

# Polysulphate: A New Enhanced Oil Recovery Additive to Maximize the Oil Recovery From Carbonate Reservoirs at High Temperature

M. A. I. Khan<sup>1\*</sup>, I. D. Piñerez Torrijos<sup>1</sup>, S. H. Aldeen<sup>1</sup>, T. Puntervold<sup>1</sup>, and S. Strand<sup>1</sup>

<sup>1</sup>University of Stavanger

## Summary

Seawater (SW) injection is an enhanced oil recovery (EOR) success in the North Sea carbonate reservoirs due to wettability alteration toward a more water-wet state. This process is triggered by the difference in composition between injection and formation water (FW). “Smartwater” with optimized ionic composition can easily be made under laboratory conditions to improve oil recovery beyond that of SW. However, in the field, its preparation may require specific water treatment processes, e.g., desalination, nanofiltration, or addition of specific salts. In this work, a naturally occurring salt called Polysulphate (PS) is investigated as an additive to produce smartwater.

Outcrop chalk from Stevns Klint (SK), consisting of 98% biogenic CaCO<sub>3</sub>, was used to investigate the potential and efficiency of the PS brines to alter wettability in chalk. The solubility of PS in SW and deionized water, and brine stability at high temperatures were measured. Energy dispersive X-ray and ion chromatography were used to determine the composition of the PS salt and EOR solutions, and to evaluate the sulphate adsorption on the chalk surface, a catalyst for the wettability alteration process. Spontaneous imbibition (SI), for evaluating wettability alteration of PS brines into mixed-wet chalk was performed at 90 and 110°C and compared against the recovery performance of FW and SW.

The solubility tests showed that the salt was easily soluble in both deionized water and SW with less than 5% solid residue. The deionized PS brine contained sulphate and calcium ion concentrations of 31.5 and 15.2 mM, respectively, and total salinity was 4.9 g/L. This brine composition is very promising for triggering wettability alteration in chalk. The SW PS brine contained 29.6 mM calcium ions and 55.9 mM sulphate ions, and a total salinity of 38.1 g/L. Compared with ordinary SW, this brine has the potential for improved wettability alteration in chalk due to increased sulphate content.

Ion chromatography revealed that the sulphate adsorbed when PS brines were flooded through the core, which is an indication that wettability alteration can take place during brine injection. The reactivity was also enhanced by increasing the temperature from 25 to 90°C. Finally, the oil recovery tests by SI showed that PS brines were capable of inducing wettability alteration, improving oil recovery beyond that obtained by FW imbibition. The difference in oil recovery between ordinary SW and SW PS imbibition was smaller due to the already favorable composition of SW.

PS brines showed a significant potential for wettability alteration in carbonates and are validated as a potential EOR additive for easy and on-site preparation of smartwater brines for carbonate oil reservoirs. PS salt, added to the EOR solution, provides the essential ions for the wettability alteration process, but further optimization is needed to characterize the optimal mixing ratios, ion compositions, and temperature ranges at which EOR effects can be achieved.

## Introduction

Carbonate reservoirs account for approximately 50% of the world’s hydrocarbon reserves, with more than 60% of the oil and 40% of the gas reserves (Bjørlykke 2015; Schlumberger 2022). Despite holding large reserves, the oil recovered from these reservoirs is usually lower than 30% of original oil in place (OOIP), thereby making the EOR potential from carbonates very attractive and high (Austad et al. 2008b; Høgnesen et al. 2005).

Carbonate reservoirs are known for being a challenging environment for oil production. The difficulties met by reservoir and production engineers are low matrix permeabilities combined with natural fractures, and unfavorable wettability as their wettability usually falls within the neutral to oil-wet range (Lucia et al. 2003), which limits capillary forces and reduces the potential for water imbibition into the rock matrices during water injection. All these conditions can lead to water fingering, early water breakthrough, and low oil recovery rates.

Wettability in carbonates is highly influenced by the presence of polar organic components (POCs) in crude oil, where the acidic components are more important than the basic components. The POCs are quantified with the acid number (AN) and base number (BN). Standnes and Austad (2000) observed a reduction in water-wetness when initially, very water-wet carbonate cores were exposed to crude oils with increasing AN. The impact of AN on carbonate wettability has been confirmed by other researchers (Hopkins et al. 2016a, 2016b, 2017; Mjos et al. 2018; Puntervold et al. 2007b; Zhang and Austad 2005). It is also important to note that the brine pH in carbonates is buffered to slightly alkaline conditions. Therefore, the species driving the wettability of the rock surfaces are dissociated carboxylic acids and nonprotonated bases.

The initial wetting of a carbonate reservoir is established when negatively charged carboxylates adsorb onto positively charged carbonate pore surfaces. This will happen during the oil migration into the reservoir. Reservoir temperature can affect the crude oil chemical composition due to decarboxylation processes that take place at high temperatures. These processes decrease the AN of the crude oil

\*Corresponding author; email: sarjilsust09@gmail.com

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(Shimoyama and Johns 1972). Therefore, a higher water-wetness observed in a carbonate reservoir can be correlated to crude oils with low AN or high reservoir temperature (Rao 1999).

