A STUDY OF SULPHATE IONS - EFFECTS ON AGEING AND IMBIBITION CAPILLARY PRESSURE CURVE

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ABSTRACT

We study the effect of sulphate ions on wettability change during ageing and the capillary imbibition curve. We use resistivity measurements during ageing to monitor the wettability change. Sulphate in the formation pore water during ageing causes less change in the resistivity index compared with cores aged with only NaCl present in the formation pore water. We interpret the difference in the resistivity index during ageing to be related to the properties of the water film. The positive imbibition capillary pressure curve has been determined for six Liège outcrop cores, four cores were aged with NaCl and two cores with Na_2SO_4 as formation water, the oil phase used was Valhall crude oil in all cases. The cores aged with NaCl as formation water and imbibed with NaCl water behaved more oil wet than cores aged with Na_2SO_4 as formation water and imbibed with Na_2SO_4 water. However, the capillary curve for the core aged with NaCl as formation water and imbibed with Na_2SO_4 water approached the capillary pressure curve of the Na_2SO_4-Na_2SO_4 case. This has the important implication that the final recovery, but not the time scale of recovery, induced by sulphate ions is only dependent on the local sulphate concentration in the pore water, and thus not at which time it was introduced into the pore water.

INTRODUCTION

One of the important research results during the last decades has been the deciphering of the fact that the wetting state of the rock is not a static parameter, and that it can be changed by the injection water. By changing the ionic composition of the injection water in field test [1, 2] and core flooding [e.g., 3, 4, 5] the oil recovery can be increased significantly. The research community seems to agree to the notion of a connection between increased recovery and changes in the wetting state of the rock [e.g., 4, 5, 6, 7, 8]. But exactly how and why this leads to increased recovery are still open questions [9].

In spontaneous imbibitions experiments, the impact of brine salinity and ionic composition on oil recovery has been observed [5, 6, 7]. However, ultimately the effect of water chemistry on oil recovery needs to be implemented in a reservoir simulator in order to estimate the impact of water chemistry on the field scale. The injection water will generally not be in equilibrium with the rock and thus induce mineralogical alteration, changes in surface charge, and oil recovery [10]. One way of introducing the effect of water/rock interactions on the oil recovery is by introducing relative

permeability and capillary pressure curves that are dependent on the aqueous chemistry [11, 12].

The aim of this work is thus to determine capillary pressure curves experimentally for different aqueous chemistries. Only the positive part of the imbibition capillary pressure curve will be presented. In this work as a first approach we have chosen to simplify the aqueous chemistry by studying the effect of individual salts. It may also be the combined effect of various ions acting together that is causing an enhanced recovery [13, 14], however, these effects will be studied in a series of future studies to follow

THEORY
Resistivity measurements
During the experiments we constantly monitor the resistivity of the core samples. Archie's correlation [15] between resistivity and saturation (S_w) is used to interpret the resistivity measurements:

$$R_t = \frac{a}{\phi^m} \frac{R_w}{S_w^n} , RI = \frac{R_t}{R_o} = S_w^{-n}, \text{ and } F = \frac{R_o}{R_w} = \frac{a}{\phi^m} \qquad (1)$$

where, R_t, R_o, and R_w is the resistivity of the rock at a certain saturation, the resistivity at 100% water saturation, and the brine resistivity respectively. F is the formation factor, RI is called the resistivity index, n is the saturation exponent and m is the cementation exponent, and a is the tortuosity factor. The saturation exponent is dependent on geological features, wettability alteration, electrical conductive minerals, vugs, and micro-porosity [16]. The resistivity measurements give an additional measurement of the brine saturation inside the cores. This is important as the experiments reported here have to run for a prolonged time, and it is crucial to have a good control of the saturation. In addition the resistivity measurements give an opportunity to monitor the wettability alteration process during ageing of the cores. If the water film collapses and loses continuity the resistivity index will increase at a given saturation, which effectively means that the saturation index is changing.

EXPERIMENTAL
Materials
Chalk
Outcrop chalk samples from Liège, Belgium have been selected for the experimental work. The geological time for Liège chalk is late Campanian age and it is composed of >95 wt% $CaCO_3$ and <5 wt% of other non-carbonate minerals [17]. The dimensions, porosity as well as effective oil permeability at S_{wi} are given for each core plug in Table 1.

