Impact of Dopants on SCAL Experiments, Phase I

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Abstract. It is a common practice in Special Core Analysis (SCAL) to add sodium iodide (NaI) to the formation brine and injection brine during laboratory waterflooding experiments. It helps in improving the contrast between water and oil for in-situ saturation monitoring using X-ray technique. Recent progress in our understanding of crude oil, brine, and rock interaction points towards a non-trivial role of NaI in wettability alteration. This alteration could introduce a significant bias in the SCAL experiments. The purpose of this study is to describe the results of experiments designed to prove or disprove the impact of NaI (inorganic dopant) at different concentrations on the oil recovery. In total, six Bentheimer samples have been tested. The samples were initially saturated with undoped or doped brines, brought to irreducible water saturation (Swi) and aged using crude oil at reservoir temperature. The samples were then loaded in Amott cells for spontaneous imbibition before being brought to residual oil saturation (Sor) during centrifuge forced imbibition. The results show a significant NaI impact on oil recovery in clastic rocks, especially during the spontaneous displacement process. Additional work is needed to assess the NaI impact on carbonate rocks, but also assess the impact of iodide in oil (organic dopant such as iododecane).

1 Introduction

To monitor saturation profiles and to accurately measure the remaining oil saturation during and at the end of a coreflooding experiment, X-ray attenuation method is used. Because oil and water have different X-ray attenuation coefficients, it is in theory possible to differentiate the two phases with X-ray or γ-ray scanners (1D linear, 3D CT or micro-CT). However, in practice, the typical brines (i.e., sea water) have attenuation coefficients a_w of 0.0208 mm^{-1} whereas typical oil attenuation coefficient a_o values are around 0.015 mm^{-1}. The closeness of these two values can be problematic as sometimes the measurement error is bigger than the delta of these two values, resulting in the impossibility to deconvolute the two signals. To remediate this problem, it is common practice in the SCAL industry/laboratories to substitute sodium chloride NaCl by sodium iodide NaI or potassium iodide KI. A 0.4 molar NaI solution has an attenuation coefficient a_w of 0.058 mm^{-1} versus 0.0208 mm^{-1} for a 0.4 molar NaCl solution, increasing the difference in attenuation between oil and brine by a factor of 7.

At the time, most authors such as [1] and [2] reported no change in wettability or variation in relative permeability due to the addition of NaI in the aqueous phase, except for [3] which stated that "it is generally undesirable to add dopants to the fluids used in the experiments because they might alter core wettability". Unfortunately, [3] never gave further explanation to this comment, and it became common practice in the industry to add NaI/KI to the connate and injection brine without worrying about any adverse effect on the wettability, oil recovery or variation in relative permeability measurements, especially for remaining oil saturation or recovery factor after a water-oil imbibition cycle.

In the early 90's, [4] started investigating the impact of the brine composition on oil recovery and wettability. It soon became apparent that in clastic system below a certain TDS threshold (5000 ppm TDS), brine composition has a major role on wettability. Nevertheless, no mention of the impact of doping with NaI/KI was ever reported. Later, [5] transposed most of the work of Morrow from clastic into carbonates and showed that adding anions (Sulphate, Phosphate, Borate…) in small quantities to the injection brine had a major impact on wettability and oil recovery. Surprisingly even with the mounting evidence of the impact of anions on wettability, no studies were started to look at the impact of doping. Guided by the observations made by [6] who concluded that only sodium iodide has a measurable influence on the effective hydrophobic interactions, [7] published a study on the role of iodide ions on oil recovery in carbonates. They showed that adding as little as 1000 ppm of NaI/KI to sea water has a drastic impact on oil recovery (between 5 to 15% incremental oil recovery). However, they failed to link this study with the common practice of using NaI/KI for doping conventional SCAL studies.

The objective of the proposed paper is to show the impact of NaI (at different concentrations in brines of same salinity), on wettability and oil recovery in Bentheimer

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outcrops. Some tests are performed with same connate and injected brines while others are performed with brines of different composition in the connate and injected brines. The results show a significant NaI impact on oil recovery, especially during the spontaneous displacement process of the tests where NaI is present in the connate brine.

2 Experimental Context

In the experimental program, two rock systems were planned to be tested, one clastic rock (Bentheimer sandstone) and one carbonate rock (Richemont limestone). A crude oil from the Middle East was selected to perform the imbibition tests.

The objective is to highlight the effect of NaI brine on oil recovery and wettability when NaI is present in:

- The initial saturating brine that we will call initial sitting brine or connate brine
- The imbibing or injected brine when performing spontaneous and forced imbibition cycles

The NaI concentration will also vary from 1g/l to 12g/l to highlight the degree of impact based on the concentration.

