OIL RECOVERY BY SPONTANEOUS IMBIBITION BEFORE AND AFTER WETTABILITY ALTERATION OF THREE CARBONATE ROCKS BY A MODERATELY ASPHALTIC CRUDE OIL

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This paper was prepared for presentation at the International Symposium of the Society of Core Analysts held in Toronto, Canada, 21-25 August 2005

ABSTRACT

Carbonate rocks can exhibit great morphological complexity at the pore, core, and reservoir scale. Cores ranging in permeability from 7 to 4000 md were cut from three outcrop limestones (two grainstones and a reef boundstone). One of the grainstones was homogeneous at the core scale and the other was distinctly heterogeneous. The rocks were characterized by permeability and porosity, thin section, scanning electron microscopy, BET surface area, and cation exchange capacity. Scaled data for the three types of outcrop limestone at very strongly water-wet conditions agreed well with correlated results for a wide range of other rock types. Mixed-wet rocks (MXW) were prepared, in the presence of initial water saturation, by adsorption from Cottonwood Creek crude oil, a moderately asphaltic crude. The crude oil was displaced by an intermediate solvent which was in turn displaced by refined oil to leave an absorbed film (F) of polar crude oil components on the rock surface. This wetting state is referred to as MXW-F. In other experiments, the crude oil was directly displaced by refined oil to obtain wetting states by surface precipitation of asphaltenes referred to as MXW-DF. The wetting states induced in the three carbonate rocks by the above methods were compared through measurements of spontaneous imbibition of brine and oil. Recoveries by forced displacement were measured to obtain Amott indices to oil and water. For all three rock types, MXW cores gave significantly higher rate and extent of imbibition than the MXW-F cores. MXW-DF cores showed the greatest wettability change. All of the MXW-F and MXW-DF cores exhibited intermediate wettability.

Keywords: Spontaneous Imbibition, Limestone, Wettability, Amott Indices.

INTRODUCTION

Carbonate reservoirs hold about one-half of the world’s oil reserves. Reported studies of oil recovery behavior from carbonate rocks are much fewer than for sandstone. Berea sandstone has been used as a model rock in by far the majority of studies on oil recovery from sandstones. To date, no comparable model rock has been adopted widely for study of carbonates. Indiana limestone, which, for example, has sometimes been employed in past studies, exhibits a large degree of macroscopic heterogeneity at the core scale [1]. In the present work, change in wettability induced by adsorption from crude oil was investigated for three selected outcrop limestones: a reef boundstone from Mt. Gambier, Australia, and two grainstones from Texas.

In wettability studies, very strongly water-wet (VSWW) cores provide the reference condition for identifying changes resulting from wettability alteration. A distinct advantage of using clean outcrop carbonates is that they are very strongly water-wet whereas, as yet, there are no reliable core cleaning techniques for restoration of reservoir carbonates to very strongly water-wet states. Several mechanisms can contribute to wettability alteration by crude oil. Non-specific interaction between oppositely charged surface sites is believed to be one of the most important factors [2]. Near neutral pH, carbonate surfaces are positively charged. Negatively charged components, such as carboxylic acids, can be expected to attach to the surface and alter the wetting [3-7]. Al-Maamari and Buckley pointed out that displacement of crude oil by a precipitant for asphaltenes could result in surface deposition which overrides various ionic interactions and render the rock surface strongly oil-wet [8].

From advancing contact angle measurements on calcite and quartz surfaces for a series of crude oils representing a wide variety of carbonate and sandstone reservoirs, Treiber *et al*. [9] and Chilingar and Yen [10] concluded that carbonate reservoirs tend more towards oil wetness than sandstones. However, Tie *et al*. [11] showed that by aging either carbonate or sandstone cores with crude oil (at 75ºC for 10 days), the wettability, assessed from recovery of crude oil by spontaneous imbibition and by Amott wettability indices, still remained in the water-wet region.

Ma *et al*. [12] used a semi-empirical scaling group to correlate spontaneous imbibition behavior of VSWW media over a wide range of conditions.

$$t_D = t\sqrt{\frac{k}{\phi}}\frac{\sigma}{\sqrt{\mu_o \mu_w}}\frac{1}{L_c^2}$$

where t_D is dimensionless time, t is time, k is permeability, ϕ is porosity, σ is the interfacial tension, and μ_o and μ_w are the oil and brine viscosities. L_c is a characteristic length that compensates for sample size, shape and boundary conditions. Use of this scaling group to compare the spontaneous imbibition rate of cores with wetting states other than VSWW (MXW [13], MXW-F [14]) provides an indication of the degree of wetting change.

In this work, spontaneous imbibition behavior is compared for three well characterized limestones, before and after inducing mixed wettability in the presence of an initial water saturation. Cottonwood Creek crude oil, a moderately asphaltic crude oil from a producing carbonate reservoir, was used to induce wetting change. Wetting alterations from very strongly water-wet to three distinct forms of mixed wettability determined by the method of treatment are compared for each rock type.

EXPERIMENTAL

Rock Characterization

Three limestone rocks selected for study are Whitestone Upper Zone (Whitestone UZ or WUZ), Edwards (Garden City) (Edwards (GC) or EGC), and Gambier (G). The limestones were characterized using various petrophysical observations and measurements. BET surface areas and cation exchange capacities (CEC) are listed in Table 1. Desorption/adsorption isotherms for water have also been reported [15]. From thin sections (see Fig. 1), according to Dunham's classification [16], both Whitestone UZ and Edwards (GC) are grainstones. Gambier rock is a reef boundstone. SEM micrographs are included in Fig. 1.