Brine
1.1 M NaCl and 0.37 M Na_2SO_4 brines were used. The ionic strength was kept constant and equal to 1.1 M. Physical properties of the brines are shown in Table 2.

Oil
Crude oil from Valhall field is used for all cores. This oil was filtered at 90°C through chalk cores with similar properties as the ones used in the experiments. This was done in order to avoid any clogging or precipitation of crude oil components. All chalk plugs were flooded with 5 pore volumes (PVs) of distilled water at ambient temperature to remove any sulfate originally present in the chalk cores before using it as a filter. The oil has a density equal to 0.86 g/cm^{3} and viscosity is 10.3 cP at 22.5^{o}C.

Experimental Procedures

Core Preparation
Twelve core plugs were drilled out in one direction from one and the same block of outcrop chalk. Thereafter the cores were shaped on a lathe, cut to the desired length, and then dried to constant weight at 90°C. After vacuum evacuating; eight plugs were saturated with NaCl brine while the four remaining were saturated with Na$_2$SO$_4$ brine. Porosity was determined from bulk measurements and difference in weights before and after saturation. Liquid permeability was measured by oil flooding during the ageing process.

Establishing Initial Water Saturations
To mimic the reservoir conditions, it was essential that samples had less than 10% initial water saturation (S_{wi}). To achieve homogeneous S_{wi}, all samples were drained with non wetting nitrogen gas using the porous plate method. Once the initial water saturation was established, the samples were loaded into Hassler-type core holders and saturated by flooding 2 PVs of crude oil under back pressure in each direction at 40°C.

Ageing Process
Oil saturated samples were aged in four different steps for approximately 10 weeks. Temperature was raised to 90°C from 40°C. Afterwards samples were flooded in three steps, 1 PV of crude oil flooding, another one-PV of oil flooding in opposite direction and finally flooding two-PVs of crude oil in the same direction as that of the first flooding. Sufficient time was given at every step providing stabilization of the water phase, i.e. constant resistivity was achieved. Electrical resistivity was measured with a frequency of 1 kHz for each sample to calculate saturation exponent (n) by using Archie's equation (Equation 1).

Spontaneous Imbibition
Spontaneous imbibition was carried out at 130°C. Figure 1 shows the schematic diagram of the equipment which is similar to that used by [18]. Six aged core plugs were chosen for three different spontaneous imbibition tests. Each test has been conducted using a pair of plugs to obtain repeatability. Each test has been named with the initial brine and the imbibing brine for each pair. Companion cores were prepared based on their S_{wi} and n values. Table 3 presents the selected plugs with their initial brine, imbibing brine, S_{wi} and n values.

Core plugs together with water-wet porous plates were mounted into a rubber sleeve with two end-pieces. Clay powder was used between the sample and the porous plate to maintain hydraulic contact during the test (see Figure 2). The samples were exposed to a net confining pressure of 20 bar. Spontaneous imbibition was carried out at four decreasing pressures (5.0, 1.0, 0.05 and 0 bar).

The pore-pressure system consists of two pressure vessels: A N_2 gas-water system, and a water-oil system. Here water was used as a buffer. Water-oil pressure vessel was installed into a heating cabinet to reach the desired temperature. N_2 gas was released (or injected) into the N_2 gas-water vessel according to the reading from the differential pressure transmitter to keep a constant differential pressure.

When the imbibition of brine over a week was < 0.3% PV and the electrical resistivity had stabilized, the capillary pressure was decreased. Water saturation at each pressure step was determined by measuring the volume of water imbibed for each sample.

RESULTS
Gas-Water Drainage
Figure 3 shows capillary pressure vs. overall saturation profile for two sets of gas-water drainage; one for NaCl saturated plugs and another for Na_2SO_4 saturated plugs. The maximum pressure applied here was 15 bar as this is the threshold pressure of gas for the porous plate. Na_2SO_4 saturated plugs reached higher S_{wi} than NaCl saturated plugs at 15 bar pressure. Values of S_{wi} for each plug have been measured from the difference in weights before and after the test. Results are presented in Table 4. Obtained S_{wi}'s for SO_4^{2-} containing plugs were more uniform as average S_{wi} is 7.3 % with 0.3 of standard deviation. Whereas S_{wi}'s for non-SO_4^{2-} containing plugs were widely spread with average S_{wi} 4.8±1.5 % (see Table 4).

