

# **SCA2003-02: THE EFFECT OF DIFFERENT CRUDE OIL/BRINE/ROCK COMBINATIONS ON WETTABILITY THROUGH SPONTANEOUS IMBIBITION**

Hongguang Tie, Zhengxin Tong and Norman R. Morrow  
Chemical & Petroleum Engineering Department, University of Wyoming  
Laramie, Wyoming

*This paper was prepared for presentation at the International Symposium of the Society of Core Analysts held in Pau, France, 21-24 September 2003*

## **ABSTRACT**

Wettability depends on crude oil/brine/rock interactions. The presence of initial water saturation can determine the areas of rock pore surface where such interactions result in adsorption of polar components from crude oil to give a condition described as mixed wettability (MXW). If crude oil is removed to leave an organic film (F) on the rock surface, the condition is referred to as MXW-F. MXW and MXW-F wetting states are compared through spontaneous imbibition measurements for crude oil/brine/rock combinations that include one sandstone and one limestone with each rock type exposed to an asphaltic and a moderately asphaltic crude oil. The solvency of the crude oils for the asphaltenes was decreased by addition of n-decane with volumetric ratio ranging from 14% to 30%. The limestone exhibited greater sensitivity to crude oil solvency than the sandstone. Whatever the crude oil or its composition, rates of recovery of refined oil by spontaneous imbibition from MXW-F cores were slower than for the corresponding MXW cores.

Key words: mixed wettability, carbonate, sandstone, crude oil solvency, asphaltene.

## **INTRODUCTION**

Although about one half of world oil reserves are held in carbonate formations, the number of laboratory studies of oil recovery from carbonate rocks are far fewer than for sandstone. Denekas *et al.* found both acidic and basic components of crude oil could change the wettability of sandstone, while the basic nitrogenous components mainly affected limestone [1]. Somasundaran noted that quartz surfaces are more sensitive to basic components in crude oil while carbonate surfaces are more sensitive to acidic components [2]. Buckley *et al.* pointed out that one mechanism for wettability alteration induced by contacting a mineral surface with crude oil is by nonspecific attraction between oppositely charged surface sites. Specific interactions, ion binding, and chelation may all contribute to crude oil/brine/rock interactions [3]. Near neutral pH, silica is negatively charged, whereas calcite is positively charged. Because of such effects, it has often been suggested that the oil recovery mechanisms controlled by adsorption from

crude oil for sandstone differ from those for carbonate. For example, it has often been suggested that carbonates are more likely to be oil wet [4].

Al-Maamari and Buckley pointed out that the stability of asphaltenes could be a dominant factor that overrides the various ionic interaction mechanisms and makes the surfaces oil-wet through asphaltene precipitation [5]. One approach to investigation of the potential reservoir wetting changes caused by such effects during production is to run laboratory tests at reservoir pressure and temperature using reconstituted live oil. However, such tests are expensive. It may be possible to design simplified laboratory tests that are relevant to reservoir conditions. For example, if the solvency of the live crude oil is matched through addition of n-decane, rather than hydrocarbon gases (mainly methane), to the dead crude oil, the effect of wettability on reservoir performance might be modeled satisfactorily simply by running tests at elevated temperature but ambient pressure.

In previous work, Xie *et al.* showed that the stability of wetting changes induced on smooth quartz surfaces by adsorption from crude oil depended on its chemical properties. Oil with moderate (~2%) to high asphaltene content (~9%) and high base numbers generally gave films that were stable to movement of the three phase line of contact back and forth across the surface [6]. For sandstones, a series of investigations were performed on correlation of MXW and MXW-F imbibition behavior that included, the effects of initial water saturation, wetting stability, and crude oil composition [7, 8, 9, 10].

In the present work, exploratory studies are reported on the effect of different crude oil/brine/rock combinations on the wettability of MXW and MXW-F cores through spontaneous imbibition measurements. Limestone outcrop samples were obtained from Mt. Gambier, Australia, and Berea sandstone was supplied by Cleveland Quarries, Ohio. These rocks were chosen mainly because of availability and the distinct difference in their surface mineralogy. An asphaltic crude oil from a sandstone reservoir and a moderately asphaltic crude oil from a carbonate reservoir were used to induce wettability changes. The effect of decrease in solvency of the crude oils on wettability alteration was investigated through addition of alkane.

## **EXPERIMENTAL MATERIALS AND PROCEDURES**

### **Cores**

Limestone: Fourteen cores, nominally of 3.8 cm diameter and 5.0 cm length, were cut from Mt. Gambier limestone (Australia). The air permeabilities of the cores ranged from 3750 md to 5420 md with twelve of the cores in the range 4000 to 4500 md. Porosities were all in the range  $54.0 \pm 1.4\%$ . One reason for use of this high permeability rock in this exploratory study was to ensure that imbibition could be measured within reasonable times even at close-to-neutral wettability. The limestone is composed of coral fossil fragments, with a minor amount of coarse sparry calcite. It is very porous and interparticle and intraparticle pores are abundant (see Fig. 1a (i) and (ii)).

