Extensive Experimental Wettability Study in Sandstone and Carbonate-Oil-Brine Systems: Part 1 – Screening Tool Development

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ABSTRACT

An extensive systematic study was designed to investigate the effect of geochemical parameters in wetting sandstone and carbonate rock-oil-brine systems. The geochemical parameters investigated in this project are: rock mineralogy (Austin chalk, Indiana limestone, Silurian dolomite, and Berea sandstone), aqueous chemistry (pH and salinity), oil chemistry and temperature. If the effects of the proposed parameters are examined with respect to each other, an overwhelming number of experiments would be required. Therefore, conventional experimental studies such as contact angle measurements and flow through porous media experiments cannot be used to study all the parameters in the allocated time for this project. This paper will present an alternative method of estimating wettability that is much faster and has high repeatability, and thus creates a well-informed screening tool to sort through different possible chemical conditions present in the reservoir and pick the parameters of interest for further study.

INTRODUCTION

Wettability is the ability of an immiscible fluid to adhere on a rock surface in the presence of another immiscible fluid [1]. This parameter has a significant impact on multiphase flow in porous media for it influences the efficiency of oil recovery methods and distribution of oil and water in the reservoir. Extensive work has been done to create effective and reliable methods to measure this parameter especially at reservoir conditions [2]. In addition, many researchers have worked on understanding how wettability influences oil recovery. Recently, different research groups have focused on understanding the effect of different reservoir parameters on the wetting state e.g. brine salinity, brine composition, oil type, rock mineralogy, temperature, etc. In the past two decades, several research groups have carried out extensive research on the effect of brine salinity on wettability [3-5]. Zhang and Austad [6] investigated the impact of potential determining ions in carbonate systems. Buckley's [7,8] group has examined crude oil's effect on wettability and in turn proposed mechanisms responsible for the observed interactions. Sayyouh et al. [9,10] investigated the effect of clay mineralogy, salinity and alkalinity on wettability. Hoeiland et al. [6] carried out IFT and contact angle experiments and found that the chemical structure of the acidic material may be more important than concentration in the oils. Rao [12] showed that in most cases, sandstone reservoirs become more oil-wet with increasing temperature, while most of the carbonate reservoirs become more water-wet. Austad's group [13-16] has done a phenomenon study of how different parameters affect the wetting state of carbonates especially chalk.

Nevertheless, the mechanisms that govern wettability are still an enigma due to its complex nature that transverse through different disciplines. An oil reservoir is composed of numerous components that create a plethora of possible chemical conditions that may influence the nature of wettability. This makes it difficult to manipulate and predict wettability reliably and consistently when chemical conditions are changed. The main project in which this study is a part of undertakes an extensive and systematic effort to study the effects of previously mentioned geochemical parameters with respect to each other. Since over 2000 experiments will be needed to complete this study, a screening process that is fast, reliable, and informative is essential.

FLOTATION EXPERIMENT

Two flotation techniques were identified in literature: (1) Wu et al. (2008) and (2) Doe and Dubey (1993), referred to as Wu and D&D, respectively (Table 1). Both procedures can give qualitative indication of chemicals effect on altering wettability. The two main differences are that Wu's procedure dries the rock powder after it is aged in oil, while D&D procedure ages the rock in brine prior to aging in oil. In addition, the D&D procedure has no drying step.

Table 1: Comparison of the two published flotation experiment procedure by Wu et al (2008) and Dubey and Doe (1993). The asterisk (*) indicates the main differences in the two procedures.

Wu et al. (2008) Procedure	**Dubey and Doe (1993) Procedure**
• Age rock in oil for two days in a test tube • Decant the oil • *Dry the remaining rock** • Add brine to the dried rock powder in test tube • Stir the brine-oil-rock mixture • Take measurements after 2 hours using the criteria represented in Figure 1	• *Age rock in brine for two days in a test tube** • Separate brine from rock and save the brine • Add oil in the test tube with rock grains • Age rock in oil for two days • Add the saved brine in oil-rock mixture • Stir the brine-oil-rock mixture Take measurements when the mixture settles.