Ageing Process
Figure 4 shows the resistivity index (RI) changes at each stage of ageing process for SO_4^{2-} and non-SO_4^{2-} containing plugs. During the first stage there seems to be no pronounced temperature effect for any sets of plug. A slight increase in saturation exponent (n) was observed when temperature was increased to 90°C (see Table 5). But after flooding 1 PV of crude oil into each plug at a rate of 7 PVs/day, non-SO_4^{2-} containing plugs showed significant changes in RI as well as n regardless of their initial water saturation. The SO_4^{2-} containing plugs show a doubling of the resistivity index during the aging process, whereas the non-SO_4^{2-} plugs show an increase by a factor of 8. The increase in resistivity index for the non-SO_4^{2-} plugs does not show any systematic correlation with the initial water saturation. The increase in resistivity during ageing indicates that the wetting state of all plugs is changing, however the plugs only saturated with NaCl seems to be more affected by the crude oil indicating that they behave more oil wet than those saturated with Na_2SO_4.

Spontaneous Imbibition
In order to have some idea of the reproducibility of our study two almost identical cores (companion cores) were prepared for each combination of brines. Figure 5 shows the production profiles (saturation vs. time) for spontaneous imbibition of all plugs. One plug (NaCl_02) from NaCl-NaCl pair did not imbibe as it might have lost contact with porous plate and/or due to any clogging of the tubing. Spontaneous imbibition of NaCl-Na$_2$SO$_4$ pair was started smoothly but NaCl_03 plug did not imbibe after P$_c$ changed to 0.05 bar (see Figure 5). The same occurred for one plug (Na$_2$SO$_4$_01) from the Na$_2$SO$_4$-Na$_2$SO$_4$ pair. Both plugs seemed to follow almost the same trend within their pair before they failed (see Figure 5). Even if some of the cores were lost during the experiment, it is still encouraging to see that the companion core followed similar trends. It is assumed that the remaining single plug from each pair is representative for each type of imbibition processes.

As expected from the resistivity measurements the cores aged with NaCl behaved more oil wet than the cores aged with Na$_2$SO$_4$. Results from the capillary pressure from three different sets of imbibition experiments are given in Table 6 and Figure 6. During NaCl-NaCl spontaneous imbibition (at zero capillary pressure), the non-SO$_4^{2-}$ plug (NaCl_01) has imbibed from S_{wi} of 0.04 to 0.28. The non-SO$_4^{2-}$ containing plug (NaCl_04) and the SO$_4^{2-}$ containing (Na$_2$SO$_4$_02) plug did, however, achieve saturation of 0.43 at zero P$_c$ point during spontaneous imbibition of Na$_2$SO$_4$ brine. Comparing spontaneous imbibition of NaCl-NaCl and NaCl-Na$_2$SO$_4$ sets, imbibing Na$_2$SO$_4$ brine is faster than imbibition of NaCl brine into non-SO$_4^{2-}$ containing plugs. However, Na$_2$SO$_4$-Na$_2$SO$_4$ set has shown a much faster imbibition of Na$_2$SO$_4$ brine. Furthermore it should be mentioned that NaCl-Na$_2$SO$_4$ set has shown a more rapid imbibition compared to Na$_2$SO$_4$-Na$_2$SO$_4$ set when capillary pressure came close to zero (see Figure 5).

DISCUSSION
Effect of SO$_4^{2-}$ during drainage and ageing
During gas-water drainage a slightly, but systematic lower water saturation was reached in the cores containing NaCl compared with the Na$_2$SO$_4$ containing plugs. This could be related to the fact that the chalk surface will obtain a negative charge in the presence of sulphate ions whereas it is more neutral in the presence of NaCl [19], and thus the properties of the diffusive layer are different in the presence of sulphate ions than only NaCl. The negatively charged surface in the presence of sulphate ions will cause a higher osmotic pressure than in the presence of NaCl only, i.e. a larger work is needed to bring negatively charged ions towards the negatively charged surface and hence a large pressure.

