of the processes involved. © 1998 Elsevier Science Inc.

Keywords: Carbonates; Surface modifications; Nuclear magnetic resonance relaxometry; Magnetic resonance imaging; Cryomicroscopy.

INTRODUCTION

Size, throat, and connectivity of pores are well known critical factors for determining transport properties of reservoir cores. However, the role of the pore surface also has to be properly considered to evaluate fluidodynamic behaviour of rock cores.¹ In fact, liquid-solid interface interactions (i.e., wettability) are strongly determined by pore surface properties and can become significant during well production, sometimes causing severe problems such as earlier water breakthrough. Moreover, surface modifications could occur during production. A well known effect is deposition of heavy fractions (e.g., asphaltenes), resulting in changing fluid distributions inside the porous structure. This aspect could be enhanced by the mineralogy of the grains and the effect on the oil entrapment, and therefore the difference in mobility needs to be understood. Conventional laboratory tests as an Ammott index could be inefficient especially if applied to heterogeneous material such as carbonates with high presence of vugs and fractures.² Nuclear magnetic resonance (NMR) techniques have

proved to be very useful in evaluating such systems, giving valuable and reliable information on pore size and heterogeneity distributions. In our work we have examined the effect of aging in crude oil on fluid distribution inside heterogeneous carbonate core samples.

MATERIALS AND METHODS

Two plugs (2.5 × 5 cm), A and B, drilled from a dolomite reservoir core, initially checked by magnetic resonance imaging to ensure absence of defects, were thoroughly cleaned by Soxhlet extraction with toluene, dried in an oven at 110°C, and fully saturated with brine (14 g/L NaCl). Petrophysical properties measured on the sample at different stages are reported in Table 1.

Chemical treatment was realised by flushing sample B with 10 pore volumes of a solution of 1000 ppm of polyacrylamide (PAM) in brine. The samples were flushed (5 cm³/min) with crude oil from the same reservoir until no more water was produced (irreducible water saturation state, Swi). After NMR measurements, the samples were aged in crude oil at 80°C for 15 days and then reflushed with fresh oil until no more water was

Address correspondence to Dr. G. Maddinelli, Eniricerche S.p.A., Via F. Maritano 26, San Donato, 20097 Milan, Italy.

E-mail: gmaddinelli@eniricerche.eni.it

Table 1. Petrophysical properties of the dolomite samples at different stages

Samples	Pore volume (cm ³)	Porosity	Swi	Swi (after aging)
A	1.21	4.3	68	48
B	1.14	4.0	77	58

produced. NMR relaxation and imaging measurements were carried out at 85 MHz on the samples at Swi and at 21°C using a SISCO instrument (Varian, Palo Alto, CA, USA) equipped with a 2-T, 31-cm bore magnet.

The Cryo-SEM measurements were conducted on a Hitachi instrument (Hitachi, Tokyo, Japan) equipped with an Oxford CT 1500 (Oxford Instruments LTD., Witney, Oxon, UK) cryogenic accessory. All measurements were performed on microplugs (4 mm in diameter) prepared as described previously and subjected to rapid freezing in liquid nitrogen to preserve fluid saturation. Backscattered electron images allowed chemical contrast between oil and water based on sensitivity to atomic number of the tracer elements, sulphur and chlorine, respectively.

RESULTS

The rock type under investigation is highly heterogeneous and, as revealed by magnetic resonance imaging, consisted of a structured porous matrix characterised by vugular regions (millimeter size) and diffuse microporous areas (a few microns in diameter) in which water is strongly trapped, as shown by the considerable amount of water retained at Swi,³ while oil appears to be mainly distributed in large vugs. Profiles of oil and water distributions inside sample A have been obtained by chemical shift imaging and are displayed in Fig. 1. A rather uniform distribution of the water (diffused microporosity) compared to highly localised oil indicates its preferential location in the vugs.

In this work we examined the effect of aging in crude oil to verify changes in fluid distribution that could be attributed to chemical modification of the pore surface, which is preferentially water wet, as confirmed by contact angle measurements. Selective T_1 relaxation measurements on the oil phase of the samples saturated at Swi, were carried out by spectroscopical discrimination between oil and water due to the moderate line broadening determined by the low magnetic susceptibility of the dolomite lithology. The relaxation curves were fitted to continuous distributions of relaxation times (Fig. 2). Two broad peaks are visible for the sample A at Swi without any treatment (Fig. 2a), which shows a high population density in the region with higher T_1 values that are close