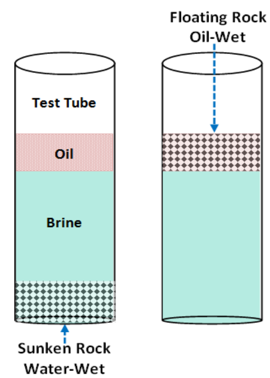

Figure 1: Schematic illustrating the flotation test results where sunken rock powder is considered water-wet and floating rock powder is oil-wet.

Both procedures were extensively tested under different conditions (Table 2). It was observed that Wu's procedure rendered all rock types water-wet, while the D&D method showed sandstone was water-wet and the carbonates were oil-wet. D&D procedure was modified to add the drying step from Wu's procedure in order to test the effect of that step, and results indicated both Berea and carbonates were water-wet for all tested conditions. In addition, when 2.5 ml oil was added at the end of Wu's procedure and the contents were vigorously stirred, the powdered limestone, chalk, or dolomite that had previously sunk to the bottom of the test tube now floated in the oleic phase. This confirmed that the drying step unique to Wu's procedure is responsible for the difference between the procedures. We concluded that the true nature of the carbonate rocks under the tested conditions is oil-wet; however, the drying process could have destabilized the oil film around the grains or evaporated the surface active compounds (SAC) in the oleic phase rendering the system water-wet. Therefore, the D&D procedure was found to be the most consistent and reliable of the two. It avoids the drying process which has tremendous effect on the observed wettability and avoids potential evaporation of SAC in the model oil. In addition, less oil (3 ml) is used in the D&D process. And finally, there is less chance of contamination because the test tubes are always closed in the D&D procedure.

Table 2: The effects of oil composition on wettability @ 70°C using Wu et al. (2008), Dubey and Doe (1993), and Dubey and Doe with drying step. WW represents water-wet conditions as OW is oil-wet.

	Aromatic A1	**Oxygen O1**	**Sulfur S1**	**Nitrogen N1**	**Decane Dec**	**Condensate Cond**
Berea: Wu	WW	WW	WW	WW	WW	WW
Berea: D&D	WW	WW*	WW	WW	WW	WW
Chalk: Wu	WW	WW	WW	WW	WW	WW
Chalk: D&D	OW	OW	OW	OW	OW	OW
Limestone: Wu	WW	WW*	WW	WW	WW	WW*
Limestone: D&D	OW	OW	OW	OW	OW	OW
Dolomite: Wu	WW	WW*	WW	WW	WW	WW
Dolomite: D&D	OW	OW	OW	OW	OW	OW
WW*: water-wet with a small fraction of rock displaying oil-wet behavior.						

Modified Flotation Test (MFT) Procedure

The rock is ground and sieved to 53 microns and 0.2 grams added to a sterilized test tube. 10ml of brine is added and the mixture is aged for 48 hours. At this stage of the process all rock sinks to the bottom of the test tube. After the aging process is completed, the pH is measured, and the brine is separated from the rock and saved for later reuse. 3ml of oil is added to the test tube containing wet rock and the mixture is aged for 48 hours, with stirring every 12 hours. The saved brine is added back to the oil-rock mixture in the test tube, stirred vigorously and allowed to settle for 24 hours. The rock at the bottom of the test tube is considered water-wet and that floating in the oleic phase is considered oil-wet (Figure 1). The rock-oil mixture is decanted followed by the pH measurement of brine. The brine solution is then poured out leaving wet rock in the test tube. The water-wet rock is then dried and weighed and mass of oil-wet rock is calculated by difference. The end result was a highly repeatable, consistent, and informative screening tool. The limitation of this technique is that it can only be conducted at ambient pressures. On the other hand, this method is much faster than conventional methods and many experiments can be conducted at the same time.