Cores

Whitestone UZ, also known as Texas Crème, quarried from the upper bench of the Whitestone Member of the Lower Cretaceous Walnut Formation, Texas, is a grainstone composed mostly of calcite. Air permeabilities and porosities varied significantly for cores cut from a 12 by 12 by 6 inch block. Air permeabilities of individual cores varied by more than an order of magnitude (<1 md to ~14 md) and porosities ranged from 18.9% to 26.4%. On the basis of this variation, Whitestone UZ is referred to as a heterogeneous limestone. In this study of comparative wetting change, three Whitestone UZ core samples of 7 md permeability were selected to avoid extreme differences in core properties (see Table 2).

Edwards (GC), which is also known as West Texas Crème, Cedar Hill Cream, or Valencia Ivory building stone, is an outcrop Cretaceous limestone from West Texas. The rock is quarried from a member of the Edwards Formation. Petrophysical property measurements on samples cut from individual 12 by 12 by 6 inch blocks showed only modest variation. Air permeabilities are around 13 md and porosities are about 21%. The rock is mainly composed of calcite crystals, which can be identified both in the bulk of the rock matrix and at pore walls (see Fig. 1(b)). Water adsorption isotherms show that only about 0.5% of the pore space is in the micropore (0 to 2.1 nm) to mesopore (2.1 to 53.0 nm) range [15].

Gambier limestone is an Oligocene-age outcrop quarried from Mount Gambier, Australia. Air permeabilities are about 4000 md and porosities about 54%. Abundant coral fossils can be readily identified from thin section (Fig. 1(a)) and SEM (Fig. 1(b)). A minor amount of sparry calcite can be seen in the rock matrix (Fig. 1(a)). Interparticle and intraparticle pores are abundant. Gambier has high CEC compared to Whitestone UZ and Edwards (GC) and abundant macro and microporosity.

Brine

In initial studies of Gambier limestone [11], 5% $CaCl_2$ was adopted to limit dissolution as recommended by Graue *et al*. for chalk [17]. Further testing indicated that consistent results for limestone could be obtained with synthetic sea water. Synthetic sea water (Table 3) was subsequently adopted as a standard brine, partly because of its widespread use as a waterflood injection brine, and was used in the present work for tests with Whitestone UZ and Edwards (GC). 100 ppm NaN_3 was added to the brine to prevent bacterial growth.

Crude Oil

Cottonwood Creek crude oil, from a Wyoming dolomite reservoir of Permian age (Cottonwood Creek, Phosphoria dolomite), was employed in this work. The oil was sparged with nitrogen to remove H_2S; the density and viscosity at room temperature (T_m = ~ 22ºC) after N_2 sparging were 0.8874 g/cm^3 and 24.1 cp respectively. The crude oil is moderately asphaltic with the n-C7 asphaltene content being 2.3 wt %. Acid and base numbers are 0.56 and 1.83 mg KOH/g oil respectively. Interfacial tensions (IFT) were measured by a drop volume tensiometer (Krüss DVT-10). The IFT of Cottonwood crude oil was 29.7 mN/m to sea water and 27.2 mN/m to 5% $CaCl_2$. Hirasaki and Zhang interpreted IFT values of this magnitude as indication that the crude oil is not likely to be contaminated by oil field chemicals such as corrosion inhibitors [18].

Mineral Oils

Two mineral oils were used in this work. Soltrol 220, with viscosity of 3.8 cp (ambient temperature), was used as the probe oil in MXW-F and MXW-DF experiments. Before use, polar impurities were removed by passing the oil through a chromatographic column packed with silica gel and alumina. After cleaning, the Soltrol 220/brine interfacial tensions were ~50 mN/m.

Heavy mineral oil, with viscosity around 180 cp (ambient temperature), was used to establish initial water saturation in the Gambier limestone samples. This oil was cleaned first by making a suspension of silica gel and alumina to remove any polar impurities followed by filtration.

Intermediate Solvent

Decalin, decahydronaphthalene ($C_{10}H_{18}$), was used as an intermediate solvent in preparation of MXW-F samples to prevent destabilization of asphaltenes by direct contact between mineral oil and crude oil.

Core Preparation

Very Strongly Water-Wet (VSWW) Cores (S_{wi} = 0%)

All VSWW imbibition reference curves were obtained for core samples initially 100% saturated with mineral oil by vacuum. Soltrol 220 was used in tests with Whitestone UZ and Edwards (GC). Heavy mineral oil was used for tests on the highly permeable Gambier cores in order to slow the rate of imbibition. Whitestone UZ and Edwards (GC) cores were pressurized up to 900 psi under oil to ensure complete saturation.

MXW Cores

Core samples were first saturated with, and soaked in, the selected brine for at least 10 days to attain ionic equilibrium. Then, for Whitestone UZ and Edwards (GC) cores, S_{wi} was established by displacing synthetic brine with crude oil at 50°C at an initial flooding rate of 0.60 PV/hr (about 3 ft/day). Details of preparation of Gambier cores are given in Reference [11]. In all tests, the direction of oil flow was reversed and a further PV of oil was injected to even out the water saturation along the length of the core.

Cores at S_{wi} were submerged in stock crude oil (oil taken directly from the sample stock) and aged in sealed pressure vessels for 10 days at 75ºC (T_a). For imbibition tests performed with crude oil as the probe oil, the wetting states of the core samples are referred to as MXW.