**Sandstone:** Seventeen cores, nominally of 3.8 cm diameter and 7.6 cm length, were cut from blocks of Berea sandstone referred to as Berea 90 [10]. Air permeabilities ranged from 80 to 123 md with 15 of the cores in the range 90 to 113 md. Porosities were all within  $18.4 \pm 0.6\%$ . This rock sample is subarkose with framework mainly composed of quartz, feldspar, and lithic fragments. Minor amounts of sparry dolomite cement and kaolinite and chlorite clays exist. Porosities are dominated by intergranular pores (see Fig. 1a (iii) and (iv)). From X-ray diffraction analysis, the ratio of chlorite to kaolinite for Berea 90 was higher than typically observed for Berea sandstone of higher permeability.

Individual core properties are listed in Tables 1 and 2. Surface areas from nitrogen adsorption (BET) and cation-exchange capacities are included in Table 3.

### **Crude Oil**

One crude oil from a Wyoming sandstone reservoir of Permian/Lower Permian age (Gibbs Field, Minnelusa formation) and one from a Wyoming dolomite reservoir of Permian age (Cottonwood Creek, Phosphoria dolomite) were selected. The Cottonwood crude oil was sparged with nitrogen to remove  $H_2S$ . Asphaltene content, acid and base numbers, viscosities and densities of the two crude oils are presented in Table 4.

### **Crude Oil with Reduced Solvency (CO/Reduced Solvency)**

The solvency of the dead Minnelusa crude oil for its asphaltene was reduced by addition of n-decane 14% and 22% by volume to provide solvencies above and below the onset of precipitation [11]. Tests on Cottonwood crude oil were run after addition of either 20% or 30% by volume of n-decane.

### **Brine**

A 5%  $CaCl_2$  brine was used for displacement tests of the limestone rock in order to limit dissolution [12]. Simulated Minnelusa reservoir brine was used for the tests on sandstone/Minnelusa oil combinations. Sea water was used in tests on sandstone/Cottonwood oil combinations.  $NaN_3$  (0.10 g/L) was added as a biocide to all brines in order to prevent bacterial growth. Brine compositions are listed in Table 5.

### **Mineral Oil**

Mineral oils (Soltrol 220 mineral oil, 3.8 cp, and a heavy mineral oil of about 175 cp), with polar components removed by exposure to silica gel and alumina, were used in core preparation and imbibition tests.

### **Oil/Brine Interfacial Tension**

Interfacial tensions (IFT), measured by drop volume tensiometer (Kruss DVT-10), were 27.0 mN/m for Minnelusa/Minnelusa brine, 25.1 mN/m for Minnelusa/5%  $CaCl_2$ , 29.7 mN/m for Cottonwood/sea water, and 27.2 mN/m for Cottonwood/5%  $CaCl_2$ . IFT values of this magnitude provide indication that the oil is not contaminated by oil field chemicals such as corrosion inhibitors [13]. Refined oil/brine interfacial tensions were ~50 mN/m.

### **Establishment of Initial Water Saturations Prior to Aging**

Initial water saturations were established by displacing brine with either crude oil or heavy mineral oil. The core samples were first saturated with, and then soaked in, the selected brines for at least 10 days to attain ionic equilibrium. Two different procedures were adopted in reaching target values of  $S_{wi}$ : (1) for sandstone samples with Minnelusa crude oil,  $S_{wi}$  of about 25% was established by displacing reservoir brine directly with crude oil at 45°C at 0.2 ml/min to 5.0 ml/min (about 0.72 to 18.75 PV/hr). (2) For limestone samples and sandstone cores treated with Cottonwood crude oil,  $S_{wi}$  was attained by displacing brine with heavy mineral oil followed by displacement of mineral oil with 5 PV decalin. The decalin was then displaced with 5 PV of the crude oil at elevated temperature ( $T_f$ ). The heavy mineral oil floods of sandstone samples were performed at 0.15 ml/min to 0.50 ml/min (about 0.6 PV/hr to 2 PV/hr). A rate of 0.20 ml/min was used for the subsequent decalin and crude oil displacements. For the limestone samples, heavy mineral oil was injected at 0.25 ml/min to 5.0 ml/min (about 0.5 to 10 PV/hr) to give  $S_{wi}$  of about 28.5%. Subsequent decalin and crude oil displacements were run at 0.25 ml/min (about 3 ft/day, 0.5 PV/hr). In all tests, the flow direction was reversed and 1 PV of the displacement oil was injected to even out the water saturation along the length of the core.

Initial water saturation is a critical parameter of wetting and imbibition [7, 10] that deserves to be investigated in its own right for carbonates. However, attempts to obtain a close match of the initial water saturations of the limestone and sandstone would not serve much purpose. The fraction of water retained by fine pores and microporosity can be expected to differ significantly between the two rock types.

### **Aging in and Replacement of the Crude Oil and CO/Reduced Solvency**

Cores containing crude oil or CO/Reduced Solvency mixtures at  $S_{wi}$  were submerged in the selected oil and aged in sealed pressure vessels for 10 days at 75°C ( $T_a$ ). If the cores are then tested with these oils, they are referred to as MXW cores.

In preparation of MXW-F cores, crude oil or modified crude oil was displaced by 5 PV of decalin at 3 ft/day (about 0.72 PV/hr for the sandstone, and about 0.5 PV/hr for the limestone) at 50°C. Decalin was then displaced with 5 PV of Soltrol 220 at ambient temperature. The effect of contact of the mineral oil with crude oil on wettability was tested by omitting the intermediate solvent (decalin) displacement so that the crude oil was displaced directly by the mineral oil.