EXPERIMENTS

Table 3 illustrates the 567 flotation experiments carried out to examine the effect of oil chemistry, rock mineralogy, and salinity on wettability at 25°C, 70°C, and 110°C. The 12 oil types consist of pure decane, condensate, and ten model oils. A set of experiments is defined as the 12 experiments for each rock type the brine and temperature. Each set of experiments has an initial condition (IC) case where pure decane is used as the oleic phase. The IC case will be used to normalize the other results in the set in order to examine if the SAC has the ability to shift wettability. The ten model oils consist of decane and 2000 ppm of surface active compound (SAC). Each SAC will be studied individually. The four groups of SAC chemicals studied are: aromatic (A1, 2,3,4-Tetrahydonaphthalene), oxygen (Acetic, Myristic, and Naphthenic acid), sulfur (Dibenzothiophene, Di-n-butyl sulfide, and 1-Tetradecanethiol), and nitrogen (Carbazole, Quinoline, Pyridine) compounds. In addition, four rock-types were used: Berea sandstone, Austin chalk, Silurian dolomite, and Indiana limestone. Three temperatures were tested (25°C, 70°C and 110°C). Lastly, four brine salinities tested were 0 ppm, 1000 ppm, 10000 ppm, 100,000 ppm as illustrated by Table 4.

Table 3: The effect of brine salinity, surface active compounds (SAC) and rock mineralogy on wettability at 25°C, 70°C, and 110°C. The rock-decane-brine cases are considered to be the initial conditions cases that other experiments in each set are compared to, in order to observe the effects of each SAC on wettability on the rocks.

SAC	**Arom.**	**Oxygen**			**Sulfur**			**Nitrogen**			**Decane**	**Condensate**
	A1	**O1**	**O2**	**O3**	**S1**	**S2**	**S3**	**N1**	**N2**	**N3**	**Dec**	**Cond**
Berea											IC	
Chalk											IC	
Limestone											IC	
Dolomite											IC	

Table 4: Brine composition for the four tested salinities.

	Total Salinity (mg/L)	**NaCl (mg/L)**	**Ca (mg/L)**	**Mg (mg/L)**	**SO4 (mg/L)**	**HCO3 (mg/L)**
Brine 1	**100,000**	90000	3000	3000	3000	1000
Brine 2	**10,000**	9000	300	300	300	100
Brine 3	**1,000**	900	30	30	30	10
Brine 4	**0**	0	0	0	0	0

RESULTS

This section presents a few selected results to indicate the type of information produced by the modified flotation technique. With such information trends can be quickly observed and parameters of interest can then be picked for further studies.

Rock-Decane-Brine

Figure 2 illustrates the initial conditions for the four rocks in the presence of four brines at 25°C, 70°C, and 110°C. Initial conditions are defined by the use of decane as the oleic phase. Decane is an alkane compound used to represent a non-reactive organic medium. Decane does not have a charge that can electrostatically interact with the rock surface. When an SAC is added to the decane, it will present reactive sites that may alter wettability.

Figure 2 illustrates that decane does not interact with Berea sandstone at the brine salinities and temperature tested. This is expected since decane does not have reactive sites present to interact with the rock. In the case of the tested carbonate rocks, a significant difference in wettability is observed between the high and low salinity (1,000 ppm and 0 ppm) brines. In the presence of high salinity brines, chalk displays water-wet conditions, but in low salinity brines exhibits oil-wet conditions. The oil-wet behavior exhibited by the low salinity brines is very peculiar, for it indicates that decane has the ability to interact with the chalk rock grains, but not the sandstone. It is hypothesized that London-van-der-Waals attractive forces may be responsible for the interaction between decane and carbonate rock surfaces at low salinity brines. These forces are weak, however, in the absence of electrostatic forces they can dominate. Once salinity is increased the electrostatic forces become more prevalent gradually diminishing the strength of London-van-der-Waals forces.

