

WETTABILITY ALTERATION OF CHALK BY SULPHATE CONTAINING WATER, MONITORED BY CONTACT ANGLE MEASUREMENT

Liping Yu, Dag C. Standnes¹ and Svein M. Skjæveland
University of Stavanger, N-4036 Stavanger, Norway
¹ Statoil ASA, Bergen, Norway

*This paper was prepared for presentation at the International Symposium of the
Society of Core Analysts held in Calgary, Canada, 10-12 September, 2007*

ABSTRACT

Observations are reported in the literature of spontaneous imbibition of seawater or modified seawater containing different concentrations of sulphate ions into preferential oil-wet chalk samples. The imbibition rate seems dependent on concentration of sulphate ions. Furthermore, the increased oil recovery from such experiments is interpreted as a wettability alteration of the chalk surface due to interaction between the chalk surface and the sulphate ions.

This paper reports the wettability alteration of chalk material by contact angle measurements on chalk slices and calcite crystal plates. Chalk slices aged with crude oil and calcite crystals aged either by crude oil or n-decane/stearic acid were exposed to seawater containing different concentration of sulphate (keeping the ion strengths constant) for different time periods at different temperatures before being transferred to a contact angle measurement cell for Drop Shape Analysis (DSA). By introducing oil droplets to the chalk slice surface immersed in the corresponding seawater used previously in the exposing procedure, contact angles were measured at room temperature for solid-fluid-fluid systems. The values were calculated by the software for DSA. The results show that the contact angle is in the oil-wet range initially and then decreases as a function of time the substrates have been exposed to sulphate containing water. The contact angles decreased in a similar way for both distilled water (DW) and sulphate containing water for temperatures below 100°C. At 130°C however, the contact angles decreased more for calcite crystals surrounded by sulphate containing water than for crystals only exposed to distilled water (DW). This observation may account for the observed spontaneous imbibition of sulphate containing water into preferential oil-wet chalk above 100°C reported in the literature.

INTRODUCTION

The wettability of a reservoir rock is of ultimate importance for oil recovery because it affects almost all types of core analysis, including capillary pressure, relative permeability, waterflooding behaviour, electrical properties, and simulated tertiary recovery (Anderson, 1986a). Wettability is of special importance for carbonate reservoirs because up to 65% of the carbonate rocks are oil-wet and 12% are intermediate-wet

(Chillingar and Yen, 1983). Furthermore, it is documented that about 50% of the world's present proven petroleum reserves are contained in carbonate reservoirs (Roehl and Choquette, 1985).

Normal waterflooding is usually not successful in carbonate fields because most of carbonate reservoirs are highly fractured with wettability conditions as neutral to preferential oil-wet (Austad et al, 1998). Seawater has, however, been injected into the naturally fractured Ekofisk chalk reservoir in the North Sea for nearly 20 years with great success (Sylte et al. 1988). Recent laboratory studies indicate that seawater appears to be an important factor regarding improved oil recovery from moderate water-wet fields such as the Ekofisk field (Austad et al., 2005; Høgnesen et al., 2005; Zhang and Austad, 2005a; Zhang and Austad, 2006). It was observed that temperature and sulphate ions from the injected seawater were the key factors for seawater to induce wettability modifications towards more water-wet conditions. The water-wetness of the chalk material increased with increasing temperature and concentration of sulphate in the seawater. The mechanism for the increased water-wetness was interpreted as due to desorption of carboxylic materials from the chalk surfaces, which was caused by making the chalk surface less positively charged due to adsorption of SO_4^{2-} and complexing the carboxylic group by Ca^{2+} on the chalk surface.

The mechanism initiating the process will be diffusion of ions in the seawater into the rock. As these ions enter the rock, surface conditions will change from oil-wet to water-wet and capillary forces will be the main driving mechanism for the imbibition process.

We are intending to build up a model to simulate spontaneous imbibition of seawater into neutral to preferential oil-wet rocks. The approach chosen is to use dynamic capillary pressure correlations implied from the work of Skjaeveland et al (1998). A modified version of the capillary pressure correlation could be

$$p_c = \frac{c_w \cos(\theta/2)}{\left(\frac{S_w - S_{wr}}{1 - S_{wr}}\right)^{a_w}} + \frac{c_o \cos((\pi + \theta)/2)}{\left(\frac{S_o - S_{or}}{1 - S_{or}}\right)^{a_o}} \quad (1)$$

Where c 's and a 's are positive constants. The expression consists of a water-wet branch and an oil-wet branch. Then the transition between water-wet and oil-wet conditions can be obtained by varying the contact angle θ .