Concerning the experimental tests, each core is initially cleaned, and wettability restored for 4 weeks of dynamic ageing, at 80°C. Spontaneous imbibition test is then carried out, at 80°C. The experiments are then concluded by centrifuging the core to determine the imbibition capillary pressure and the residual oil saturation Sor with an adapted design according to the investigated rock. A centrifuge temperature of 80°C is also applied to keep consistency.

The testing program can be summarized as follows:

NaI clastic program, Phase 1:

Reference test

- Bentheimer sandstone rock with Middle Eastern oil and connate brine containing no Iodide. Imbibition done with connate brine containing no iodide

Impact of NaI in imbibing brine only

- Bentheimer sandstone rock with Middle Eastern oil and connate brine containing no Iodide. Imbibition done with imbibing brine containing 1g/l NaI
- Bentheimer sandstone rock with Middle Eastern oil and connate brine containing no Iodide. Imbibition done with imbibing brine containing 12g/l NaI

Impact of NaI concentration in initial sitting brine (initial saturating brine)

- Bentheimer sandstone rock with Middle Eastern oil and connate brine containing 1g/l NaI. Imbibition done with imbibing brine containing 1g/l NaI
- Bentheimer sandstone rock with Middle Eastern oil and connate brine containing 6g/l NaI. Imbibition done with imbibing brine containing 6g/l NaI
- Bentheimer sandstone rock with Middle Eastern oil and connate brine containing 12g/l NaI. Imbibition done with connate brine containing 12g/l NaI

NaI carbonate program, Phase 2:

Reference test

- Richemont carbonate rock with Middle Eastern oil and connate brine containing no Iodide. Imbibition done with connate brine containing no iodide

Impact of NaI in imbibing brine only

- Richemont carbonate rock with Middle Eastern oil and connate brine containing no Iodide. Imbibition done with imbibing brine containing 1g/l NaI
- Richemont carbonate rock with Middle Eastern oil and connate brine containing no Iodide. Imbibition done with imbibing brine containing 12g/l NaI.

Impact of NaI concentration in saturating brine (connate brine)

- Richemont carbonate rock with Middle Eastern oil and connate brine containing 1g/l NaI. Imbibition done with imbibing brine containing 1g/l NaI.
- Richemont carbonate rock with Middle Eastern oil and connate brine containing 6g/l NaI. Imbibition done with imbibing brine containing 6g/l NaI.
- Richemont carbonate rock with Middle Eastern oil and connate brine containing 12g/l NaI. Imbibition done with connate brine containing 12g/l NaI.

The same programs are later planned on the same rock systems to test the effect of organic dopant (iododecane added in the oil phase) on oil recovery and wettability of clastic and carbonate rocks, phase 3 and phase 4 respectively.

As explained before, the program progress did not allow to finish all phases. In this paper, only results from the tests performed on Bentheimer rocks and use of sodium iodide NaI are presented (Phase 1).

3 Rock and Fluid Properties

a) Rock properties

Bentheimer sandstone rock was chosen for the clastic program. It is composed of around 90 to 95% of quartz, with small amount of feldspar and illite/kaolinite. Because it is a homogeneous rock that shows constant mineral composition and intrinsic properties (uniform pore throats and bodies, with porosity ranging from 21 to 27% and permeability ranging from 0.5 to 3 Darcy), it is a perfect candidate for such comparative experimental study.

Six Bentheimer sandstone outcrops were selected for this program. Their properties are listed in Table 1.

Table 1: CCA properties

Sample Id	Diameter Cm	Length cm	Porosity φ frac.	Kkl D
Be1	3.80	5.03	0.246	2.07
Be2	3.79	5.02	0.244	2.14
Be3	3.81	5.03	0.248	2.16
Be4	3.80	5.03	0.249	2.49
Be5	3.80	5.02	0.243	2.02
Be6	3.80	5.05	0.246	2.06

As shown in the table, all samples have same geometry and same intrinsic properties φ and Klinkenberg permeability Kkl.

b) Brine

The different brines were prepared according to the original sea water composition SW. Its composition was first simplified (SW→SW*). Based on this simplified sea water SW*, different concentrations of NaI were added to it (SW*1 with 1 g/l NaI, SW*6 with 6 g/l NaI, SW*12 with 12 g/l NaI), as shown in Table 2.