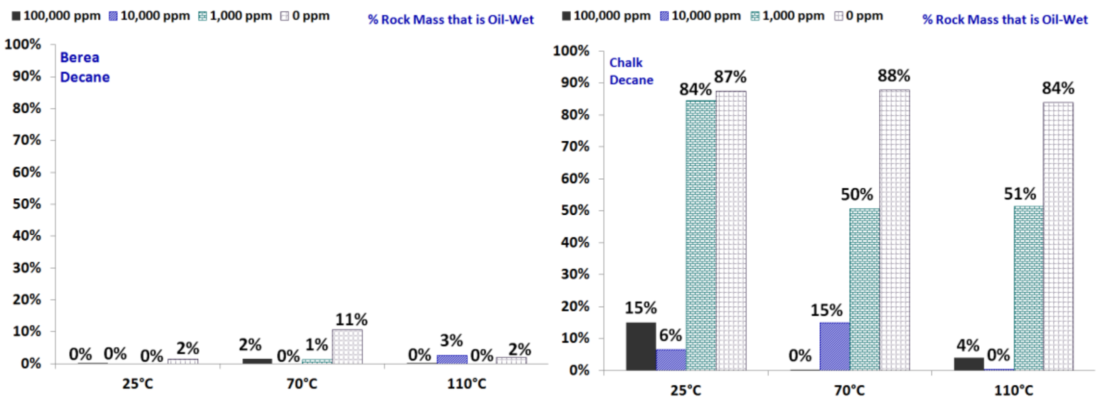

Figure 2: Reports the fraction of rock grains that are oil-wet when decane and brine are used with Berea sandstone and Austin chalk.

Chalk-Brine-Oxygen SAC

Figure 3 illustrates the effect of two oxygen SAC on chalk. Acetic acid is a short-chained fatty acid and one of the simplest carboxylic acids, while naphthenic acid is a mixture of cyclopentyl and cyclohexl carboxylic acids. Acetic acid seems to render chalk water-wet for all brine salinities especially the low ones. The opposite effect is observed for the long- chained fatty acids where they shift the wettability towards oil-wet especially at higher salinity. It seems that as brine salinity is increased the long-chained fatty acids shift the wettability more towards oil-wet conditions. There are minor contradictions in both cases presented, which calls for further study and understanding why certain conditions present opposite results. The contradictions may be a result of an experimental error, or a certain mechanism is active at these conditions and thus altering the wettability differently.

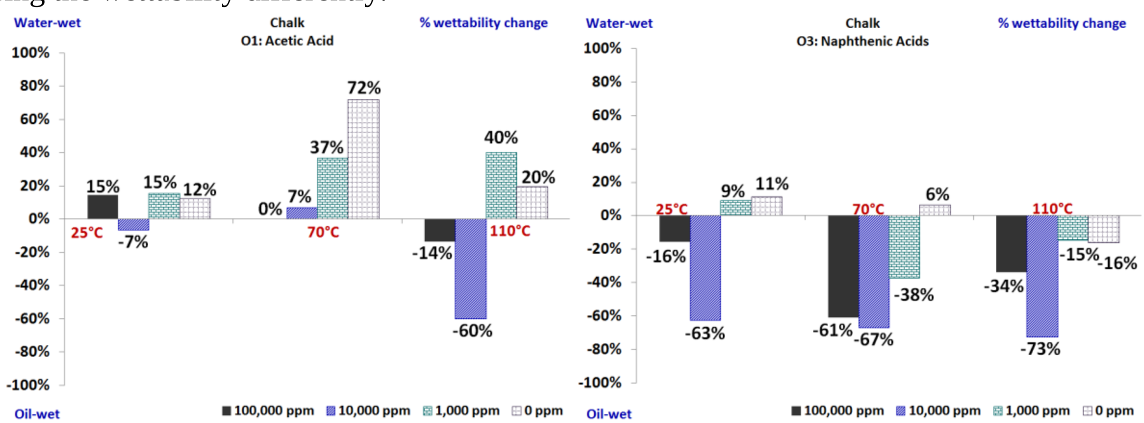

Figure 3: Reports the effect of acetic and naphthenic acid on the wettability of chalk at four different salinities.