This paper reports how the contact angle changes with time and temperature for brines containing different amount of sulphate. The ultimate purpose is to use these functions in the above mentioned capillary pressure correlation to be able to account for time dependant wettability and thereby model spontaneous imbibition caused by dynamic wettability modifications.

Based on the literature data on surface wettability (Anderson, 1986b), we take the following categories of contact angles as references to describe the surface wettability: (i) water-wet behaviour: $0^\circ < \theta < 70^\circ$, (ii) neutral behavior: $70^\circ < \theta < 110^\circ$ and (iii) oil-wet behavior: $110^\circ < \theta < 180^\circ$.

EXPERIMENTAL

Materials

Chalk: outcrop chalk from Stevns Klint nearby Copenhagen, Denmark, which is a soft and highly porous material of the Maastrichtian age. This chalk is generally homogenous. The permeability is low (2-5mD). It has been previously applied as a medium mimicking the properties of the chalk in the North Sea reservoirs (Frykman, 2001).

Calcite crystal: Calcite (Island-spar) from India supplied by J. Brommeland AS, Norway, is used to prepare calcite crystal plates for contact angle measurement.

Brine: The brine termed EF-Brine, has a model composition close to the initial brine in the Ekofisk field, was used as initial water, synthetic seawater with normal SO_4^{2-} content (SSW) and seawater with four times normal SO_4^{2-} content (SSW-4S) was used as fluids that chalk slices and calcite crystal plates were exposed to. All chemicals were P.A. grade ($\geq 99.8\%$) provided by Sigma-Aldrich. The composition is given in Table 1.

Oils: Crude oil, with an AN=3.01 mgKOH/g and BN= 0.95 ± 0.05 mgKOH/g, was diluted with n-heptane in the ratio of 40/60 n-heptane/crude oil by volume, named Oil A. The oil was filtrated through a 5 μm Millipore filter and no precipitation of asphaltenes was observed at ambient conditions. The AN was then analyzed to be 2.07 mgKOH/g. 0.01 mol/l Stearic acid ($\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$) with purity 99.6% was dissolved to n-decane and this mixture was named as Oil B.

Experimental Procedures

Chalk Slice Preparation

The cylindrical chalk cores were drilled out from the chalk block by an oversized bit, shaved in a lathe to a diameter of ~ 38 mm and cut to a length of ~ 70 mm. The cores were dried to constant weight at 90°C .

- Approach 1: The dried cores were saturated with Oil A under vacuum, placed in a Hassler core holder at room temperature, and flooded with Oil A (2 pore volume (PV) at rate 1 ml/min) in each direction. After flooding, the core was immersed in the same kind of oil inside a sealed steel container and aged at 90°C for 5 days. After aging, chalk slices with thickness of ~ 2 mm were cut from the core and they were then exposed to the same oil again for several hours.
- Approach 2: The chalk slices were cut from the dried chalk core and then saturated with Oil A under vacuum for 3 hours.

Afterwards, the chalk slices were brought out of the oil, stayed in air for ~ 1 minute to get rid of the bulk oil on the surface, then they were put into the sealed container with

seawater at different temperatures. They were moved to the special glass cell used for contact angle measurement after exposing to seawater for different time periods.

Calcite Crystal Plate Preparation

Calcite crystals used for contact angle measurements were prepared according to the following procedures:

- The calcite crystals were naturally split or cut into smaller pieces with a diamond saw. They were then carefully polished using polishing machine with sand papers to achieve smooth surfaces.
- The calcite crystals were cleaned by toluene, n-heptane, distilled water and air-dried. Then they were exposed to EF-brine for at least 1 hour, afterwards, they were aged in Oil A at 50°C for several days or in Oil B at room temperature for 1 day. The influence of aging time in Oil A was observed.
- After aging, the calcite crystals were moved out from the oil, and rinsed with n-heptane to remove the bulk oil on the surface, then air-dried.
- Afterwards, the calcite crystals were exposed to pre-heated seawater in a sealed cell at different temperatures, after different time periods, they were moved to the special glass cell where they were placed horizontally with supporters and surrounded by seawater. Then oil droplets (n-decane for the calcite crystals aged in Oil B, droplets of n-heptane or oil A for calcite crystals aged in Oil A) were introduced onto the bottom surface of the calcite crystal and contact angles were measured.