Table 2: ionic brine compositions & salt concentrations

	SW	SW*	SW*1	SW*6	SW*12
Ion	C (mg/l)	C (mg/l)	C (mg/l)	C (mg/l)	C (mg/l)
Na+	12066	10542	10696	10675	10691
K+	503.5	503.5	503.5	503.5	503.5
Ca2+	819.2	817.8	817.8	817.8	817.8
Mg2+	1482	1482	1482	1482	1482
Ba2+	2.8	0	0	0	0
Sr2+	16.4	0	0	0	0
Cl-	22505	22486	22486	21272	19877
SO42-	3047	0	0	0	0
HCO3-	168	0	0	0	0
I-	0	0	846.6	5079.8	10159
TDS	40593	35831.3	36831.9	39830.1	43530.3
I	0.81	0.72	0.72	0.72	0.72

Salt	SW C (g/l)	SW* C (g/l)	SW*1 C (g/l)	SW*6 C (g/l)	SW*12 C (g/l)
NaCl	26.8	26.8	26.8	24.8	22.5
KCl	0.96	0.96	0.96	0.96	0.96
CaCl2, 2H2O	3	3	3	3	3
MgCl2, 6H2O	12.4	12.4	12.4	12.4	12.4
Na2SO4	4.5	0	0	0	0
NaHCO3	0.23	0	0	0	0
SrCl2, 6H2O	0.05	0	0	0	0
BaCl2, 2H2O	0.004	0	0	0	0
NaI	0	0	1	6	12

For the addition of NaI in SW* at different concentrations, it was decided to keep the ionic strength I as for the simplified sea water SW*: as the maximum addition of NaI was 12g/l, it does not impact much the resulting TDS.

Table 3 summarizes the brine properties, density ρw and viscosity µw at 80°C (based on correlation).

@80°C	ρw (g/cc)	µw (cP)
SW*	0.995	0.38
SW*1	0.997	0.39
SW*6	1.000	0.39
SW*12	1.002	0.39

c) Oil

A dead oil from Middle Eastern reservoir was used in the study. Before analysis, the oil was filtered at 0.1µm and centrifuged at 10000 RPM, at 50°C. Before using it in our different tests, the crude oil was placed in oven at 100°C for 2 days to ensure no evaporation of light components happens at 80°C.

SARA analysis (chromatographic technique) was performed to assess the capacity of this crude oil to alter wettability (from water-wet towards oil-wet rock or less water-wet). As mentioned by [8], there are 2 main groups of components in crude oils that are responsible for reservoir rock wettability alteration. Group 1 corresponds to polar heteroatoms such as organic acids and bases, while group 2 corresponds to the asphaltenes.

The results from the crude oil analysis are reported below.

Table 4: Crude oil SARA analysis, TAN and TBN

Saturates wt%	42.5
Aromatics wt%	48.8

Resins wt%	8.7
Asphaltenes wt%	2.7
TAN mg KOH/g	0.07
TBN mg KOH/g	0.62

Despite a low total acid number TAN and not high concentration of asphaltenes, previous internal studies have shown that this crude oil was efficient to make reservoir rock slightly oil-wet (after initial core cleaning and Swi establishment with the same crude oil): the reported Amott-Harvey and USBM wettability indexes were both between -0.5 and -0.1. The wettability change was mainly attributed to the total base number TBN (>0.5 mg KOH/g).

Table 5 summarizes the measured oil properties, density ρo and viscosity μo at 80°C.

Table 5: measured oil properties

@80°C	ρo (g/cc)	μo (cP)
Crude oil	0.831	3.10

4 Experimental Protocol

After the preliminary characterization, the samples were brine saturated. Because it was planned to test the effect of the connate water with and without NaI, three samples were initially saturated with SW* and the remaining three samples were saturated with 1, 6, and 12 g/l NaI respectively (Table 6).

All the samples were then loaded in centrifuge for a primary drainage cycle using mineral oil as displacing phase. A multistep method was performed to determine the primary drainage capillary pressure Pc up to the irreducible water saturation Swi. At the end of the forced drainage, the samples were unloaded and reloaded in reverse position to flatten the saturation profiles: this additional step is of importance to ensure that the wettability is better distributed along the samples.

Mineral oil was then replaced sequentially by toluene and dead oil at 80°C using a conventional coreflooding system. This system was used to dynamically age the samples for four weeks.

After the ageing period, the samples were loaded in Amott cells for the spontaneous imbibition (SPI) at 80°C, for 42 days. The samples, saturated with dead oil, at Swi, were immersed in brines of different NaI concentrations.

Finally, the samples were loaded in centrifuge again for forced imbibition (FI), with multistep centrifuge method, up to remaining oil saturation ROS. The maximum applied Pc ensures an asymptotic Pc curve: ROS may be assumed to be the residual oil saturation Sor. Note that the imbibing brines for the forced imbibition (FI) are the same brines tested on the same samples during the spontaneous imbibition (SPI).

Table 2 and Table 6 help in understanding what the compositions of each initial “connate” brines and imbibing brines are.