### **Spontaneous Imbibition**

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

## Amott Indices

After brine imbibition, some of the MXW and MXW-F cores were selected for measurement of Amott wettability indices [14]. The cores were flushed with the test brine at rates up to 48 ft/day (for sandstone) and 60 ft/day (for limestone) ft/day (2.4 ml/min and 5.0 ml/min respectively). The flow direction was reversed and one additional PV of brine was injected to even out the fluid distribution along the length of the core. Then the core was immersed in oil and recovery of brine by spontaneous imbibition was recorded. After completion of the imbibition step, the cores were flooded with oil at rates equal to those used in the corresponding brine flood to determine the amount of brine recovered by forced displacement.

## RESULTS AND DISCUSSION

Previous studies showed that a semi-empirical scaling group initially developed for strongly water wet conditions [15], can be used to compare changes in imbibition rate as a result of changes in wettability for a variety of MXW [7] and MXW-F [10] wetting conditions. The following scaling group is used in the present work to assess changes in wettability from spontaneous imbibition behavior.

$$t_D = t \sqrt{\frac{k}{f}} \frac{s}{\sqrt{m_o m_w}} \frac{1}{L_c^2}$$

where  $t_D$  is dimensionless time,  $t$  is time,  $k$  is permeability,  $f$  is porosity,  $s$  is the interfacial tension, and  $m_o$  and  $m_w$  are the oil and brine viscosities.  $L_c$  is a characteristic length that compensates for sample size, shape and boundary conditions [15].

Mixed-wet cores often do not exhibit clear-cut imbibition end points. In the present work the imbibition recovery,  $V_{o,imb}$  for oil and  $V_{w,imb}$  for brine, used in calculation of Amott indices was operationally determined by the recovery at a cutoff dimensionless time of  $10^5$  (This corresponds to imbibition time ranging from about 3 days for the Mt. Gambier limestone MXW-F cores to about 80 days for Berea sandstone MXW cores). The largest value of  $V_{oe,imb}$  ( see Table 6, Core 5B8) was obtained after 12 months. Post-cutoff recovery, if any, by spontaneous imbibition,  $V_{oe,imb}$  and  $V_{we,imb}$ , was added to the recoveries obtained by force displacement,  $V_{o,f}$  for oil recovery and  $V_{w,f}$  for brine recovery to obtain Amott indices from the following equations [16].

$$I_w = \frac{V_{o,imb}}{V_{o,imb} + V_{oe,imb} + V_{o,f}}$$

$$I_o = \frac{V_{w,imb}}{V_{w,imb} + V_{we,imb} + V_{w,f}}$$

$$I_{w-o} = I_w - I_o$$

### **Comparison of imbibition by limestone and sandstone MXW cores**

MXW Cores – Recovery of Minnelusa and Cottonwood Crude Oils Fig. 1b presents scaled imbibition data for MXW limestone cores for Minnelusa and Cottonwood crude oils. Results for sandstone cores are presented in Fig. 1c. The rate of recovery for Cottonwood oil is less than for the Minnelusa oil for both the sandstone and limestone cores. One contributing reason for this behavior is that, although the Minnelusa crude oil has higher asphaltene content than Cottonwood oil (9.0% vs. 2.3%), the ratio of acid and base number to asphaltene content of the Cottonwood oil is comparatively high.

Imbibition rates (normalized with respect to rates for very strongly water-wet (VSWW) conditions) vs. oil recovery for the two oils and two rocks are shown in Fig. 1d. For the same fraction of oil recovery, the relative rate of recovery for the sandstone falls between the relative rates measured for the limestone.

Minnelusa Crude Oil Plus Alkane MXW imbibition rates for limestone samples decrease with addition of n-decane (see Fig. 2a). For the sandstone cores, Fig. 2b, noticeable decrease was only achieved when 22% of n-decane was added to the crude oil. Also, an obvious induction time was observed for Minnelusa crude oil containing 22% of n-decane.

Cottonwood Crude Oil Plus Alkane In MXW (Cottonwood) limestone cores, imbibition rates decrease significantly with the increase in the added volume of n-decane (Fig. 2c). For sandstone cores, Fig. 2d, decreases in imbibition rates were also observed but were small relative to those observed for the limestone. No significant differences were observed in imbibition behavior between cores prepared with 20% and 30% of n-decane added to the crude oil except after long imbibition time.

### **Comparison of imbibition for limestone and sandstone MXW-F cores**

Direct Displacement of Crude Oil by Mineral Oil For both limestone and sandstone core samples, and either Minnelusa or Cottonwood crude oil, the MXW-F samples prepared by direct flush of crude with 5 PV of Soltrol 220 mineral oil (MO) show very low imbibition rate and recovery (see Fig. 3a and 3b). The likely cause of the large change in wetting is surface precipitation of asphaltenes [5]. Conditions for surface precipitation propagate through the core as the injected refined oil mixes with the crude oil to give a composition that results in surface precipitation. This composition is close to that for the onset of asphaltene precipitation [5].

MXW-F for Different Crude Oils Comparison of imbibition results for MXW-F limestone and sandstone cores are presented in Fig. 3a and Fig. 3b respectively. Compared to MXW results, the rate and extent of imbibition for MXW-F cores were consistently lower for all tests. For example, the recovery from Cottonwood MXW-F cores is about 10% for limestone and 11% for sandstone, while the recovery from Cottonwood MXW cores is 28% for limestone and 33% for sandstone. (cf. Fig. 1b, 1c and 3a, 3b respectively). For sandstone samples, the imbibition rate for MXW-F (Minnelusa) cores is faster than for MXW-F (Cottonwood) cores. Except at early time,

the scaled imbibition rates of MXW-F (Cottonwood) cores are almost the same for both limestone and sandstone cores.