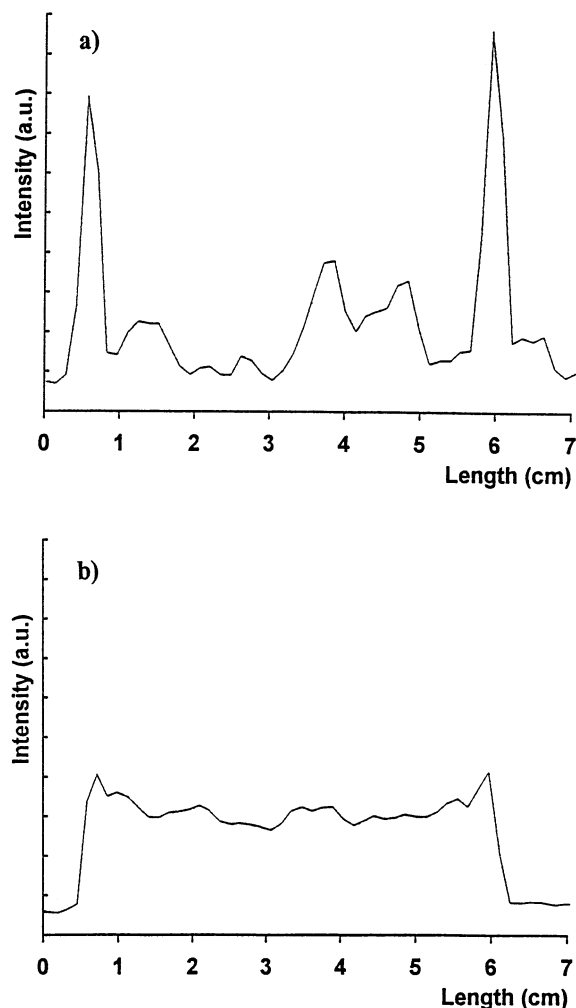


Fig. 1. Signal profiles obtained by one-dimensional chemical shift imaging, showing distribution of oil (a) and water (b) inside a dolomite core sample at irreducible water saturation (Swi).

to relaxation of bulk oil ($T_1 = 0.87$ s). This result is consistent with preferential oil distribution on large vugs with only a slight amount situated in the microporous area. After aging in crude oil (Fig. 2b), a consistent shift of population density to intermediate values is found, indicating either migration of oil to smaller pores or closer contact to the surface with consequent enhanced relaxation.⁴ The treatment with polyacrylamide (sample B in Fig. 2c) reveals a significant reduction of such effects, showing a relaxation distribution more similar to that of the nonaged sample.

Cryo-SEM provided pore scale imaging of the phenomena involved. Images shown in Fig. 3 refer to representative vugular (Fig. 3a) and microporous (Fig. 3b) regions, showing a clear picture of pore spaces and corresponding filling fluids. In detail, after aging in crude