Mixed-Wet with Film (MXW-F and MXW-DF) Cores

Imbibition experiments were also performed with cores using mineral oil (Soltrol 220) instead of crude oil as the probe oil. If the crude oil was displaced first with decalin (5 PV) to avoid destabilization of asphaltenes, and then clean mineral oil (5 PV Soltrol 220), the samples are referred to as MXW-F. If the crude oil was directly displaced with mineral oil, the cores are referred to as MXW-DF samples. All displacements of one oil by another were performed at 3 ft/day.

Spontaneous Imbibition

The prepared VSWW, MXW, MXW-F, and MXW-DF core samples were set in glass imbibition cells filled with the selected brine. Oil volume, expressed as percentage of original oil in place (%OOIP), was recorded vs. time. All imbibition tests were performed at ambient temperature (T_m).

Amott Indices

After brine imbibition tests, Amott index measurements [19, 20] were performed on all core samples. After spontaneous imbibition of brine, forced displacement tests were performed at rates ranging from 3 ft/day up to 50 ft/day for Whitestone UZ limestone, 3 ft/day up to 25 ft/day for Edwards (GC) limestone, and 2 ft/day up to 50 ft/day for Gambier limestone. One additional pore volume of brine was injected with the flow direction reversed to even out the fluid distribution along the core. After determining the Amott index to water, oil imbibition was followed by forced displacement with oil to determine the Amott index to oil.

Measurement of Amott wettability indices involves spontaneous imbibition tests. It is sometimes stated that imbibition of either brine or oil should be allowed to reach equilibrium [21]. However, imbibition by mixed-wet cores does not usually give clear cut end points. Reported Amott indices in this work were based on an operational end point definition given by a dimensionless imbibition time, t_D, of 10^5 [11].

RESULTS AND DISCUSSION

VSWW Imbibition

All the VSWW imbibition experiments were carried out with 0% initial water saturation. In contrast to MXW cores, the presence of initial water saturation has only moderate effect on VSWW imbibition behavior [13, 22]. Scaled spontaneous imbibition results for the three limestones are compared in Fig. 2(a). The final oil recoveries show significant differences, 62.8%, 53.8%, 41.5% for Gambier, Whitestone UZ, and Edwards (GC) respectively. Thus trapped oil varies by a factor of up to 1.5. The low recovery from Edwards (GC) is ascribed to the numerous small vugs of about 200 μ diameter formed by selective dissolution of fossils (see Figs. 1(a) and 1(b)).

If all the curves are normalized by final recovery, as shown in Fig. 2(b), it can be seen that they fall in a narrow range and are close to the correlated results for Berea 500 sandstone [23] and also the spread in results for a wide range of other rock types [22]. Whitestone UZ showed slightly faster imbibition at early time; this could be related to the inherent heterogeneity of this rock. The agreement between scaled imbibition behavior of the three tested limestones and many other outcrop rocks is strong indication that the outcrop limestones are free of organic contaminants.

Comparison of Imbibition for Different Rock Types

Initial water saturation (S_{wi}) is a key factor in the development of mixed wettability. It controls the amount of rock surface exposed to adsorption from crude oil [24]. Xie and Morrow showed that mixed-wet cores become increasingly less water-wet, as indicated by orders of magnitude decrease in scaled imbibition rate, with decrease in initial water saturation established prior to aging in crude oil [13]. This is good reason for keeping the initial water saturation constant for the same rock type when investigating other aspects of crude oil/brine/rock interactions. However, for different rock types with distinct difference in pore structure and size distribution, as in the present work, attempting to bring all cores to the same S_{wi} would serve little purpose. The S_{wi} values for each rock type were ~28.7% for Whitestone UZ, ~16.1% for Edwards (GC), and ~28.5% for Gambier. These values represent a compromise between rock petrophysical properties and technical convenience. For example, S_{wi} for Whitestone UZ and Edwards (GC) was established by essentially the same displacement conditions, whereas injection of heavy mineral oil was needed to attain an S_{wi} of ~28.5% for Gambier cores.

Figs. 3(a) and 3(b) present, respectively, the scaled imbibition results for Whitestone UZ and Edwards (GC) cores for MXW, MXW-F, and MXW-DF wetting states. For both of these grainstones, at any given dimensionless imbibition time, excluding induction time, MXW cores gave the highest rate and recovery of oil by spontaneous imbibition and MXW-DF cores showed the least. The same sequence of rate and recovery was given by the Gambier samples (Fig. 4(a)) [11]. Amott index measurements (see Table 4) were consistent with decrease of water wetness in the sequence MXW, MXW-F, and MXW-DF for all the three tested rock types. The same sequence was obtained for Berea sandstone [11].

Spontaneous Imbibition of Oil by Gambier Cores – Cottonwood and Minnelusa Crudes

After forced displacement of oil by water in the Amott test, cores were tested for imbibition of oil. From the Amott wettability index measurements in Table 4, it is seen that only Gambier MXW-F and MXW-DF cores showed production of water by spontaneous imbibition of oil. Fig. 4(b) presents the oil imbibition curves for Gambier cores at the three tested wetting states given by Cottonwood crude oil. Oil imbibition results for a core prepared with Minnelusa crude oil [11] are also included. The high degree of oil wetness may be related to asphaltene content of crude oil (9% for Minnelusa vs. 2.3% for Cottonwood) used in preparation of the core sample. The value of I_o of 0.93 for Gambier core prepared by direct displacement of asphaltic Minnelusa crude oil by mineral oil is the highest value of I_o yet seen for an outcrop rock after exposure to crude oil. In fact, no additional recovery of water was measured for forced displacement of oil. The value of I_o of 0.93, rather than 1, results from using a cut-off at $t_D = 10^5$. An I_{w-o} of -0.6 for MXW-F Edwards (GC) after aging with a North Sea crude oil at an S_{wi} of ~17% has been observed [25].