Minnelusa Oil Plus Alkane For both limestone and sandstone MXW-F (Minnelusa plus alkanes) core samples respectively, the imbibition rates are dramatically suppressed compared to the results for MXW (Fig. 3c and Fig. 3d). For limestone core samples, the imbibition rates for MXW-F cores prepared with 14% and 22% of n-decane in Minnelusa crude oil were low and showed no significant differences. (The MXW-F core prepared with Minnelusa crude oil even showed slightly lower imbibition rate and recovery.) For sandstone MXW-F cores, no differences in the imbibition behavior were observed for cores prepared with 0%, 14%, and 22% n-decane added to Minnelusa crude oil.

Cottonwood Oil Plus Alkane In MXW-F (Cottonwood), for both limestone and sandstone core samples (cf. Fig. 3e, 3f and Fig. 2c, 2d respectively), the imbibition rates are suppressed compared to corresponding MXW combinations ( Fig. 2c and 2d). For both rock types, addition of alkanes had essentially no effect on imbibition behavior.

### **Amott Indices**

For both limestone and sandstone, Table 6, the Amott index of MXW cores lay in the water-wet range (0.3 to 1) by Cuiec's classification [16]. For the MXW-F cores, all the values of  $I_{w-o}$  fell in the range of intermediate-wet (-0.3 to 0.3). Moreover, limestone MXW-F cores all had neutral wettability (-0.1 to 0.1).

The largest change in wettability from the original VSWW state was observed for an MXW-F limestone core prepared by direct displacement of Minnelusa crude oil with mineral oil ( $I_w = 0.05$ ,  $I_o = 0.93$ ,  $I_{w-o} = -0.88$ ). This provides strong evidence for wettability alteration by asphaltene precipitation, a mechanism which was first identified through contact angle behavior [5].

## **CONCLUSIONS**

1. A crude oil with intermediate asphaltene content (Cottonwood, 2.3%) but high acid and base number relative to asphaltene content caused larger reduction in imbibition rate than a high asphaltene content oil (Minnelusa, 9.0%) for both sandstone and limestone cores.
2. Modification of both Cottonwood and Minnelusa crude oil composition through addition of an alkane resulted in systematic decrease in rate of recovery with increase in alkane content for the limestone. For sandstones, the overall changes, if any, in wetting with addition of alkanes were small except for the Minnelusa oil above the onset of precipitation.
3. For any combination of Cottonwood oil and Minnelusa oil and sandstone or limestone, direct displacement of crude oil by mineral oil resulted in almost

complete suppression of spontaneous imbibition. The behavior is ascribed to generation of strongly oil-wet surfaces by surface precipitation.

4. Comparison of crude oil recovery at MXW conditions with recovery of mineral oil for MXW-F conditions generated by the corresponding parent crude oil, showed the latter to be distinctly less water-wet for any of the tested combinations.

## NOMENCLATURE

$D$	Diameter of core samples, cm	$T_m$	imbibition temperature, °F
$k$	gas permeability, md	$V_{o,f}$	Oil recovery by forced displacement
$I_o$	Amott oil index	$V_{o,imb}$	Oil recovery by spontaneous imbibition
$I_w$	Amott water index	$V_{w,f}$	Brine recovery by forced displacement
$I_{w-o}$	Amott relative wettability index	$V_{w,imb}$	Brine recovery by spontaneous imbibition
$L$	Length of core samples, cm	$f$	porosity, %
$L_c$	characteristic length, cm	$\sigma$	oil/water interfacial tension, mN/m
$S_{wi}$	initial water saturation, %	$V_{oe,imb}$	Post-cutoff oil recovery by imbibition
$t$	imbibition time, min	$V_{we,imb}$	Post-cutoff brine recovery by imbibition
$t_D$	dimensionless imbibition time	$m_w$	water viscosity, cp
$T_a$	aging temperature, °F	$m_o$	oil viscosity, cp
$T_f$	decaline flush temperature, °F		

## ACKNOWLEDGEMENT

Support for this work was provided by BP/Amoco (U.K./U.S.A.), Chevron, ELF/Total/Gas de France/Institut Francais du Petrole (France), Phillips, Shell (The Netherlands), Statoil (Norway), the Enhanced Oil Recovery Institute of the University of Wyoming, and the U.S. Department of Energy through the National Petroleum Technology Office. We thank Eric Robertson of Idaho National Engineering and Environmental Laboratory and Kyle True of True Oil Company for providing Minnelusa crude oil, Continental Resources Inc. for providing Cottonwood oil, Jill Buckley for crude oil analysis and valuable discussion, Lincoln Patterson, CSIRO, Melbourne, for providing the limestone rock, and Peigui Yin for obtaining petrographic data.

## REFERENCES

1. Denekas, M.O., Mattax, C.C., and Davis, G.T., "Effects of Crude Oil Components on Rock Wettability," *Trans., AIME* (1959) **216**, 330-333.
2. 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.