An effect of the water film properties can also be seen from the resistivity measurements during ageing, see Figure 4. At least two effects could cause an increase of the resistivity; 1) collapse of water films 2) change of the water film geometry (tortuosity). Collapse of water film should be similar for cores with NaCl and Na$_2$SO$_4$, due to similar residual water saturation. Even if there is a higher adsorption of active components from the oil,

the water film has collapsed and may not be very conductive. The significant change in resistivity happens when oil is flooded through the core after the initial ageing. If there has been a wettability change during that period, new oil and water channels may be formed when oil is flooded and thus affect the tortuosity of the water film. The resistivity change happens to a less degree when Na_2SO_4 is present in the core, indicating that in this case the water film is more stable.

Effect of SO_4^{2-} on the imbibition capillary pressure
The core aged with NaCl brine and imbibed with NaCl brine (NaCl_01) behaves least water-wet, whereas the cores aged with Na_2SO_4 and imbibed with Na_2SO_4 (Na2SO4_01) behaves more water-wet. When a brine with the same composition as the formation water is imbibed into the core it is reasonable to assume that the wetting state of the core does not change over time, and at any given capillary pressure the Na_2SO_4_01 core imbibes more water and faster than NaCl_01 (see Figures 5 and 6). However, the core aged with NaCl and imbibed with Na_2SO_4 (NaCl_04) does not follow the NaCl_01 core, rather it approaches the capillary pressure curve of Na_2SO_4_01. This is an interesting observation since it means that the wettability alteration induced by sulphate seems only to be dependent on the local sulphate concentration inside the core. If this is the case it would simplify any future modelling.

CONCLUDING REMARKS
In this work we have used simple brines only consisting of one type of salt in order to make a first approach at systematically studying the mechanisms behind wettability alteration induced by changing the ionic composition of the aqueous phase. In addition we have used the porous plate method, with the purpose of generating a set of capillary pressure curves that are dependent on the water chemistry. These curves can then be used to model any spontaneous imbibition experiments where similar rock and brine chemistry is used, by the methods introduced in [11, 12].
To summarize:
- We have demonstrated that resistivity measurements can be used as an indication of wettability change during ageing.
- Core plugs having SO_4^{2-} in formation brine have shown more water-wet behaviour.
- Wettability alteration induced by sulphate ions seems to be only dependent on the local concentration of sulphate and not at which time it was introduced, i.e. in the formation water or injection water.

ACKNOWLEDGEMENT

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Table 1. Physical properties of core plug samples

Sample	Dia-meter (cm)	Length (cm)	Porosity (%)	Effective Oil Permea--bility, k_o (mD) at S_{wi}
Na2SO4_01	3.81	7.22	42.9	2.74
Na2SO4_02	3.81	7.00	43.6	2.75
Na2SO4_03	3.81	7.25	43.1	2.83
Na2SO4_04	3.81	6.99	43.2	2.84
NaCl_01	3.80	7.00	41.7	2.89
NaCl_02	3.81	6.98	43.2	3.19
NaCl_03	3.81	7.00	41.7	2.68
NaCl_04	3.81	6.99	42.9	2.80
NaCl_05	3.81	6.99	43.6	2.43
NaCl_06	3.81	7.00	42.7	2.72
NaCl_07	3.81	6.99	43.0	2.44
NaCl_08	3.81	6.99	43.5	2.72

Table 2. Physical properties of brines @ 22.5^{o}C

	NaCl Brine	Na_2SO_4 Brine
Concetration (M)	1.1	0.37
Density (gm/cm^3)	1.042	1.043
Viscosity (cP)	1.042	1.095
Resistivity (ohm*m)	0.115	0.230

Table 3: List of core plugs and imbibing fluids for spontaneous imbibition

Spontaneous Imbibition	Initial Brine	Imbibing Brine	Sample	Swi (%) at 22°C	Saturation Exponent, n
Na$_2$SO$_4$ - Na$_2$SO$_4$ pair	Na$_2$SO$_4$	Na$_2$SO$_4$	Na2SO4_01	7.1	2.00
	Na$_2$SO$_4$	Na$_2$SO$_4$	Na2SO4_02	7.0	1.89
NaCl – NaCl pair	NaCl	NaCl	NaCl_01	3.7	1.90
	NaCl	NaCl	NaCl_02	3.5	1.90
NaCl - Na$_2$SO$_4$ pair	NaCl	Na$_2$SO$_4$	NaCl_03	6.0	2.37
	NaCl	Na$_2$SO$_4$	NaCl_04	6.3	2.38