CONCLUSION

The objective of this paper was to present an alternative method of measuring/estimating wettability that is much faster, quantitative with high precision, and thus creates a well-informed screening tool to sort through different possible chemical conditions present in the reservoir and pick the parameters of interest for further study. In addition, this paper presents the type of information that can be obtained from the proposed modified flotation technique. Trends can be identified and conditions of interest can be studied further.

REFERENCES

1. Rao, D.N. “Fluid-fluid and solid-fluid interfacial interactions in petroleum reservoirs,” *Petroleum Science and Technology*, (2001) **19**(1&2), 157-188
2. Rao, D.N. and Girard, M.G., “A new technique for reservoir wettability characterization”, *Journal of Canadian Petroleum Technology*, (1996), 31-39
3. Tang, G.Q. and Morrow, N.R., “Salinity, Temperature, oil composition, And Oil Recovery by Waterflooding.” *SPE Reservoir Eng.*, (1997), 269-276
4. Lager, A., Webb K.J., Black, C.J. Singleton, M., Sorbie, K.S. “Low Salinity Oil Recovery - An Experimental Investigation,” *Society of Core Analyst*, (2006) , SCA2006-36,1-12
5. Zhang, Y. and Morrow, N.R., “Comparison of secondary and tertiary recovery with change in injection brine composition for crude oil/sandstone combinations,” (2006), SPE 99757 presented at the 2006 SPE/DOE Symposium on Improved Oil Recovery, 22-26.
6. Zhang, P.M., Austad, T., “Wettability and oil recovery from carbonates: Effects of temperature and potential determining ions.” *Colloid and surface A*, (2006), **279**, 179–187
7. Buckley, J.S., Takamura, K., Morrow, N., “Influence of Electrical Surface Charges on the Wetting Properties of Crude Oils”. *SPE Reservoir Engineering*, (1989), **4**, 332-340.
8. Buckley, J.S., Liu, Y., and Monsterleet, S., “Mechanisms of Wetting Alteration by Crude Oils” *SPE Journal (37230)*, (1998), **3**(1), 54-61.
9. Sayyouh, M.H., Dahab, A.S. and Omar, A. “Effect of Clay Content on Wettability of Sandstone Reservoir.” *Journal of Petroleum Science*, (1990), **4**(2), pp. 119-125
10. Sayyouh, M.H., Hemeida, A.M., Al Blehed, M.S. and Desouky, S.K., “Role of Polar Compounds in Crude Oils on Rock Wettability” *Journal of Petroleum Science*, (1991), **6**, 225-233
11. Hoeiland S., Barth T., Blokhus A. M., Skauge A., “The effect of crude oil acid fractions on wettability as studies by interfacial tension and contact angles,” *Journal of Petroleum Science and Engineering*, (2001), **30**, 91-103.
12. Rao, D.N., “Wettability effects in thermal recovery operations.” *SPE Reservoir Evaluation. & Engineering.*, (1999) **2**, 420-430
13. Austad, T., Shariatpanahi, S.F., Strand, S., Black, C.J.J. and Webb, K.J., 2011. Condition for low salinity EOR-effect in carbonate oil reservoirs. 32nd Annual IEA EOR Symposium and Workshop, 17-19 October.
14. Austad, T., RezaeiDoust, A. and Puntervold, T., “Chemical mechanism of low salinity water flooding in sandstone reservoirs” SPE 129767 prepared for presentation at the 2010 SPE Improved Oil Recovery Symposium, 24-28 April 2010.
15. Austad, T., Strand, S., Madland, M.V., Puntervold, T. and Korsnes, R.I., “Seawater in chalk: An EOR and compaction fluid,” *SPE Reservoir Evaluation & Engineering*, (2008), **11**(4), 648-654.
16. Austad, T., Strand, S., Puntervold, T. and Ravari, R.R., “New method to clean carbonate reservoir cores by seawater,” SCA2008-15 presented at the International Symposium of the Society of Core Analysts, 29th October to 2nd Nov 2008.