3. Buckley, J.S., Liu, Y., and Monsterleet, S., "Mechanisms of Wetting Alteration by Crude Oils," *SPEJ* (Mar. 1998) **3**, 54-61.
4. Anderson, W.G., "Wettability Literature Survey—Part1: Rock/Oil/Brine Interactions and the Effects of Core Handling on Wettability," *JPT*, (Oct. 1986), 1125-1144.
5. Al-Maamari, R.S.H. and Buckley, J.S., "Asphaltene Precipitation and Alteration of Wetting: the Potential for Wettability Changes during Production," SPE 59292, *2000 SPE/DOE IOR Symposium*, Tulsa, OK, U.S.A., 2-5 Apr.
6. Xie, X., Morrow, N.R., and Buckley, J.S., "Contact Angle Hysteresis and the Stability of Wetting Changes Induced by Adsorption from Crude Oil," *J. Pet. Sci. & Eng.*, 33 (2002), 147-159
7. Xie, X. and Morrow, N.R., "Oil Recovery by Spontaneous Imbibition from Weakly Water-Wet Rocks," *Petrophysics*, (July-August 2001) **42**, 4, 313-322.
8. Tong, Z., Morrow, N.R., and Xie, X., "Spontaneous Imbibition of Mixed-Wettability States in Sandstones Induced by Adsorption from Crude Oil," *Proceedings of the 7<sup>th</sup> International Symposium on Reservoir Wettability*, Tasmania, Australia, March 2002 (*J. Pet. Sci. & Eng.*, in press, 2003)
9. Tong, Z., Xie, X., and Morrow, N.R., "Crude Oil Composition and the Stability of Mixed Wettability in Sandstones," *Proceedings of the International Symposium of the Society of Core Analysts*, Monterey, CA, U.S.A. Paper SCA-2002-31, Sept. 2002 (*Petrophysics*, in press, 2003).
10. Tong, Z., Xie, X. and Morrow, N.R., "Scaling of Viscosity Ratio for Oil Recovery by Imbibition From Mixed-Wet Rocks," *Petrophysics*, (July-August 2002) **43**, 4, 338-346.
11. Wang, J.: Personal communication, Mar. 2002.
12. Graue, A., Tonheim, E., and Baldwin, B., "Control and Alteration of Wettability in Low-Permeability Chalk", *Proceedings of the 3<sup>rd</sup> International Symposium on Evaluation of Reservoir Wettability and Its Effect on Oil Recovery*, Ed. Morrow, N. R., Laramie, WY, U.S.A., 21-23 Sep. 1994.
13. Hirasaki, G. and Zhang, D. L., "Surface Chemistry of Oil Recovery from Fractured, Oil-Wet, Carbonate Formation," SPE 80988, *2003 SPE International Symposium on Oilfield Chemistry*, Houston, TX, U.S.A., 5-8 Feb.
14. Amott, E., "Observations Relating to the Wettability of Porous Rock," *Trans., AIME* (1959) **216**, 156-62.
15. Ma, S., Morrow, N.R., and Zhang, X., "Generalized Scaling of Spontaneous Imbibition Data for Strongly Water-wet Systems," *J. Pet. Sci. & Eng.*, (1997) **18**, 165-178.
16. Cuiec, L. E., "Evaluation of Reservoir Wettability and Its Effect on Oil Recovery", *Interfacial Phenomena in Petroleum Recovery*, Ed. Morrow, N. R., Marcel Dekker, Inc., New York, 1991, 319-375.

Table 1. Minnelusa crude oil

Core	L,cm	D,cm	k, md	$\phi$	$S_{wi},\%$	$\mu_o, cp$	$\sigma, mN/m$	Rec. oil (imb.)
Berea sandstone								
5B2	7.745	3.784	92.5	0.179	24.6	77.2	27.0	crude
5B3	7.506	3.783	97.9	0.180	25.0	3.8	49.5	mineral oil
5B8	7.394	3.785	103.7	0.185	24.6	77.2	27.0	crude
5B32	7.668	3.782	94.3	0.185	25.7	3.8	49.5	mineral oil
5B33	7.719	3.782	99.0	0.187	25.2	3.8	49.5	mineral oil
3B3	8.118	3.799	99.3	0.184	25.8	19.1	22.1	14 (v)% decane + crude
3B4	7.776	3.799	92.3	0.183	25.5	3.8	49.5	mineral oil
3B5	7.878	3.798	93.7	0.182	26.1	3.8	49.5	mineral oil
3B6	7.854	3.798	94.2	0.182	25.6	14.5	25.1	22 (v)% decane + crude
3B20	7.827	3.798	123.3	0.188	25.3	3.8	49.5	mineral oil
Mt Gambier limestone								
G25	5.334	3.765	4530	0.550	28.7	70.6	25.1	crude
G02	5.006	3.782	5420	0.532	28.5	3.8	49.5	mineral oil
G07	4.961	3.776	4220	0.541	28.4	3.8	49.5	mineral oil
G12	4.917	3.778	4090	0.528	28.6	3.8	49.5	mineral oil
G13	5.055	3.778	4420	0.554	28.6	19.1	25.1	14 (v)% decane + crude
G26	5.181	3.774	4270	0.530	28.4	3.8	49.5	mineral oil
G15	5.017	3.770	3990	0.533	28.6	14.5	25.4	22 (v)% decane + crude