Table 6: Symbols of connate brine and imbibing brines per sample test

Sample Id	Brine at Swi	SPI and FI brine
Be1	SW*	SW*
Be2	SW*	SW*1
Be3	SW*	SW*12
Be4	SW*1	SW*1
Be5	SW*6	SW*6
Be6	SW*12	SW*12

For the first three samples, we will look at the impact of the NaI presence (at different concentrations in the imbibing brine) on oil recovery when the initial sitting brine at Swi is not doped with NaI (only simplified brine composition SW*). For the last three samples, the combined effect of NaI presence in the connate brine and varying concentrations of NaI in the imbibing brine, on the oil recovery, will be investigated.

5 Experimental Results

The primary drainage was first performed to set Swi and to determine the capillary pressure curve. Our objective was not to determine Pc but at least ensure all mineral oil-brine Pc curves are similar, with close Swi values. The reported averaged water saturation <Sw> values were volumetrically obtained (from interface recording in centrifuge vial, with final control of produced brine volume in vial at the end of the tests).

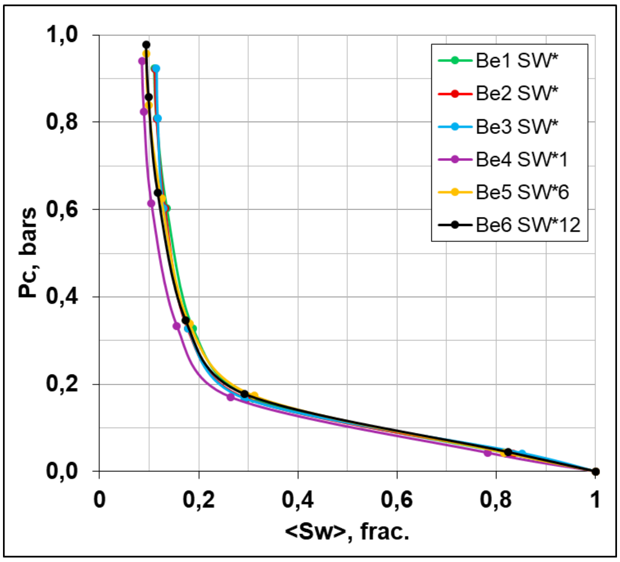

Figure 1: Primary drainage brine-mineral oil Pc curves

Figure 1 shows that all the primary drainage capillary pressure Pc curves are overlapping: it confirms that the samples behave similarly.

The samples were then reloaded in the centrifuge but in reverse position to try reducing the non-uniform fluid distribution due to the capillary end-effect post centrifugation: preliminary studies have been done to determine/calibrate the duration of the maximum reversal Pc step to flatten the saturation profile (visualization under NMR pre and post reversal). Reversal time is important because it may reverse the water holdup on the other side of the rock. For this program, it was observed a small additional production on all samples, reducing the Swi values (equivalent to 5 s.u. reduction). To avoid this tedious protocol, it is preferable to perform a primary drainage porous plate test to obtain flat saturation profiles. The final Swi values, post-reversal, are listed in Table 7:

Table 7: Swi values post-reversal

Sample Id	Brine at Swi	Swi frac.
Be1	SW*	0.075
Be2	SW*	0.066
Be3	SW*	0.098
Be4	SW*1	0.028
Be5	SW*6	0.042
Be6	SW*12	0.084

The core plugs were then loaded in core holders for fluid replacement at 80°C. Mineral oil was first replaced with 10PV of toluene then 10PV of crude oil: the intermediate step is required to avoid any precipitation of asphaltenes. The samples were kept under dynamic ageing for 4 weeks before being loaded in the Amott cells at 80°C. Unfortunately, oil permeability at Swi was not recorded before and after ageing. During the dynamic ageing, there was no observed production of brine. At the end of the ageing period, the samples were placed in Amott cells, immersed in different brines (Table 6). Figure 2 shows the oil production versus time for 42 days.

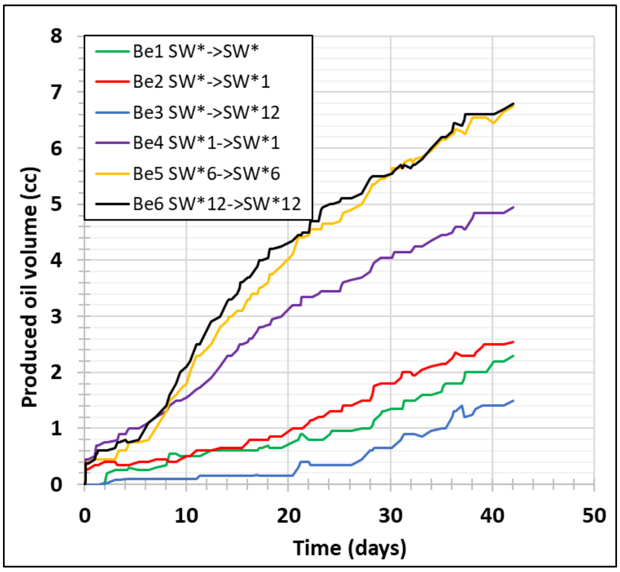

Figure 2: Spontaneous imbibition rates

Despite the production equilibrium was clearly not reached, Figure 2 shows different imbibition rates according to the different initial brines in place and imbibing brines. There are clearly two trends:

- The 3 samples initially saturated with SW* (no NaI addition) have the lowest spontaneous oil production rate. It is difficult to state that there is an imbibition rate dependency to the NaI concentration in the imbibing brine
- The 3 samples initially saturated with doped brines at different and not nil NaI concentrations show a significant spontaneous oil production rate. When imbibing the rocks with a brine of concentration in NaI >6g/l, the production rates appear to be similar. For the sample with 1g/l of NaI in connate brine and imbibing brine, production rate is lower than the 2 other samples but outperform the 3 samples with no NaI in the connate brine

With these simple observations, it is already obvious that the presence of NaI or not in the irreducible brine has a huge impact on the spontaneous oil recovery. When the initial sitting brine is not doped with NaI, the oil production rate does not seem dependent on the NaI concentration in the imbibing brine: if it was the case, we would have expected the blue curve from Figure 2 being above the red one.

After the spontaneous imbibition, the samples were loaded in centrifuge for multistep forced imbibition. Six increasing Pc steps were applied to obtain Pc and Pc asymptotic trend at the highest speed (2900 RPM max., equivalent to a Bond number Nb of 4.10^{-4}), leading to Sor. Note that, at 1400 RPM, corresponding to Bond number around 9.10^{-5}, almost no additional oil production was observed, proving the non-violation of the Hassler-Brunner condition at the highest speed.

Figure 3 shows the 6 Pc curves as a function of the averaged water saturation <Sw>.

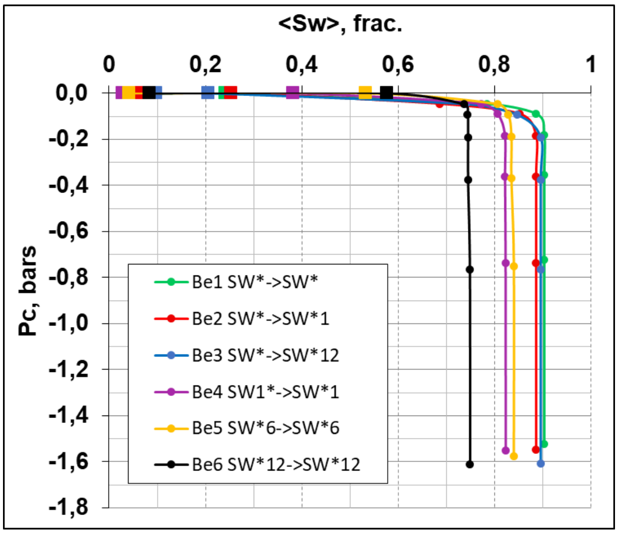

Figure 3: Pc curves of the six samples (square points for spontaneous imbibition and circle points for forced imbibition), full scale plot

To confirm the wettability impact on the Pc curves, same Pc curves are plotted on limited scale in Figure 4:

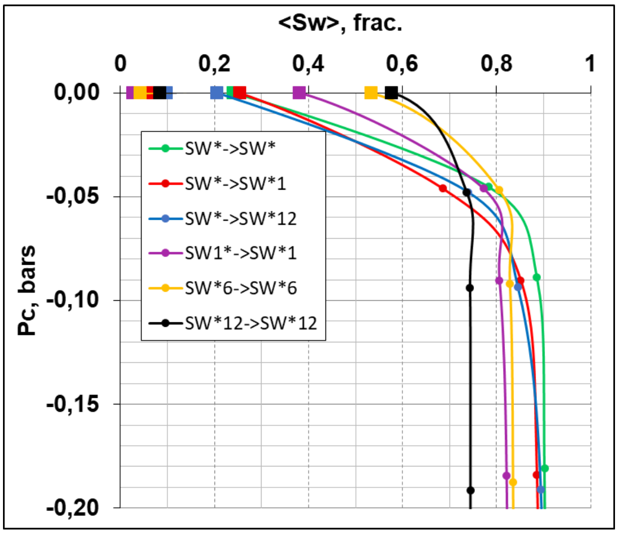

Figure 4: Pc curves of the six samples on limited Y-axis scale

The assumed Sor values (no Forbes correction applied here) are different according to the tests: the highest Sor value is obtained for the test with 12g/l of NaI in the initial and imbibing brine while the lowest Sor is obtained for the reference test using undoped brine, called the reference test (the most representative of the series, with undoped sea water and crude oil).