DSA Equipment

It is conventional to measure contact angles through the denser phase. Thus, for a drop of oil against seawater, the contact angle would be measured through seawater. Therefore, the contact angle values indicate that a decrease in the contact angle implies a decrease in the oil-wet behaviour. The cell used for measurement and the photo of the equipment are shown in Figure 1 and Figure 2. Equilibrium contact angle (the contact angle for the introduced oil droplet when the three phase line is not moving anymore) was measured for the oil-brine-calcite system with the photos taken by DSA system.

RESULTS AND DISCUSSION

Contact Angle Measurement Using n-Heptane and Oil A On Calcite Crystal Aged With Oil A

Aging time influenced the surface wetting state. Figure 3 shows the development of the contact angle for calcite crystals aged in Oil A at 50°C. The results show that the wettability of the calcite crystals became stable after 4 days of aging. The change in wetting behavior is induced by adsorption of Oil A components onto the calcite crystal surface initially covered with a film of brine. Increasing the aging time of calcite crystals in Oil A to 12 days did not reflect any significant change in contact angle value compared to the value obtained after 4 days of aging. Moreover, by observing the contact angle on

calcite crystal aged in Oil A for different times, we can conclude that Oil A can only change the calcite crystal surface to neutral-wet.

Almost no contact angle change was observed for the same oil droplet with exposing to seawater at 70°C. Shown by Figure 5, even after 32 hours exposing, the contact angle did not change significantly. The situation changes when different oil droplets are introduced at different times. Figure 4 and 6 present contact angles measured on refreshed oil droplets after they are introduced onto the calcite crystal bottom surface at different time. The contact angles decrease with increasing exposure time to seawater, which means that the calcite surface has changed from neutral-wet to more water-wet. Compare Figure 4, 5 and Figure 6, seawater can change the property of aged calcite crystal where no oil droplet covers, and it is reflected by the contact angle value decrease when introduce refreshed oil droplet. The following results are observed by introducing refreshed oil droplet after different exposing time.

Contact Angle Measurement On Chalk Slice

Generally, contact angle measurement is operated with smooth crystal surfaces in place of reservoir rocks. The disadvantage is that the smooth surface may not represent the real performance of reservoir rocks which are usually not only rough but also mineralogically heterogeneous. Here we tried contact angle measurement on the chalk slices intending to check if it is possible to measure the wettability of the real chalk surface directly.

Figure 7 shows how the contact angle changes on chalk slice surfaces (prepared with Approach 1) with different exposing time to seawater at 90°C. The contact angle decreased drastically during the first hour's exposing to seawater. After 4 hours, the contact angle decreased to about 38°, which is in the range of water-wet. Figure 8 shows how the contact angle changed on the chalk slice surface (prepared with Approach 2) with different exposing time to seawater at 90°C. The decrease in contact angle after 4 hours was significant. Figs. 7 and 8 again confirm the importance of aging time and temperature. An initial contact angle of about 140° was observed on the chalk slice prepared with Approach 1 which can be compared to the angle 80° measured using Approach 2. The higher contact angle utilizing Approach 1 is due to more polar components being adsorbed onto the chalk surface at higher temperature and with longer aging time.

One major challenge regarding the observed contact angles is to relate the measured changes directly to alteration in the wettability of the porous medium. The porosity of chalk used for the experiments is nearly 50%, which means that the initial surface that the contact angle of the oil droplet is measured on contains a very high fraction of oil in the pores. After exposing the chalk slices to seawater some of this oil was displaced by seawater. Thus, the surface that the oil droplet is placed on gradually contains more water present in the pores, and the contact angle will surely decrease drastically. The rough nature of the porous medium will influence the measured value of the contact angle.