Table 2. Cottonwood crude oil

Core	L,cm	D,cm	k, md	$\phi$	$S_{wi},\%$	$\mu_o, cp$	$\sigma, mN/m$	Rec. oil (imb.)
Berea sandstone								
3B11a	7.050	3.798	113.6	0.190	24.6	3.8	49.5	mineral oil
3B12a	7.261	3.798	107.1	0.190	25.6	3.8	49.5	mineral oil
3B13a	7.158	3.798	109.2	0.190	25.2	9.2	28.6	20 (v)% decane + crude
3B15a	7.038	3.798	103.7	0.188	24.6	24.1	29.7	crude
3B16a	7.279	3.784	100.0	0.187	25.5	3.8	49.5	mineral oil
3B16b	7.064	3.785	80.7	0.182	24.2	3.8	49.5	mineral oil
3B17a	7.061	3.788	101.4	0.186	25.2	6.4	28.9	30 (v)% decane + crude
Mt Gambier limestone								
G08	5.103	3.772	4350	0.542	28.8	24.1	27.2	crude
G10	4.897	3.773	4140	0.548	28.2	3.8	49.5	mineral oil
G11	5.087	3.780	4160	0.526	28.4	3.8	49.5	mineral oil
G16	4.948	3.770	4060	0.531	28.5	3.8	49.5	mineral oil
G17	4.904	3.770	3750	0.538	28.7	9.2	27.0	20 (v)% decane + crude
G18	5.056	3.767	4170	0.550	28.5	3.8	49.5	mineral oil
G19	5.050	3.764	4120	0.544	28.4	6.4	26.9	30 (v)% decane + crude

Table 3. Selected properties of sandstone and limestone cores

Cores	BET, m <sup>2</sup> /g	CEC, meq/100g
Berea sandstone	1.2	0.0030
Mt. Gambier limestone	0.77	0.00065

Table 4. Selected properties of crude oil samples

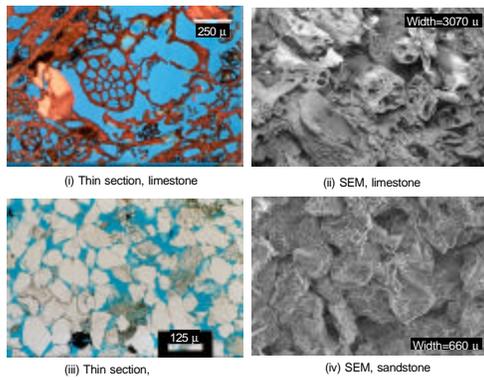
Crude oil	Density, g/ml	$\mu_o$ at 22°C, cp	n-C7 asphalt., wt%	Acid #, mg KOH/g oil	Base #, mg KOH/g oil
Minnelusa	0.9062	77.2	9.0	0.17	2.29
Cottonwood	0.8874	24.1	2.3	0.56	1.83

Table 5. Synthetic brine composition

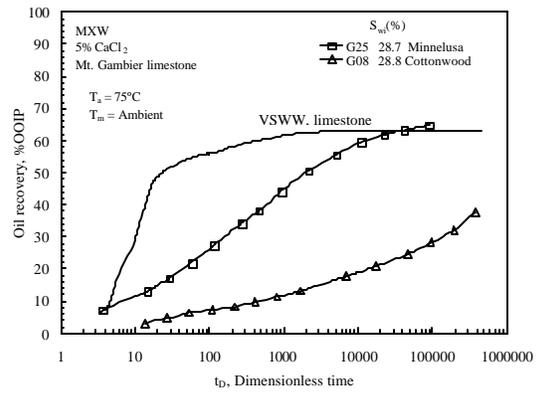
Brine	NaCl (g/L)	KCl (g/L)	CaCl <sub>2</sub> (g/L)	MgCl <sub>2</sub> (g/L)	MgSO <sub>4</sub> (g/L)	Na <sub>2</sub> SO <sub>4</sub> (g/L)	NaN <sub>3</sub> (g/L)	pH	TDS (mg/L)
Minnelusa	29.8	-	2.1	-	0.394	5.903	0.1	6.8	38297
Sea water	28	0.935	2.379	5.365	-	-	0.1	6.6	36779
5% CaCl <sub>2</sub>	-	-	50	-	-	-	0.1	6.9	50100