It is noted that the capillary pressure curves of the samples with no NaI in the initial brine are overlapping and have almost same Sor values: it shows that the addition of NaI in the imbibing brine is not affecting the final oil recovery.

On the other hand, the samples with NaI in the initial sitting brine show higher Sor, with around 8% higher Sor values for the samples containing 1 and 6g/l, in comparison with undoped initial brine samples, up to 15% higher Sor for the sample with the highest NaI concentration.

The Swi, Sw sp. after spontaneous imbibition and Sor values are reported in Table 8.

Table 8: Endpoint water saturation

Sample Id	Brine at Swi	Imbib. brine	Swi frac.	Sw sp. frac.	Sor frac.
Be1	SW*	SW*	0.075	0.241	0.098
Be2	SW*	SW*1	0.066	0.254	0.115
Be3	SW*	SW*12	0.098	0.206	0.105
Be4	SW*1	SW*1	0.028	0.381	0.177
Be5	SW*6	SW*6	0.042	0.533	0.161
Be6	SW*12	SW*12	0.084	0.577	0.252

It shows some consistency between the resulting Sw values obtained post spontaneous imbibition and Sor values post forced imbibition: increasing value of Sw sp. leads to higher Sor value.

Based on all above results, 4 histograms help in clarifying the findings: the variation of average water saturation d<Sw> pre/post spontaneous imbibition, Sor, recovery factor RF and water wettability index Iw as a function of the tests.

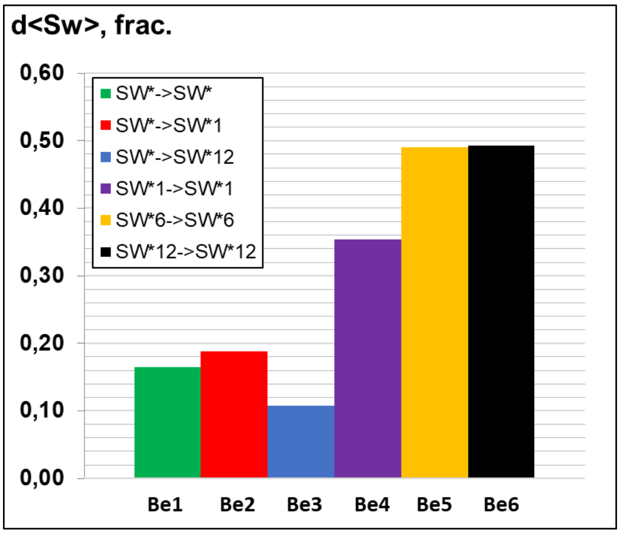

Figure 5: Spontaneous dSw histograms

Figure 5 shows the spontaneous imbibition contribution (d<Sw> = <Sw> value post spontaneous displacement – Swi). The lowest spontaneous imbibition occurs on the samples initially saturated with undoped brine Be1, Be2 and Be3. The highest spontaneous imbibition contribution is observed on the samples with doped initial sitting brines Be4, Be5 and Be6, highlighting a more water-wet behaviour compared to the other samples. It shows that the samples containing NaI in the connate water at Swi behave more water-wet, the ability of the oil to modify the rock wettability after the ageing period being certainly reduced.

The histogram plot in Figure 6 represents the Sor values according to the 6 tests.

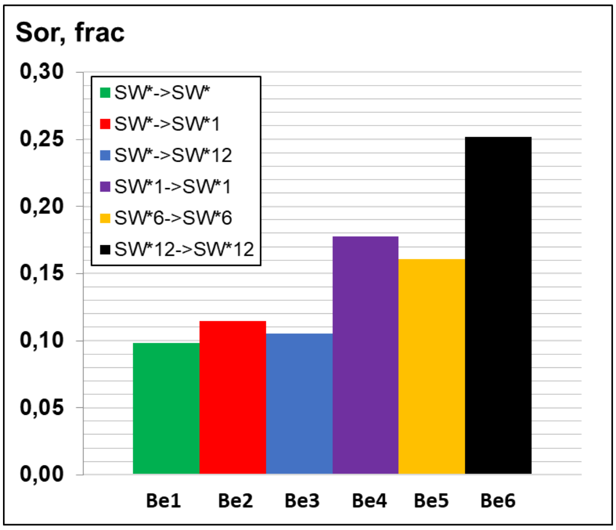

Figure 6: Sor histograms

The histogram shows that the three samples with no NaI in the sitting brines have lower Sor compared to the three samples containing NaI: it confirms the observations made during the spontaneous imbibition. Be1, Be2 and Be3 behave less water-wet compared to Be4, Be5 and Be6. Sample Be6 (the one with 12g/l brine in connate and imbibing brine) has the highest value of Sor.

The final oil recovery factor RF histogram can be plotted.