Due to the above discussion it may be difficult to assess the wettability of chalk directly by contact angle measurements on sliced chalk.

Contact Angle Measurement With n-Decane On Calcite Crystal Prepared With Oil B

Contact angle measurements on the smooth calcite crystal surfaces aged in Oil B are reported. Stearic acid dissolved in n-decane has very high affinity to calcite surfaces and can render the surface oil-wet (Gomari and Hamouda, 2006). Figure 9 and 10 show how the contact angles change with time when exposed to the fluid systems SSW, SSW-4S and DW at different temperatures. It is interesting to observe that the initial values of the contact angles only differ between 124° and 136° for all measurements indicating good reproducibility.

Temperature is a major factor influencing the results. For calcite crystals exposed to the fluid systems SSW, SSW-4S and DW at 20°, the contact angle change was not stable and only changed within a very limited range about 20°. With exposure temperature increasing to 50°C and 90°C, the calcite crystal surfaces became more water-wet as a function of time for all the three fluid systems investigated (SSW, SSW-4S and DW). The contact angle decreased to about 72° at 50°C and to 58° – 63° at 90°C. No significant difference was observed between DW and sulphate containing water at these temperatures. Differences were however observed at 130°C. Contact angle using DW stabilized at approximately 80° compared to 70° for SSW and 68° for SSW-4S. The differences are small but this temperature is the only one where different performances were observed. It should be noticed that sulphate containing water only imbibed significantly into chalk cores for temperatures above 100°. Further investigations are needed to conclude whether these small contact angle differences can cause the observed improved oil recovery by imbibition test for chalk cores at 130°C.

CONCLUSIONS

- Contact angle change observed with refreshed oil droplets reflects that the properties of calcite crystal surface are changed by surrounded brines (DW, SSW and SSW-4S). The area covered by oil droplets can't have access to brines, which explains that almost no contact angle change for non-refreshed oil droplets.
- Oil A is only able to modify the wettability of calcite crystals to neutral-wet conditions. Longer aging time and higher aging temperature will induce more water-wet conditions.
- It is maybe difficult to assess wettability by contact angle measurements on chalk slices due to changes in fluid saturation and surface roughness.
- Stearic acid dissolved in n-decane (Oil B) can render the calcite crystal (to) oil-wet. Contact angle measurements show that the calcite crystal surface wetting state before exposing the calcite crystals to seawater/DW is reproducible and in the range from 124° to 136°.

- Increasing temperature from 20 to 90°C in the Oil B/calcite crystal system makes the calcite crystal more water-wet due to accelerate desorption of stearic acid from the calcite crystal surface for all fluid systems investigated (DW, SSW and SSW-4S).
- Different performance between DW and SSW, DW and SSW-4S was found at 130°C for the stearic acid/n-decane/calcite crystal system. Further studies are however necessary to confirm whether this difference can lead to improved oil recovery for chalk core imbibition test.
- The experimental results show a clear trend for the contact angle change at different temperature, with different time of exposing the calcite crystals to bath fluid. It can be used as important reference for the modified capillary pressure correlation.

NOMENCLATURE

θ	Contact angle
p_c	Capillary pressure
S_w	Water saturation
S_{wr}	Residual (irreducible) water saturation
S_o	Oil saturation
S_{or}	Residual oil saturation
AN	Acid number
BN	Base number
Ca^{2+}	Calcium cation
SO_4^{2-}	Sulphate anion
SSW	Synthetic seawater with normal amount of sulphate ions present
SSW-4S	Synthetic seawater with four times the normal concentration of sulphate
DW	Distilled water

REFERENCES

- Anderson, W.G., “Wettability literature survey – part 1: rock/oil/brine interactions and the effects of core handling on wettability”, *JPT*, (1986a), pp. 1125-1144.
- Anderson, W.G., “Wettability literature survey – part 2: wettability measurement”. *JPT*, (1986b), pp 1246– 1262.
- Austad, T., Strand, S., Høghesen, E. J., and Zhang, P., “Seawater as IOR Fluid in Fractured Chalk”. Paper SPE 93000, presented at the 2005 SPE International Symposium on Oilfield Chemistry held in Houston, Texas, U. S. A., 2-4 February.
- Austad, T., Matre, B., Milter, J. Sævareid, A. and Øyno, L., “Chemical flooding of oil reservoirs 8. Spontaneous oil expulsion from oil- and water-wet low permeable chalk material by imbibition of aqueous surfactant solutions”, *Colloids Surf. A: Physicochem. Eng. Aspects* (1998) **137**, pp. 117–129.