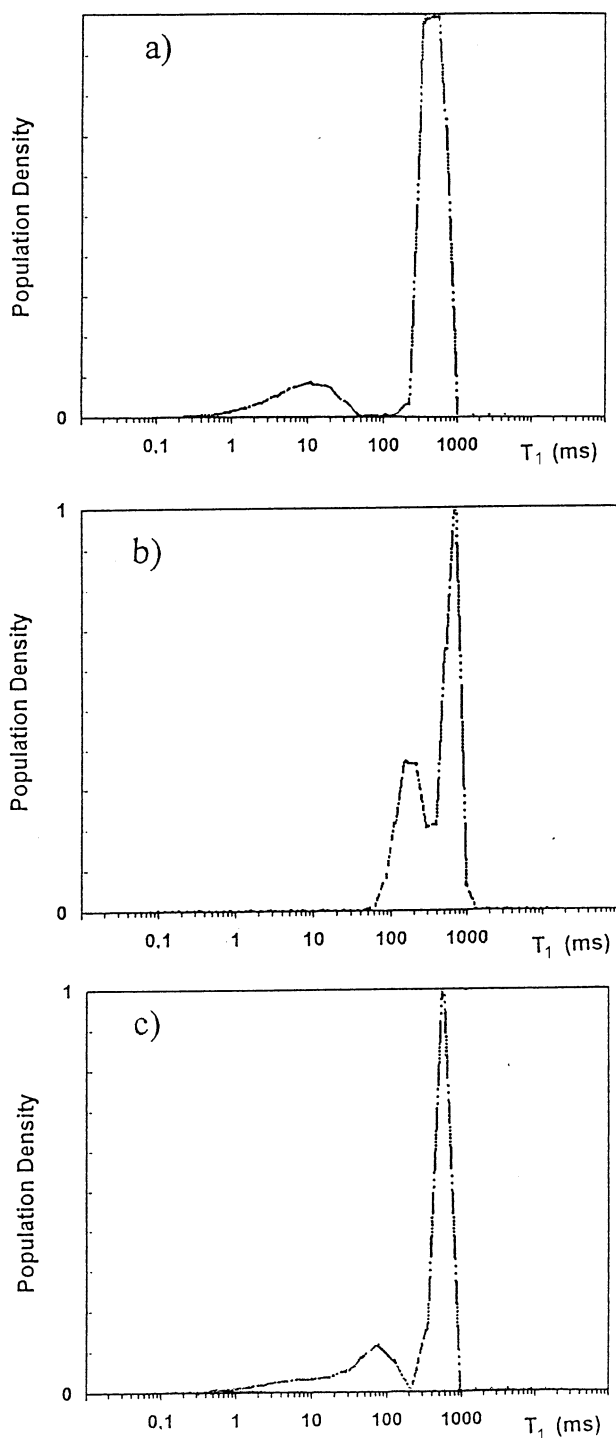


Fig. 2. Population density of T_1 obtained by continuous distribution analysis computed for a logarithmic time scale and normalized to unit area, relative to sample A saturated at S_{wi} (a); sample A aged in crude oil (b); and sample B treated with PAM to prevent surface alteration and aged in crude oil (c).

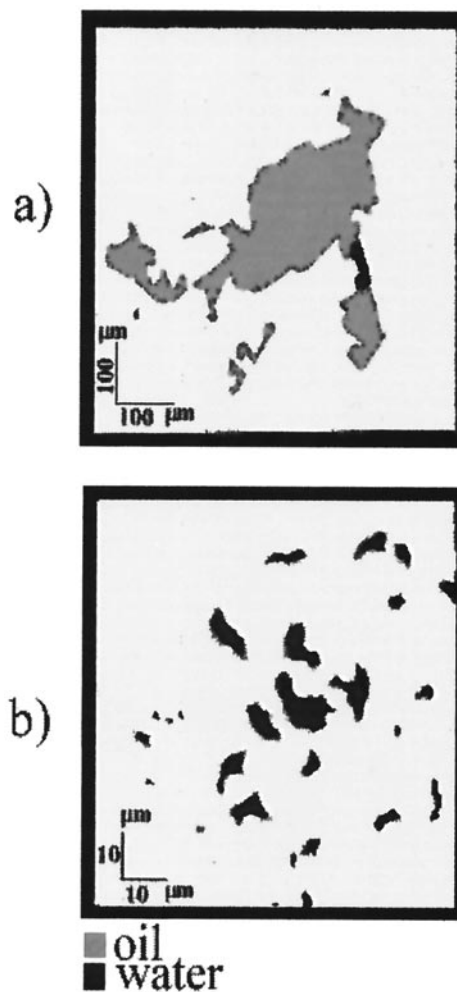


Fig. 3. Processed images obtained by Cryo-SEM showing water (dark) and oil (light) distributions at the pore scale in two selected representative porous regions inside microplugs (4 mm in diameter) after aging in crude oil. (a) Selected vugular region; (b) selected microporous area.

oil, vugs appear preferentially filled by oil with some water entrapment, whereas micropores are completely occupied by water.

CONCLUSIONS

An effective change in oil distribution was observed after aging of dolomite core samples as observed by the increased relaxation rate indicated by the shift toward smaller values of a fraction of population observed in T_1 distribution of Fig. 2b. This increased relaxation rate observed on a fraction of oil is more likely due to enhanced surfacial contact with the pore walls.^{4,5} This is consistent with the decrease in water content after aging

treatment and the lack of migration of oil toward the microporous areas excluded by Cryo-SEM observations. The alteration of surface properties induced by aging appears to be efficiently prevented by protecting pore surface with appropriate chemicals (PAM) active against asphaltene adhesion. The polymer (PAM) has a high affinity with the dolomite pore surface due to favourable electrostatic interactions.⁶ This points out the important role of pore surface in determining fluid phase distribution and the mechanisms of entrapment.

Acknowledgments—The authors acknowledge the management of Agip S.p.A. and Eniricerche S.p.A. for sponsorship and permission to publish the work. A special thanks to Mrs. A. Lyne of Agip S.p.A. for helpful suggestions.

REFERENCES

1. Anderson, W.G. Effects of wettability on waterflooding. *J. Petroleum Technol.* 39:1605–1622; 1987.
2. Sprunt, E.S. Arun core analysis: Special procedures for vuggy carbonates. *Log Analyst.* 30:353–362; 1989.
3. Borgia, G.C.; Brancolini, A.; Camanzi, A.; Maddinelli, G. Capillary water determination in core plugs: A combined study based on imaging techniques and relaxation analysis. *Magn. Res. Imaging* 12:221–224; 1994.
4. Kleinberg, R.L.; Kenion, W.E.; Mitra, P.P. Mechanism of NMR relaxation of fluids in rock. *J. Magn. Reson.* 108: 206–214, 1994.
5. Howard, J.J. Wettability and fluid saturation determined from NMR T1 distributions. *Magn. Reson. Imaging* 12: 197–200; 1994.
6. Hirasaki G.J. Wettability: Fundamentals and surface forces. *SPE Formation Eval.* 6:217–226; 1991.