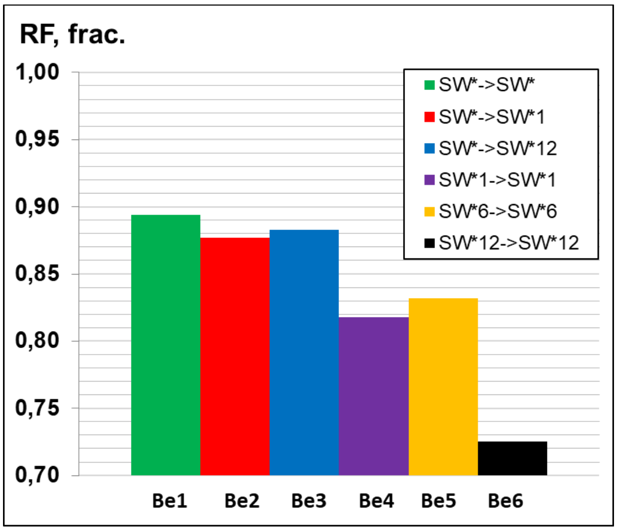

Figure 7: RF histograms

Figure 7 shows that the three samples with no NaI in the initial sitting brine have the highest and almost equal RF. The two samples containing NaI in sitting and imbibing brine, 1g/l and 6g/l have a lower RF, around 5-6% lower than the first three samples. Then sample Be6 (12g/l in sitting and imbibing brine) shows the lowest recovery factor, around 15% less than the reference sample Be1. It is also an indication of the samples with doped brine in connate water being more water wet or less oil-wet than the samples with no NaI in the sitting brines.

Based on the spontaneous displacement and forced imbibition saturation ranges, the Amott water wettability index Iw can be calculated. Figure 8 shows the Iw histogram as a function of the tests.

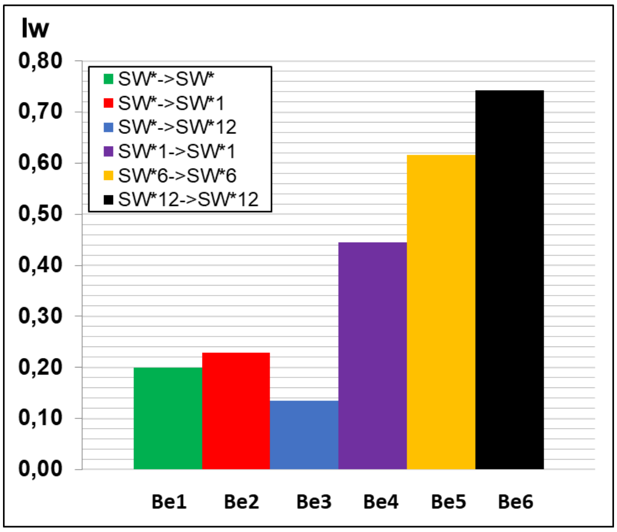

Figure 8: Iw histograms

This plot is probably the most relevant indication of the effect of NaI doping agent on wettability: all samples with no NaI in the sitting brine, and despite the doped imbibing brine, have same Iw between 0.13 and 0.23. For the samples with NaI in the sitting brines, Iw are much higher, from 0.44 and 0.74, with increasing Iw and with increasing NaI concentration. Important to note that with 1g/l only of NaI in connate water (Be4), Iw value is double compared to the Iw values of the tests with no NaI in connate water (Be1, Be2, Be3).

6 Discussion

Regarding the observed results and their explanations, a list of possible mechanisms can be provided. It may be split in two types: petrophysics and physico-chemistry.

About the possible petrophysics mechanisms, all tests were performed with the exact same protocol, same fluids, and same conditions. The main difference between the tests is the Swi difference. The dispersion of the post-reversal Swi values is indeed not negligible but cannot fully explain the high degree of the difference between the different tests. It may explain the trend of Be4, test with the lowest Swi value of 3% and the lowest NaI concentration in the connate brine, behaving less water-wet than Be5 and Be6 that have higher Swi values and higher NaI concentrations in the connate brine.

It is more likely a physico-chemistry effect that leads to the observed results: salinity change, IFT/contact angle change, pH change, ionic interaction.

As the TDS does not change significantly between the different tests, there is no osmosis effect expected: salinity is not the reason of the differences.

An IFT change could occur when replacing some NaCl with NaI in the brine: though measurements are not available, the very small addition of NaI in the brine should not lead to a significant change of IFT. Also, [10] showed there was no significant change in IFT when adding various iodide concentrations in brine. Nevertheless, they made some contact angle measurements and pointed that the presence of iodide in brine could make the rock (carbonate in this study) less oil-wet.

A change in pH could also be an explanation of the observed differences: no change of pH is expected by adding iodide in the brine (no change in concentration of H+ and OH-).