- Chilingar, G.V. and Yen, T.F., "Some notes on wettability and relative permeability of carbonate rocks. II". *Energy and Sources*, (1983) **7**, pp 67-75.
- Frykman, P., "Spatial variability in petrophysical properties in Upper Maastrichtian chalk outcrops at Stevns Klint, Denmark". *Marine and Petroleum Geology*, (2001) **18**, pp 1041-1062.
- Høgnesen, E. J. Strand, S. and Austad, T., "Waterflooding of preferential oil-wet carbonates: Oil recovery related to reservoir temperature and brine composition", Paper SPE 94166, presented at the 14th Europec Biennial Conference held in Madrid, Spain, June 13-16, 2005.
- Rezaei Gomari, K. A. and Hamouda, A.A, "Effect of fatty acids, water composition and pH on the wettability of calcite surface". *Journal of Petroleum Engineering*, (2006) **50**, pp 140-150.
- Roehl, P. O. and Choquette, P. W., *Carbonate Petroleum Reservoirs*. Springer-Verlag, New York, (1985) pp 622.
- Roehl, P. O. and Choquette, P. W., *Carbonate Petroleum Reservoirs*. Springer-Verlag, New York, (1985) pp 622.
- Skjæveland, S.M., Siqveland, L.M., Kjosavik, A., Hammervold, W.L., Virnovsky, G.A., "Capillary Pressure Correlation for Mixed-Wet Reservoirs", Paper SPE 77328, presented at the 1998 SPE India Oil and Gas Conference and Exhibition held in New Delhi, India.
- Sylte, J. E., Hallenbeck, L. D., and Thomas, L. K., "Ekofisk Formation Pilot Waterflood", Paper SPE 18276, presented at the 63th Annual Technical Conference and Exhibition held in Houston, TX, U. S. A., October 2-6, 1988.
- Zhang, P. and Austad, T., "The Relative Effects of Acid Number and Temperature on Chalk Wettability". Paper SPE 92999, presented at the International Symposium on Oilfield Chemistry held in Houston, TX, U. S. A., February 2-4, 2005.
- Zhang, P. and Austad T., "Wettability and Oil recovery from Carbonates: Effects of Temperature and Potential Determining Ions". *Colloids and Surfaces A: Physicochem. Eng. Aspects* (2006) **279**, pp179–187.

Ion	EF-brine (mol/l)	SSW (mol/l)	SSW-4S (mol/l)
Na ⁺	0.684	0.450	0.419
K ⁺	--	0.010	0.010
Mg ²⁺	0.025	0.045	0.045
Ca ²⁺	0.231	0.013	0.013
Cl ⁻	1.196	0.525	0.350
HCO ₃ ⁻	--	0.002	0.002
SO ₄ ²⁻	--	0.024	0.096
TDS, g/l	68.01	33.39	33.39

Table 1. Molar compositions of the brines used

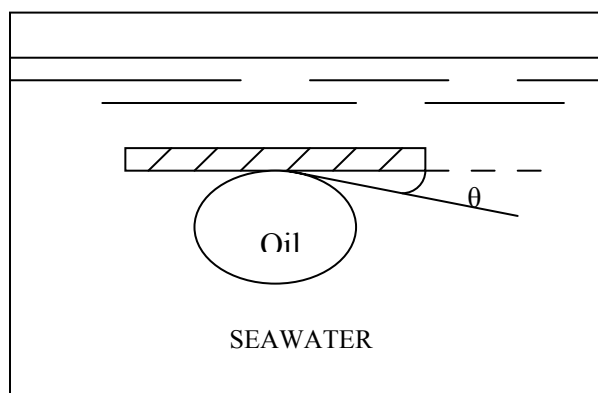


Figure 1. Illustration of phase arrangement in the cell for contact angle measurement



Figure 2. DSA system

2 days aging	4 days aging	6 days aging	7 days aging	12 days aging
35.2°	70.1°	70.1°	64.2°	72.5°