Table 4: Obtained results from gas-water drainage experiments

SO$_4^{2-}$ containing plugs			Non SO$_4^{2-}$ containing plugs		
Sample Name	S$_{wi}$ (%) at 22°C	Corrected S$_{wi}$ (%) at 90°C *	Sample Name	S$_{wi}$ (%) at 22°C	Corrected S$_{wi}$ (%) at 90°C *
Na2SO4_01	7.1	7.4	NaCl_01	3.7	3.8
Na2SO4_02	7.0	7.3	NaCl_02	3.5	3.6
Na2SO4_03	7.4	7.7	NaCl_03	6.0	6.1
Na2SO4_04	7.6	7.8	NaCl_04	6.3	6.5
			NaCl_05	6.9	7.1
			NaCl_06	5.0	5.2
			NaCl_07	3.3	3.4
			NaCl_08	3.4	3.5
Average S$_{wi}$ (%)	7.3±0.3	7.5±0.3		4.8±1.5	4.9±1.5

Corrected Swi at 90°C= (Swi at 22°C)(brine density$_{@22^oC}$ /density$_{@90^oC}$)*(1-PV correction)*

Where, brine density$_{@22^oC}$ /density$_{@90^oC}$ = 1.0336 and Pore volume (PV) correction factor for 20 bar confining pressure = 0.002

Table 5: Calculated saturation exponent (n) from Archie's correlation (3) for all Liège plugs during the ageing process

Sample name and conditions	Different stages of ageing process					
	Reference point: T= 40°C	Increasing temperature to 90°C	Flooding 1 PV of crude oil	Reverse flooding 1 PV of crude oil	Flooding 2 PV of crude oil	Overall changes (%)
SO$_4^{2-}$ containing plugs						
Na2SO4_01	1.70	1.72	1.77	1.84	2.00	18
Na2SO4_02	1.67	1.69	1.75	1.80	1.89	13
Na2SO4_03	1.71	1.73	1.77	1.82	1.93	13
Na2SO4_04	1.69	1.70	1.75	1.82	1.93	14
Non- SO$_4^{2-}$ containing plugs						
NaCl_01	1.29	1.33	1.51	1.52	1.90	48
NaCl_02	1.31	1.41	1.61	1.64	1.90	45
NaCl_03	1.68	1.70	2.33	-	2.37	42
NaCl_04	1.53	1.63	1.91	1.99	2.38	55
NaCl_05	1.80	1.85	2.14	2.22	2.71	50
NaCl_06	1.58	1.60	1.91	1.95	2.36	49

| NaCl_07 | 1.34 | 1.39 | 1.62 | 1.62 | 1.89 | 42 |
| NaCl_08 | 1.40 | 1.44 | 1.69 | 1.75 | 2.02 | 45 |