MXW Imbibition

Fig. 5(a) presents a comparison of the scaled MXW imbibition data for the three limestones. The Whitestone UZ core exhibited the fastest scaled imbibition behavior of the three rock types; Gambier imbibed slightly faster than Edwards (GC). The Whitestone UZ sample was more water-wet, $I_{w-o} = 0.63$, than Edwards (GC) and Gambier (I_{w-o} = 0.44 and 0.48 respectively). All three MXW rocks had values of I_{w-o} in the water-wet range (1.0 to 0.3) according to Cuiec's classification [20].

MXW-F and MXW-DF Imbibition

Scaled spontaneous imbibition data for MXW-F and MXW-DF cores for the three selected rock types are presented in Figs. 5(b) and 5(c). Clearly, for all three rock types, MXW-DF cores gave slower scaled imbibition than MXW-F cores. The slow imbibition of MXW-DF cores is ascribed to surface precipitation of asphaltenes resulting from direct displacement of crude oil by mineral oil [8]. But even with almost complete suppression of brine imbibition, I_{w-o} for the three MXW-DF cores are still very close to zero (-0.05 to -0.1).

Induction Time

From Figs. 5(a), 5(b) and 5(c) (see also Figs. 3(a), (b) and (c)), for MXW, MXW-F, and MXW-DF cores, both Edwards (GC) and Whitestone UZ cores showed induction times prior to noticeable imbibition. For Edwards (GC), the induction times for MXW and MXW-F cores were about 30 mins compared to under 5 min. for Whitestone UZ cores. The Gambier cores showed no delay in brine imbibition for all tested samples.

Oil Recovery

Total oil recovery by spontaneous imbibition followed by forced displacement is compared for Whitestone UZ and Edwards (GC) rocks at all the tested wettability states (see Fig. 5(d)). It can be seen that for the conditions tested, highest recovery of the probe oil was obtained for MXW-F grainstones that are weakly water-wet. (The wetting category which exhibits maximum recovery can be expected to shift with decrease in initial water saturation.) Recovery from VSWW, MXW, MXW-F, MXW-DF Gambier boundstone did not match the trend obtained for the grainstones.

Oil Wetness of Carbonate Rocks

In general, carbonate reservoir rocks are widely reported to be less water-wet than sandstones. However, for the three rocks of the present work, MXW cores exhibited extensive imibibiton of water (I_w from 0.44 to 0.63) with Cottonwood crude oil at the tested initial water saturations.

Several possible factors may contribute to this overall difference. Reservoir connate water and wettability can be difficult to re-establish in the laboratory. Reservoir carbonates often have lower initial water saturation (sometimes as low as 5% or even less) than the values used in this work. In general, the lower the initial water saturation, the higher the fraction of rock surface that is exposed to adsorption from crude oil. Factors governing the retention of water by capillarity in the reservoir, for example, change in the free water level, could also have changed over geologic time.

Restored state procedures are commonly used to reestablish reservoir wettability in the laboratory. In principle, the first step is to achieve a strongly water-wet state comparable to that exhibited by the outcrop limestones used in this study. Cleaning usually involves solvent flow or extraction using a series of organic solvents, such as chloroform, methanol, toluene, tetrahydrofuran, etc. [20]. In practice, so-called clean cores are usually found to be neutral-wet. If the traditional rock cleaning process includes Dean-Stark extraction with toluene, the high boiling point of toluene (110.6ºC) will cause removal of connate water before extracting the crude oil so that areas of rock previously overlain by bulk water may become exposed to adsorption from the crude oil [26]. This may further compromise the restored state procedure.

Model Limestone

A search some fifty years ago for a readily available outcrop sandstone lead to widespread adoption of Berea sandstone as a model rock for oil recovery and a wide variety of other topics. Results of the present study indicate that Edwards (GC) may be suited for use as a model limestone. The rock has low BET surface area, is low in microporosity, and satisfies criteria often used to describe sandstone as clean. Cores from a single block have been found to be uniform in permeability and porosity (about 11 md and 21% for the tested block). The high residual saturation of about 60% OOIP for VSWW cores and reduction to 30% at intermediate wettability is of special value to parametric studies such as determining relationships between oil recovery and wettability.

CONCLUSIONS

1. VSWW imbibition results for three tested outcrop limestone rock types, that span variation in permeability of three orders of magnitude and in porosity by a factor of two and a half, were scaled closely with correlated data for a wide variety of rocks and synthetic porous media.

2. Three selected outcrop limestones were very strongly water-wet (unlike fresh or cleaned carbonate cores from oil reservoirs) and provide a definitive initial condition for study of wettability change caused by adsorption from crude oil.

3. Wettability alteration from VSWW by commonly used core preparation techniques resulted in a consistent pattern of wettability change indicated by three distinct spontaneous imbibition curves. Rate and recovery was highest with crude oil as the probe oil (MXW), less if crude oil was displaced by a solvent followed by mineral (probe) oil (MXW-F), and least for direct displacement of crude oil by mineral (probe) oil (MXW-DF).

4. Oil recovery from grainstones by a combination of spontaneous imbibition followed by forced displacement (of the Amott test) was highest at slightly water-wet conditions.