Figure 3. Contact angle by duplicate n-heptane droplets on calcite crystal with different aging time in Oil A

0 hour exposing	11.6 hours exposing	22 hours exposing
72.5°	49.1°	30.2°

Figure 4. Contact angle by refreshed n-heptane droplets on calcite crystal with different exposing time to seawater

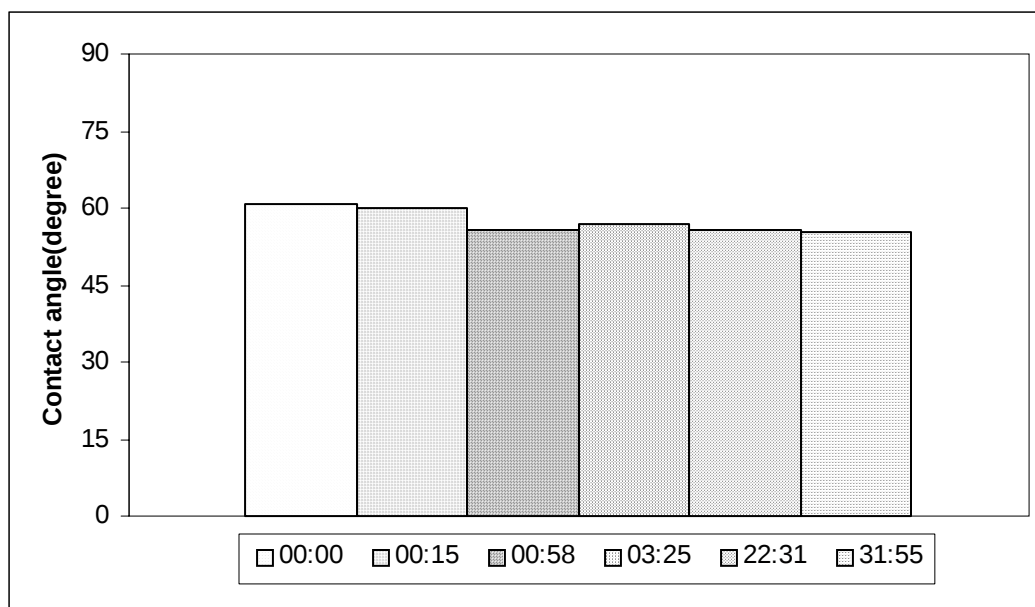


Figure 5. Contact angles observed by the same non-refreshed n-heptane oil droplet with exposing time to SSW

00:00	00:10	00:25	00:52	01:16
63.8°	39.7°	35.5°	36.8°	31.9°

00:00	00:04	00:28	00:55	01:14
63.2°	55.2°	40.6°	37.6°	35.0°

Figure 6. Contact angles observed by refreshed Oil A droplets on calcite crystal surface with exposing time to SSW, duplicate crystal plates are used to this measurement.

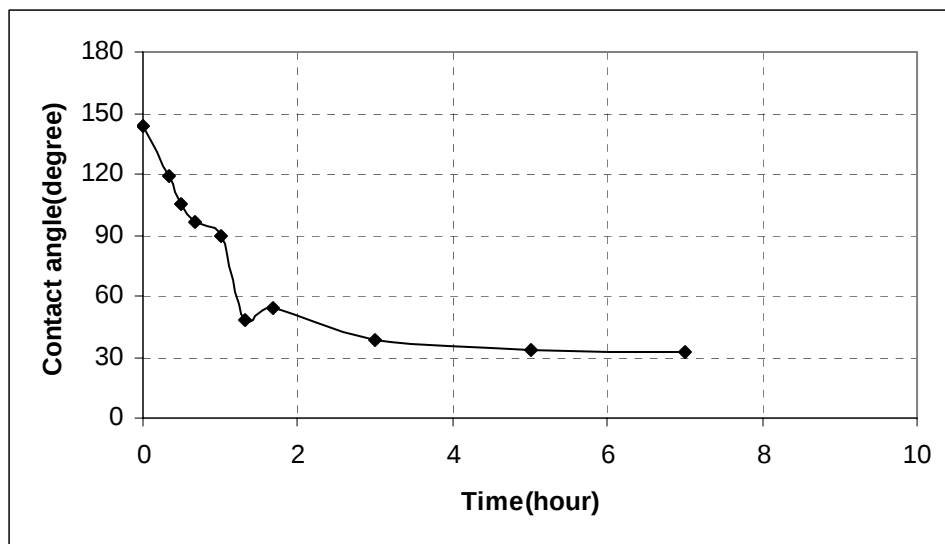


Figure 7. Contact angle with refreshed n-decane droplets on chalk slice (prepared with Approach 1) with different exposing time to seawater at 90°C