Table 6, Amott Indices

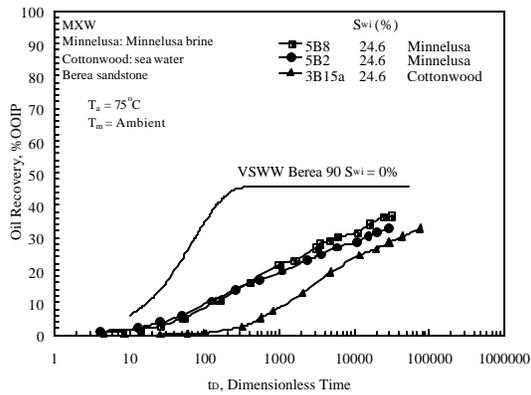
Core	V <sub>o, imb</sub> mL	V <sub>oe, imb</sub> mL	V <sub>o, f</sub> mL	I <sub>w</sub>	V <sub>w, imb</sub> mL	V <sub>wε, imb</sub> mL	V <sub>w, f</sub> mL	I <sub>o</sub>	I <sub>w-o</sub>	Wetting State
Mt Gambier limestone										
G07	0.43	0.17	8.40	0.05	6.80	0.55	0	0.93	-0.88	MXW -F (Minnelusa Direct Flood)
G12	2.03	0.67	10.54	0.15	1.45	0.10	9.70	0.13	0.02	MXW -F (14% Decane + Minnelusa)
G08	6.26	3.54	3.15	0.48	0.10	0	12.50	0.01	0.48	MXW (Cottonwood Crude)
G11	1.00	0.03	10.80	0.08	1.37	0.03	8.70	0.14	-0.05	MXW -F (Cottonwood Direct Flood)
G10	2.23	0.72	10.90	0.16	2.20	0.40	9.40	0.18	-0.02	MXW -F (Cottonwood)
Berea sandstone										
5B8	4.15	0.35	1.20	0.73	0	-	-	0	0.73	MXW (Minnelusa)
3B3	4.50	2.90	0.05	0.6	0	-	-	0	0.60	MXW (22% Decane + Minnelusa)
3B12b	2.07	0.41	5.03	0.28	0.28	0	6.42	0.04	0.24	MXW -F (Minnelusa)
3B15a	3.80	0.65	0.85	0.72	0	-	-	0	0.72	MXW (Cottonwood)
3B13a	4.60	2.00	0	0.70	0	-	-	0	0.70	MXW ( 20% Decane + Cottonwood)
3B16b	0.42	0.16	7.13	0.05	0.65	0.07	6.30	0.09	-0.04	MXW -F (Cottonwood Direct Flood)
3B12a	1.30	0.37	7.00	0.16	0.30	0.10	7.50	0.04	0.12	MXW -F (Cottonwood)



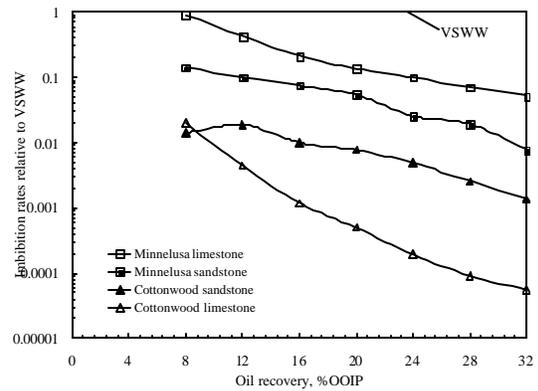
a) Thin section and SEM photos



b) Limestone

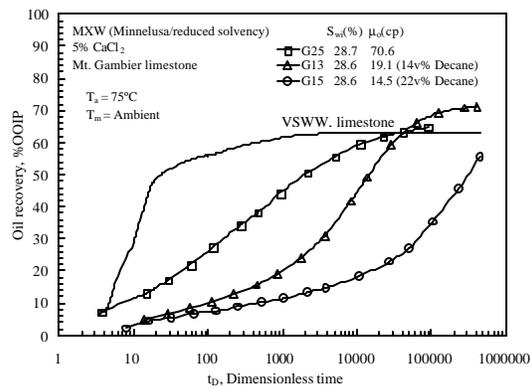


c) Sandstone

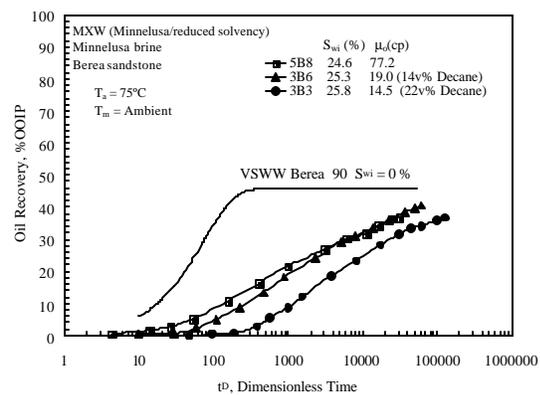


d) Relative reduction in imbibition rates

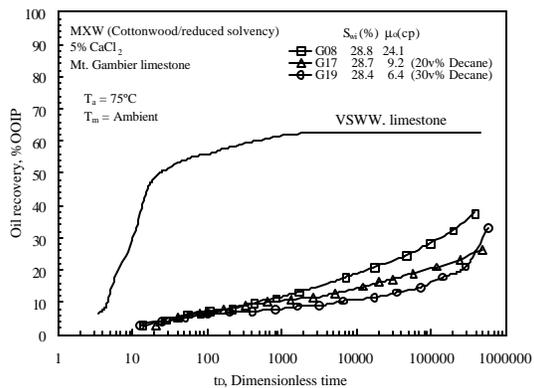
Fig. 1 Thin section and SEM photos and recovery of crude oil from MXW limestone and sandstone by spontaneous imbibition