ACKNOWLEDGEMENT

Support for this work was provided by BP/Amoco, Chevron Texaco, Total, Conoco Phillips, Statoil (Norway), EORI of the University of Wyoming, and the U.S. Department of Energy. We thank Continental Resources Inc. for providing Cottonwood oil, Jill Buckley for crude oil analysis, Lincoln Patterson, CSIRO, Melbourne, for providing the Gambier limestone rock, and Peigui Yin and Norman Wardlaw for discussions and petrographic analysis.

REFERENCE

1. Churcher, P.L., P.R. French, J.C. Shaw, and L.L. Schramm, “Rock Properties of Berea Sandstone, Baker Dolomite, and Indiana Limestone,” SPE 21044, presented at the SPE International Symposium on Oilfield Chemistry, Anaheim, CA, U.S.A., Feb. 20-22, 1991.
2. Buckley, J.S., Y. Liu, and S. Monsterleet, “Mechanisms of Wetting Alteration by Crude Oils,” *SPEJ* (Mar. 1998) **3**, 54-61.
3. Block, A. and B. B. Simms, “Desorption and Exchange of Adsorbed Octadecylamine and Stearic Acid on Steel and Glass,” *J. Colloid Interface Sci*., (1967) **25**, 514-18.
4. McCaffery, F.G. and N. Mungan, “Contact Angle and Interfacial Tension Studies of Some Hydrocarbon-Water-Solid Systems,” *J. Cdn. Pet. Tech.* (July-Sept. 1970) **9**, No. 3, 185-96.
5. Lowe, A.C., M.C. Phillips, and A.C. Riddiford, “On the Wetting of Carbonate Surfaces by Oil and Water,” *J. Cdn. Pet. Tech.* (April-June 1973) **12**, No. 44, 33-40.

6. Somasundaran, P., "Interfacial Chemistry of Particulate Flotation," *Advances in Interfacial Phenomena of Particulate/Solution/Gas Systems; Applications to Flotation Research*, P. Somasundaran and R.B. Grieves (eds.), AIChE Symposium Series (1975) **71**, No. 150, 1-15.
7. Cuiec, L.E., "Rock/Crude-Oil Interactions and Wettability: An Attempt to Understand Their Interrelation," SPE 13211 presented at the 1984 SPE Annual Technical Conference and Exhibition, Houston, TX, U.S.A., Sept. 16-19.
8. Al-Maamari, R.S.H. and J.S. Buckley, "Asphaltene Precipitation and Alteration of Wetting: the Potential for Wettability Changes during Production," *SPE REE* (August 2003) 210-214.
9. Treiber, L.E., D.L. Archer, and W.W. Owens., "A Laboratory Evaluation of the Wettabiltiy of Fifty Oil-Producing Reservoirs," *SPEJ*, (December, 1972), 531-540.
10. Chilingar, G.V. and T.F. Yen, "Some Notes on Wettability and Relative Permeability of Carbonate Reservoir Rocks, II," *Energy Sources* (1983) **7**, No. 1, 67-75.
11. Tie, H., Z. Tong, and N.R. Morrow, "The Effect of Different Crude Oil/Brine/Rock Combinations on Wettability through Spontaneous Imbibition," Proceedings of the 2003 International Symposium of Society of Core Analysis, Pau, Fance, Sept. 22-25.
12. Ma, S., N.R. Morrow, and X. Zhang, "Generalized Scaling of Spontaneous Imbibition Data for Strongly Water-wet Systems," *J. Pet. Sci. & Eng.*, (1997) **18**, 165-178.
13. Xie, X. and N.R. Morrow, "Oil Recovery by Spontaneous Imbibition from Weakly Water-Wet Rocks," *Petrophysics*, (July-August 2001) **42**, 4, 313-322.
14. Tong, Z., X. Xie, and N.R. Morrow, "Scaling of Viscosity Ratio for Oil Recovery by Imbibition From Mixed-Wet Rocks," *Petrophysics*, (July-August 2002) **43**, 4, 338-346.
15. Fischer, H., N.R. Morrow, and G. Mason, "Application of Water Desorption/Adsorption Isotherm Data to Characterization of Micro- and Meso-porosity in Sandstone and Carbonate Rocks," presented at the 7th International Symposium on the Characterization of Porous Solids, COPS VII, Aix-en-Provence, France, May 26-28, 2005.
16. Dunham, R.J., "Classification of Carbonate Rocks According to Depositional Texture", Ed. W.E. Ham, *Classification of Carbonate Rocks*. *Memoir 1*, AAPG, 1962, 108-121.
17. Graue, A., E. Tonheim, and B. Baldwin, "Control and Alteration of Wettability in Low-Permeability Chalk", Proceedings of *the 3rd International Symposium on Evaluation of Reservoir Wettability and Its Effect on Oil Recovery*, Ed. N.R. Morrow, Laramie, WY, U.S.A., Sep. 21-23, 1994.
18. Hirasaki, G. and D.L. Zhang, "Surface Chemistry of Oil Recovery from Fractured, Oil-Wet, Carbonate Formation," *SPEJ*, (June, 2004), 151-164.
19. Amott, E., "Observations Relating to the Wettability of Porous Rock," *Trans.*, AIME (1959) **216**, 156-62.
20. Cuiec, L.E., "Evaluation of Reservoir Wettability and Its Effect on Oil Recovery", *Interfacial Phenomena in Petroleum Recovery*, Ed. N.R. Morrow, Marcel Dekker, Inc., New York, 1991, 319-375.
21. Anderson, W.G., "Wettability Literature Survey – Part II: Wettability Measurement," *JPT* (Nov. 1986) **38**, No. 12, 1246-1262.