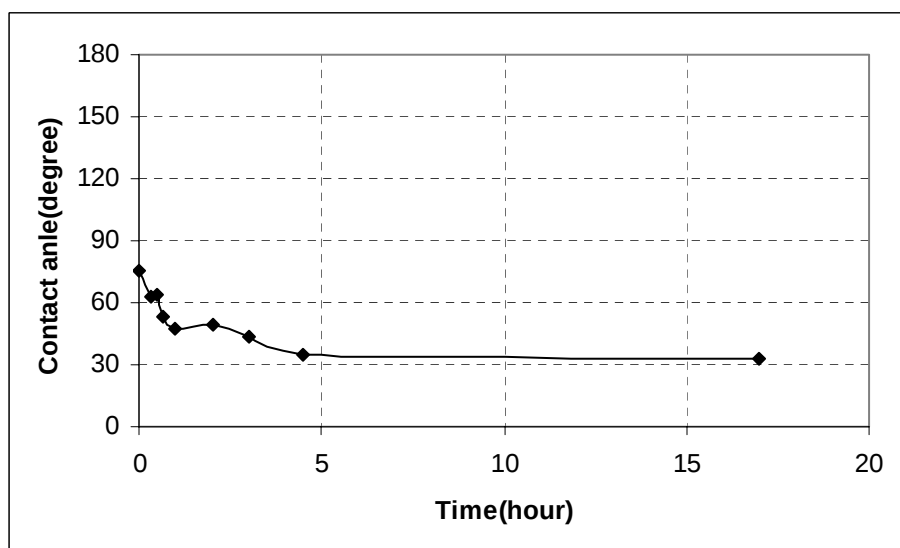


Figure 8. Contact angle with refreshed n-decane droplets on chalk slice (prepared with approach 2) with different exposing time to seawater at 90°C