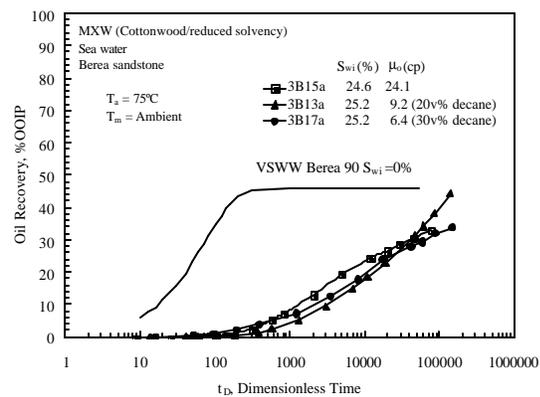
a) Minnelusa/Limestone



b) Minnelusa/Sandstone

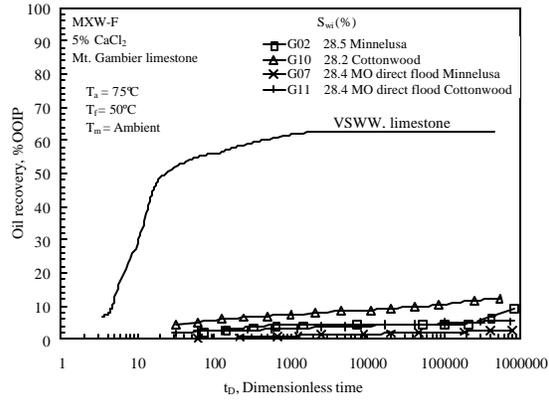


c) Cottonwood/Limestone

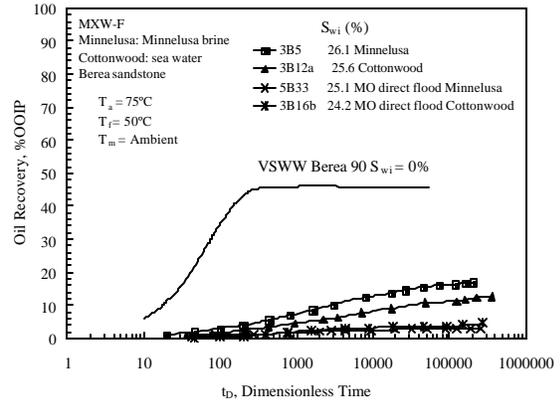


d) Cottonwood/Sandstone

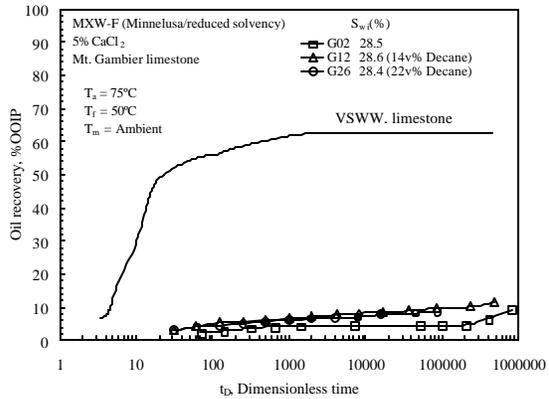
Fig. 2 Recovery of crude oil from MXW (CO/Reduced Solvency) limestone and sandstone by spontaneous imbibition



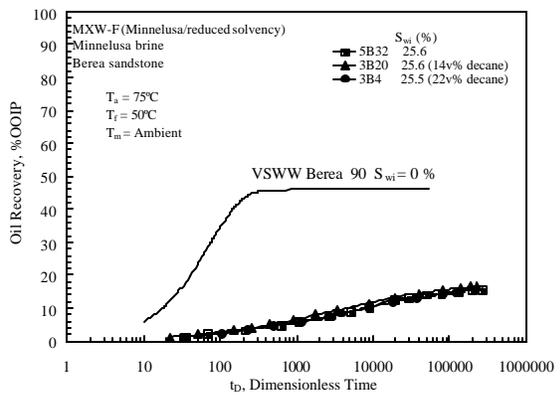
a) Limestone



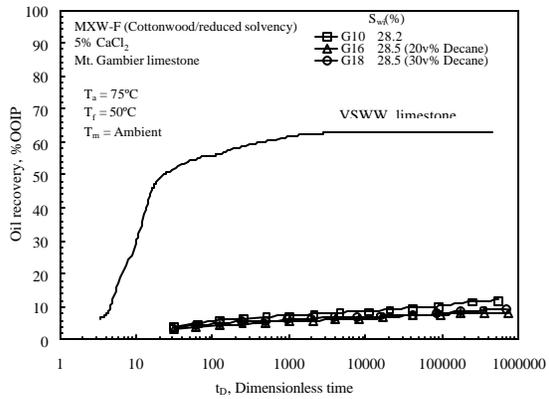
b) Sandstone



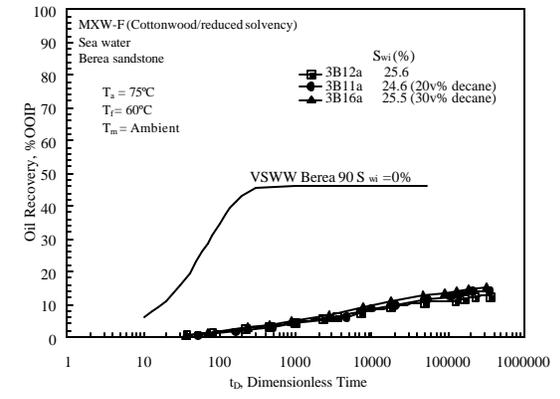
c) Minnelusa/Limestone



d) Minnelusa/Sandstone



e) Cottonwood/Limestone



f) Cottonwood/Sandstone

Fig. 3 Recovery of mineral oil from MXW-F (direct displacement) and MXW-F (CO/reduced solvency) limestone and sandstone by spontaneous imbibition