22. Viksund, B.G., N.R. Morrow, S. Ma, W. Wang, and A. Graue, "Initial Water Saturation and Oil Recovery from Chalk and Sandstone by Spontaneous Imbibition," Proceedings of the 1998 International Symposium of Society of Core Analysis, the Hague, Netherlands, Sept.
23. Zhang, X., N.R. Morrow, and S. Ma, "Experimental verification of a modified scaling group for spontaneous imbibition," *SPE Reservoir Evaluation*, *(*Nov. 1996) Vol. **11,** No. 4, 280-285.
24. Salathiel, R.A., "Oil Recovery by Surface Film Drainage in Mixed-Wettability Rocks," *JPT* (Oct. 1973) 1216-24; *Trans.*, AIME, 255.
25. Graue, A., personal communication.
26. Hirasaki, G.J., J.A. Rohan, and S.T. Dubey, "Wettability Evaluation During Restored-States Core Analysis," SPE 20506 presented at the 1990 SPE Annual Technical Conference and Exhibition in New Orleans, LA, U.S.A., Sept. 23-28.

Table 1. Selected properties of three rocks

Cores	BET, m^2/g	CEC, meq/100g
Whitestone UZ	0.90	0.00029
Edwards (GC)	0.20	0.00026
Gambier	0.77	0.00065

Table 2. Cores

Sample No.	L cm	D cm	k_g md	ϕ	S_{wi} %	μ_o cp	σ mN/m	Wetting
Whitestone UZ								
3WUZ02A	3.74	6.30	7.42	0.26	28.7	24.1	29.7	MXW
3WUZ01A	3.75	6.05	6.90	0.25	28.7	3.8	49.6	MXW-F
3WUZ01B	3.75	6.36	7.58	0.24	28.8	3.8	49.6	MXW-DF
Edwards (GC)								
1EGC05A	3.80	6.26	11.6	0.21	16.0	24.1	29.7	MXW
1EGC06B	3.80	6.37	10.4	0.21	16.3	3.8	49.6	MXW-F
1EGC06A	3.80	6.38	12.9	0.21	16.3	3.8	49.6	MXW-DF
Gambier [11]								
G08	5.10	3.77	4350	0.54	28.8	24.1	27.2	MXW
G10	4.90	3.77	4140	0.55	28.2	3.8	49.5	MXW-F
G11	5.09	3.78	4160	0.53	28.4	3.8	49.5	MXW-DF

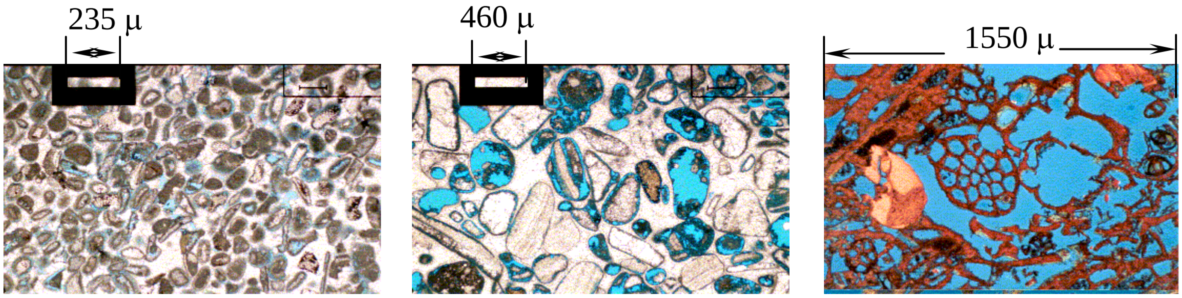
Table 3. Synthetic brine composition

Brine	NaCl (g/L)	KCl (g/L)	$CaCl_2$ (g/L)	$MgCl_2$ (g/L)	NaN_3 (g/L)	pH	TDS (mg/L)
Sea water	28	0.935	2.379	5.365	0.1	6.6	36779

Table 4. Amott indices

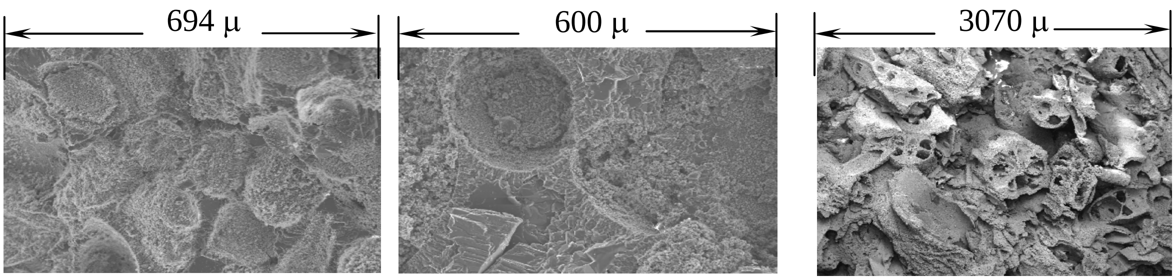
Sample No.	$V_{o,\,imb}$ mL	$V_{o\varepsilon,\,imb}$ mL	$V_{o,\,f}$ mL	I_w	$V_{w,\,imb}$ mL	$V_{w\varepsilon,\,imb}$ mL	$V_{w,\,f}$ mL	I_o	$I_{w\text{-}o}$	Wetting
Whitestone UZ										
3WUZ02A	4.70	0	2.72	0.63	0	-	-	-	0.63	MXW
3WUZ01A	2.35	0.08	5.50	0.30	0	-	-	-	0.30	MXW-F
3WUZ01B	0.53	0.09	7.07	0.07	1.20	0	5.80	0.17	-0.10	MXW-DF
Edwards (GC)										
1EGC05A	2.95	0	3.70	0.44	0	-	-	-	0.44	MXW
1EGC06B	1.65	0.52	6.90	0.18	0	-	-	-	0.18	MXW-F
1EGC06A	0	0	6.95	0.00	0.78	0.05	7.70	0.09	-0.09	MXW-DF
Gambier [11]										
G08	6.26	3.54	3.15	0.48	0.10	0	12.50	0.01	0.48	MXW
G10	2.23	0.72	10.90	0.16	2.20	0.40	9.40	0.18	-0.02	MXW-F
G11	1.00	0.13	10.80	0.08	1.37	0.03	8.70	0.14	-0.05	MXW-DF