The ionic strength was kept constant for the brine preparations. But interaction between ions and interaction with oil components should be investigated. [10] showed for instance that iodide ions can influence the electrophoretic mobility on a carbonate rock.

The presence of clay (1-2% of illite/kaolinite), even at low concentration, may play a role on the observed results. Clays are negatively charged, while the tested oil surface contains positive species such as 3RNH+: we can imagine that iodide I^- may interact with 3RNH+, inhibiting somehow the ageing process. In our case, when iodide is present in the connate brine, it may reduce the interactions between the oil and the rock, which would lead to a more water-wet state. This statement must be validated, though it is similar approach to the accepted multi-component ion exchange mechanism.

Further investigations of all possible reasons must be done. It does not prevent to conclude that the collected data results clearly show an effect of NaI on the oil recovery and wettability. This can be a problem when using doping agent to monitor the in-situ X-ray saturation changes during the coreflooding experiments. Based on common practices for SCAL tests, the maximum NaI concentration tested in this study (12g/l) corresponds to a very low concentration value. The question of the NaI effect on wettability and oil recovery arises even more when increasing this concentration: this case may happen according to research objectives (pore scale level), nature of the rock and fluid systems being studied, and X-ray scanner equipment such as 1D linear X-ray system, 2D X-ray system, 3D CT scanner, micro-CT scanner.

Advanced developments were successfully implemented by [9] to monitor fluid saturation during SCAL HPHT coreflooding tests on large cores without doping the fluids: this avoids the risk of establishing an unrepresentative wettability state in the rock and so possible unrepresentative relative permeability result for instance.

In this study, NaI was used as doping agent but other dopants such as potassium iodide KI or caesium chloride CsCl (in that case with no iodide) may be tested.

7 Conclusions

The objective of the study was to monitor the impact of the NaI addition in brine at different concentrations on wettability and oil recovery of Bentheimer sandstone samples. Effect of NaI presence or not in the connate brine was also tested.

During the spontaneous imbibition cycle, high imbibition rates were observed for the samples containing NaI in connate water. If the two tests with highest NaI concentration in resident brine have same imbibition rate, the test with low NaI concentration still highly outperform the samples with no NaI in the connate water. The samples with no NaI in connate brine had low imbibition rates and no clear rate arrangement according to the NaI concentration in the imbibing brine.

During the imbibition cycle, the three samples with no NaI in the connate brine had similar water saturation variation during the spontaneous displacement and similar final residual oil saturation post centrifuge forced imbibition, final recovery factor, and final water wettability index: important to note that the NaI addition in the imbibing brine does not seem to impact the oil recovery and wettability. On the other hand, for the three samples containing various NaI concentrations in the connate brine, all results show more water wetness than the three samples with no NaI in the connate brine. It is proven by the dependency of water wettability index to the amount of NaI: the Iw values increase with the increase of NaI concentration in connate brine. There is an obvious effect of the NaI presence on oil recovery and wettability.

In sandstone rocks, if the salinity of the connate brine is among the primary factors controlling the oil recovery as mentioned by [11] and [12], brine composition may also play an important role.

In this study, all observations are made on a specific type of rock, rock wettability state, with a specific couple of fluids: it may vary according to their properties, but the findings remain important to ensure all coreflooding tests and measurements are truly representative. It is a point of vigilance. Note that the second phase of the program is ongoing: it consists in repeating the protocol on carbonate rocks. Iododecane dopant will be tested later for both clastic and carbonate rocks during a third and fourth phase.

Finally, further work needs to be done to understand the dynamic mechanisms involved in the wettability alteration of sandstone and carbonate rocks when using iodide as dopant for the SCAL studies involving ISSM.

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Nomenclature

a_w: attenuation coefficient
CCA: conventional core analysis
CsCl: caesium chloride
CT: computed tomography
FI: forced imbibition
HPHT: high pressure high temperature
I: ionic strength
IFT: interfacial tension
ISSM: in-situ saturation monitoring

Iw: water wettability index
Kkl: Klinkenberg permeability
KI: potassium iodide
NaCl: sodium chloride
NaI: sodium iodide
Nb: Bond number
NMR: nuclear magnetic resonance
Pc: capillary pressure
ROS: remaining oil saturation
RPM: revolutions per minute
SARA: saturates, asphaltenes, resins, aromatics
SCAL: special core analysis
SPI: spontaneous imbibition
Sor: residual oil saturation
s.u.: saturation unit
Sw: water saturation
<Sw>: average water saturation
SW: sea water
SW: simplified synthetic sea water*
Swi: irreducible water saturation
TAN: total acid number
TBN: total base number
TDS: total dissolved salt
USBM: US Bureau of Mines

µw: brine viscosity
µo: oil viscosity
ρw: brine density
ρo: oil density
φ: porosity

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