Table 6: Pc characteristics for spontaneous imbibition at 130°C

	Spontaneous Imbibition Conditions (initial -imbibing brine)				
	NaCl-NaCl pair	*NaCl-Na2SO4 pair*		*Na2SO4-Na2SO4 pair*	
Sample name	*NaCl_01*	*NaCl_03*	*NaCl_04*	*Na2SO4_01*	*Na2SO4_02*
Pc (bar)	Sw (fraction)	Sw (fraction)	Sw (fraction)	Sw (fraction)	Sw (fraction)
5	0.04	0.06	0.07	0.08	0.08
1	0.07	0.14	0.15	0.19	0.21
0.05	0.21	-	0.35	-	0.40
0	0.28	-	0.43	-	0.43
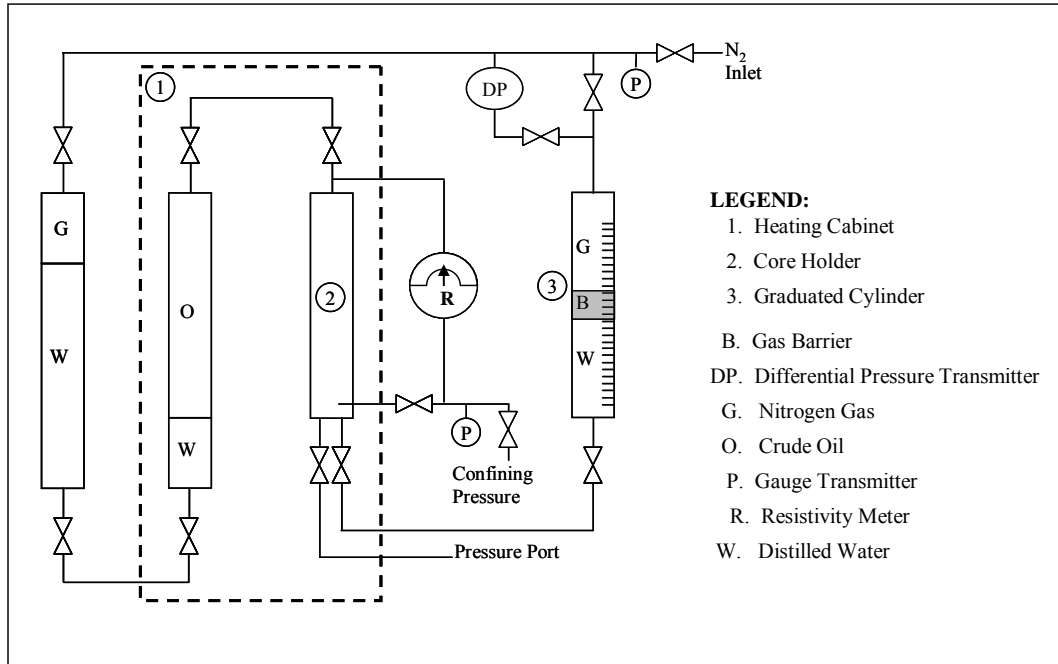
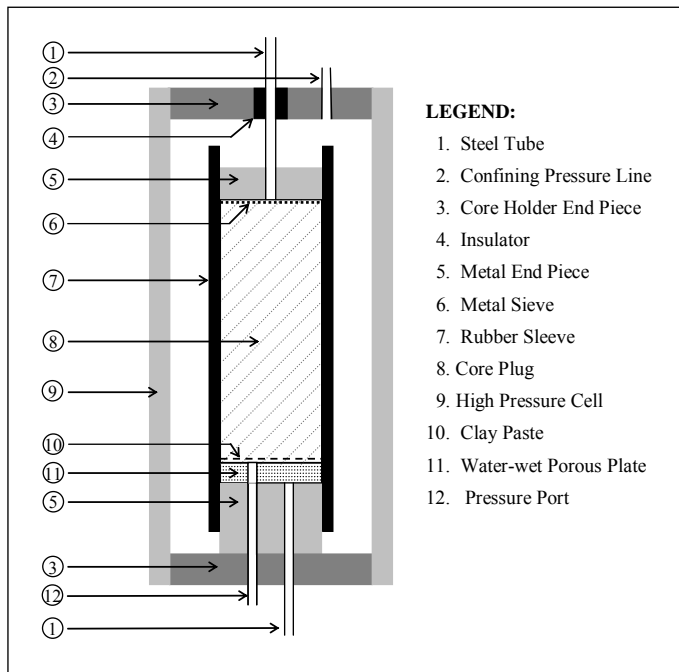Figure 1: Schematic diagram of the apparatus for capillary pressure measurement under reservoir conditions.

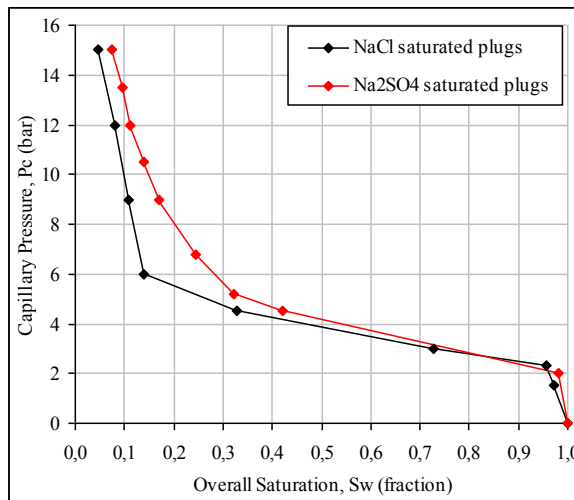Figure 2: Schematic diagram of the Hassler type core holder.