Note: $V_{o,\,imb}$ and $V_{w,\,imb}$ are oil and water recovery from brine and oil imbibition tests at the chosen 10^5 cut-off dimensionless time. $V_{o\varepsilon,\,imb}$ and $V_{w\varepsilon,\,imb}$ are oil and water production after $t_D = 10^5$. $V_{o,f}$ and $V_{w,f}$ are forced displacement recovery of oil and water.



Whitestone UZ Edwards (GC) Gambier

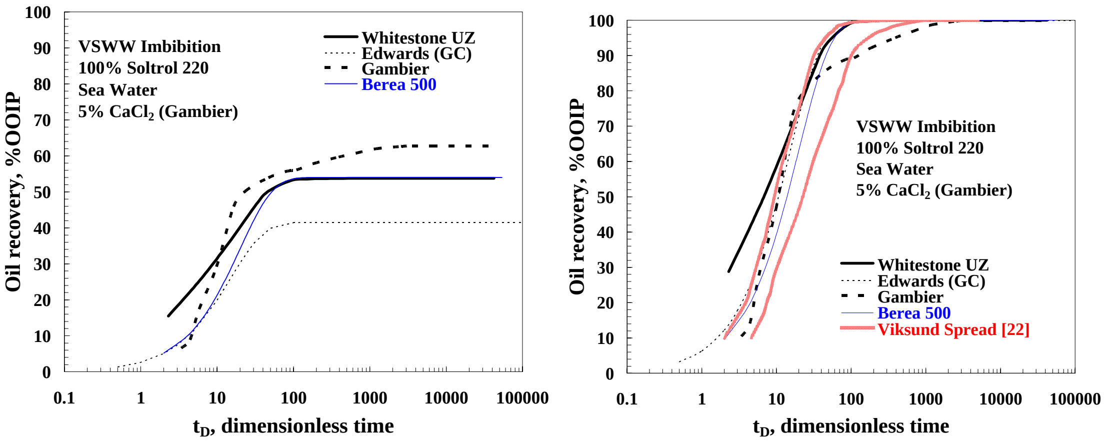
(a) Thin section



Whitestone UZ Edwards (GC) Gambier

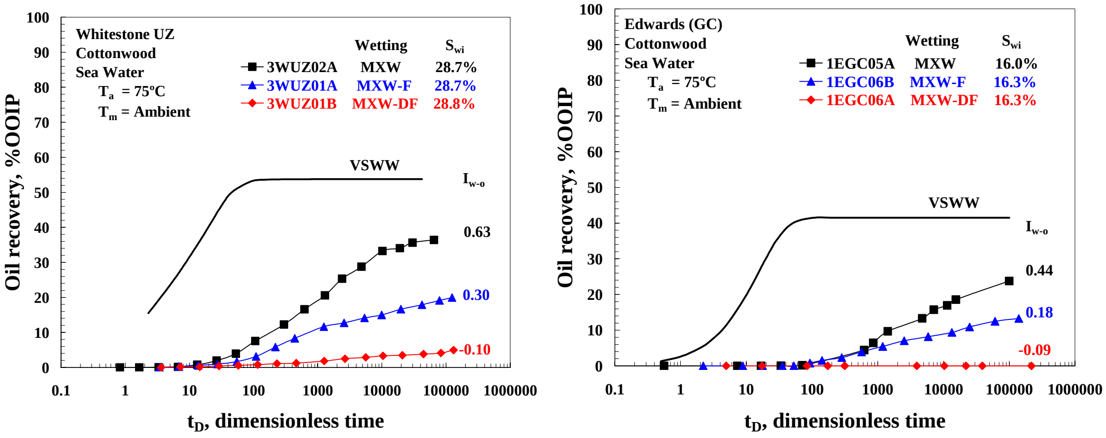
(b) SEM

Fig. 1 Thin section and SEM



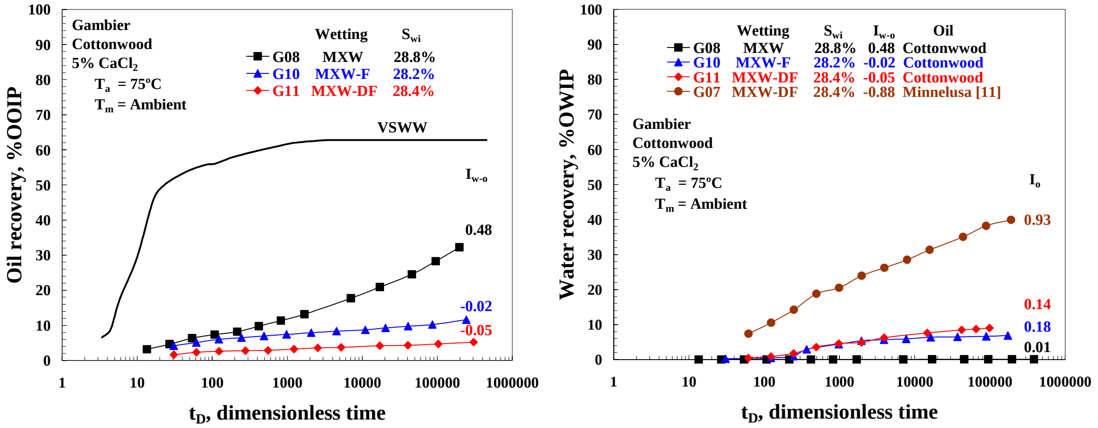
(a) Correlated VSWW imbibition (b) Normalized to final recovery