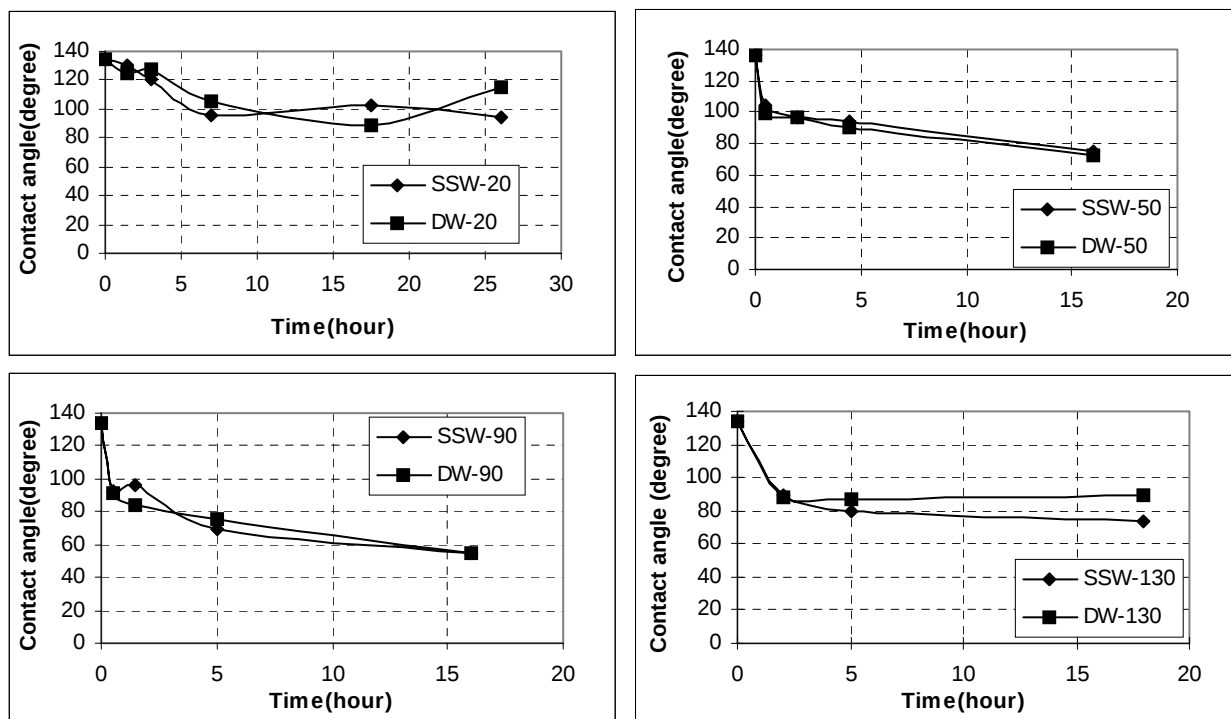


Figure 9. Contact angle with refreshed n-decane droplets on calcite crystals exposed to SSW and DW for different time at different temperatures

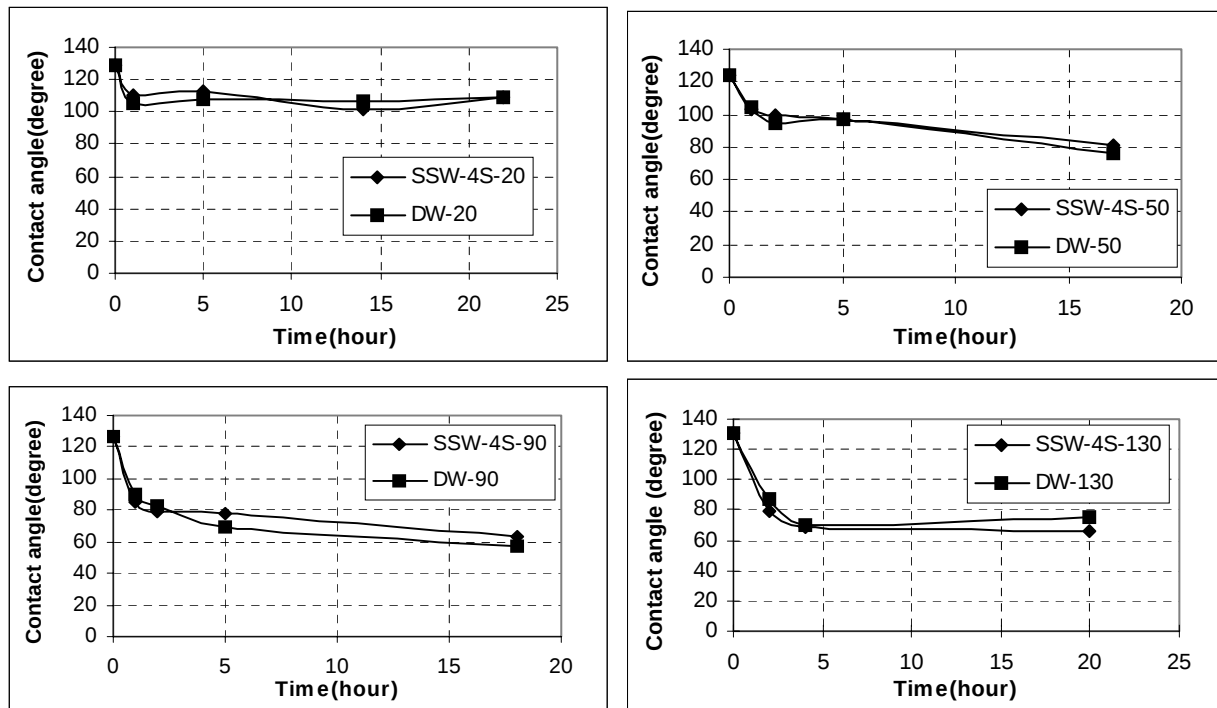


Figure 10. Contact angle with refreshed n-decane droplets on calcite crystals exposed to SS and DW for different time at different temperatures