LEGEND:
1. Steel Tube
2. Confining Pressure Line
3. Core Holder End Piece
4. Insulator
5. Metal End Piece
6. Metal Sieve
7. Rubber Sleeve
8. Core Plug
9. High Pressure Cell
10. Clay Paste
11. Water-wet Porous Plate
12. Pressure Port

Figure 3: Capillary pressure vs saturation profile for two gas-water drainage experiments at room temperature. Eight NaCl brine saturated and four Na_2SO_4 brine saturated Liège chalk plugs were used.
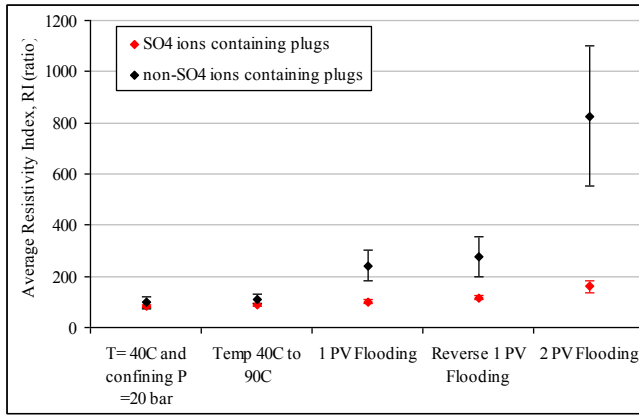
Figure 4: Changes of resistivity index (RI) during each stage of ageing process for SO_4^{2-} and non- SO_4^{2-} containing plugs. Red and black marks are represented for SO_4^{2-} and non- SO_4^{2-} containing plugs, respectively.
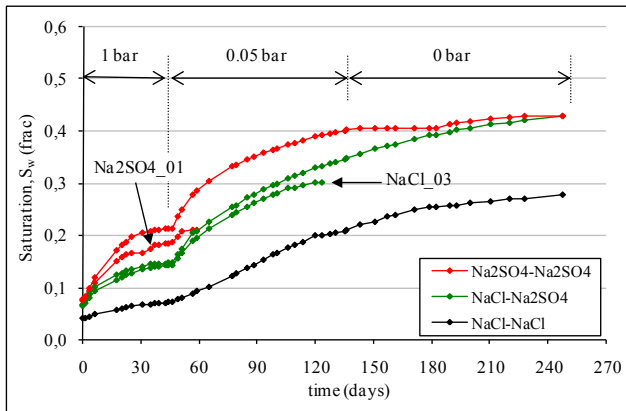

Figure 5: Production profile (saturation vs. time) for three different sets of spontaneous imbibition. Nomenclatures are made as 'initial brine – imbibing brine' for Liège chalk plugs.
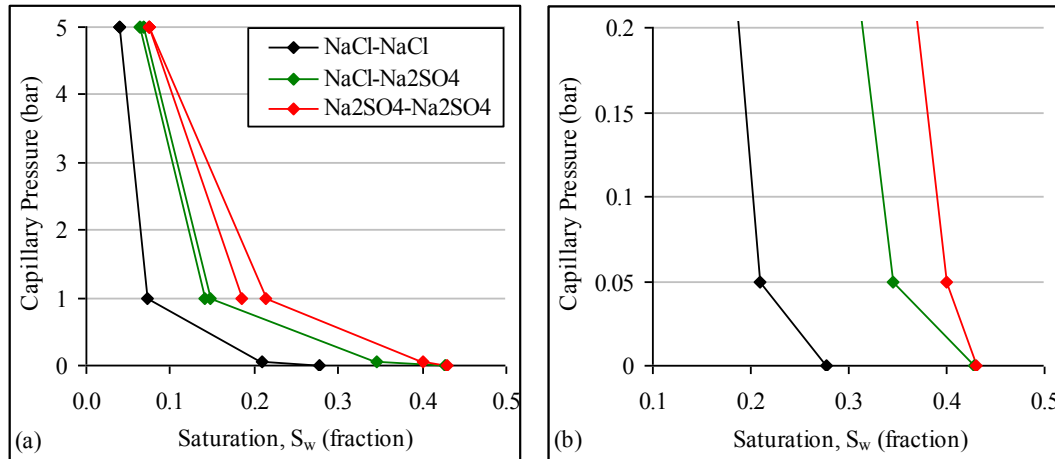

Figure 6: (a) Capillary pressure diagram for three different sets of spontaneous imbibition. (b) Magnified section of capillary pressure range from 0.2 bar to 0 bar. Nomenclatures are made as 'initial brine – imbibing brine' for Liège chalk plugs.