Fig. 2 (a) Scaled VSWW imbibition results for the three limestones and Berea sandstone, and (b) comparison with range of normalized results for a variety of rock types.



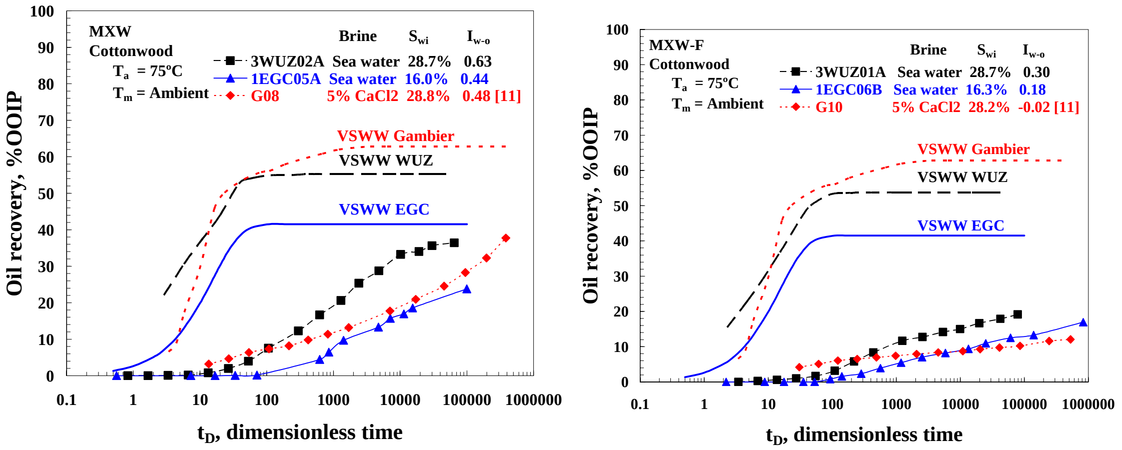
(a) Whitestone UZ cores (b) Edwards (GC) cores

Fig. 3 Comparison of spontaneous imbibition for two grainstones with MXW, MXW-F, and MXW-DF wetting states induced by Cottonwood crude oil



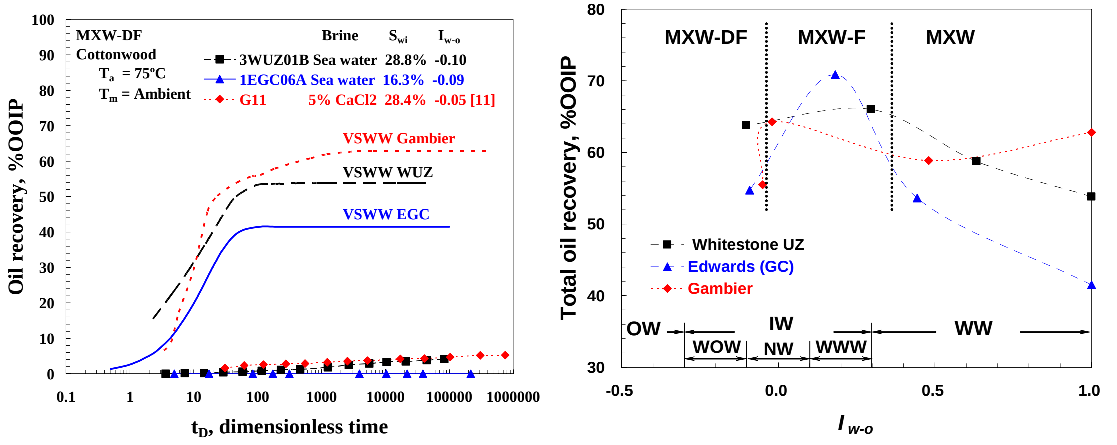
(a) Brine imbibition (b) Oil imbibition

Fig. 4 Comparisons of (a) spontaneous imbibition of brine for Gambier cores with MXW, MXW-F, and MXW-DF wetting states induced by Cottonwood crude oil [11] and (b) spontaneous imbibition of oil after forced displacement (MXW-DF imbibition for Gambier and Minnelusa crude oil is included)



(a) Scaled MXW imbibition

(b) Scaled MXW-F imbibition



(c) Scaled MXW-DF imbibition

(d) Total recovery vs. wettability

Fig. 5 Comparison of recovery of oil with VSWW for (a) MXW, (b) MXW-F, (c) MXW-DF by spontaneous imbibition for three carbonate rocks, and (d) total oil recovery (spontaneous imbibition plus forced displacement) versus Amott-Harvey wettability index.
(WW – water-wet, WWW – weakly water-wet, NW – neutral wet, WOW – weakly oil-wet, IW – intermediate wetting, OW – oil-wet [7])