A water-based EOR method that can contribute with a wettability alteration toward more water-wet state is very important in heterogeneous reservoirs. Increased capillary forces will promote SI of brine from fractures into the matrix and mobilize trapped oil. Delayed water breakthrough by taking benefit of reservoir heterogeneity is highly valuable in the pursuit for increased oil production from carbonate reservoirs. Smartwater is a method that meets all these requirements, and it is only prepared by changing the ionic composition of the injection water (Fathi et al. 2010, 2011; Strand et al. 2006a, 2006b).

Different authors proposed different mechanisms explaining the smartwater EOR effect seen in carbonate cores depending on minerals, oil properties, and brine compositions (Bartels et al. 2019; Hao et al. 2019; Liu and Wang 2020; Tetteh et al. 2020). The smartwater EOR effect can be divided into rock/fluid interaction (mainly wettability alteration) and fluid/fluid interaction effects. Several mechanisms related to fluid/fluid interactions have been proposed for injection brine-induced EOR: Formation of water-in-oil microdispersions/microemulsions (Sohrabi et al. 2017), osmosis (Fredriksen et al. 2018; Sandengen et al. 2016), and reduction of interfacial tension. Sohrabi et al. (2017) noticed the formation of water-in-oil microemulsions due to the presence of surface-active agents in crude oil. The authors proposed that these microdispersions/microemulsions would improve the oil recovery by making the carbonate rocks more water-wet and also by swelling the oil phase, which will reconnect the isolated oil droplets in the pore space resulting in improved sweep efficiency. However, the oil swelling effect in microdispersion formation was observed only in glass micromodels, not in real porous rock. Therefore, according to Tetteh and Barati (2018), these observations might not directly influence EOR processes in actual reservoir cores. Alhammedi et al. (2017) experienced higher oil recovery by injecting low-salinity (LS) water in carbonate reservoir cores from the Middle East and linked it to microdispersion formation. Tetteh and Barati (2018) also observed microdispersions in the produced samples of waterflooding in Indiana Limestone. While Sohrabi et al. (2017) and Tetteh and Barati (2018) referred to the formation of these microdispersions as due to the presence of surface-active agents of crude oil; Sandengen et al. (2016) proposed that they were formed due to osmotic movement caused by the salinity difference of LS injection brine and high-salinity formation brine. These brines are separated by crude oil acting as a semipermeable membrane, resulting in the movement of water ions from the LS brine to the oil. This forms emulsification and water-in-oil microdispersions, resulting in oil swelling that leads to fluid displacement. Sandengen et al. (2016) claimed that the osmosis mechanism could be the reason for the formation of the water-in-oil microdispersions observed by Sohrabi et al. (2017) in the glass micromodel visualization experiments. However, the rock mineralogy was not considered while investigating the osmosis mechanism for EOR, and only single salt brines were used during experiments, while most of the formation brines are a combination of several salts.

McGuire et al. (2005) proposed that decrease in interfacial tension between the brine and oil could improve the capillary number and enhance oil recovery in LS brine injection in sandstone, which might be relevant for carbonate as well. Nevertheless, many researchers did not see any significant EOR effect in the case of lower interfacial tension between oil and brine (Mahani et al. 2015; Tetteh and Barati 2018; Yousef et al. 2011).

Proposed mechanisms related to rock/fluid interactions or wettability alteration processes have been classified mainly as either electrostatic interactions or mineral dissolution. Wettability alteration associated with the electrostatic interaction between the rock surface, oil, and brine, is inspired by the Derjaguin-Landau-Verwey-Overbeek theory, which can be further classified into different mechanisms: Electrostatic bond linkages, multivalent ion exchange and electrical double layer expansion, and surface charge variation. Tetteh et al. (2020) pointed out that these mechanisms are similar to the mechanism of the chemically induced wettability alteration process proposed by Zhang et al. (2007), but in the mechanism, the specific ion properties are of utmost importance. This mechanism will be discussed later in this introduction. Mineral dissolution during water flooding has been proposed as mechanisms for the higher oil recovery by smartwater injection, e.g., dissolution of calcite ( $\text{CaCO}_3$ ) (Chandrasekhar et al. 2018; den Ouden et al. 2015) and anhydrite ( $\text{CaSO}_4$ ) (Austad et al. 2015; Chandrasekhar et al. 2018). In the latter case, dissolution of anhydrite provided the most important ions ( $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$ ) for chemically induced wettability alteration originally proposed by Zhang et al. (2007) to the injection brine. The proposed recovery mechanism by Zhang et al. (2007) has been verified in several parametric studies, showing that the presence of both  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  facilitates wettability alteration toward more water-wet conditions and significantly improves the oil mobilization from heterogeneous pore systems. By modifying the SW composition, more efficient smartwater compositions can be made. Studies have shown that smartwater can be made by increasing the concentration of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  in SW or by lowering the salinity while maintaining the  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  concentration of SW.

The wettability alteration is induced by the specific ions present in SW, calcium ( $\text{Ca}^{2+}$ ), magnesium ( $\text{Mg}^{2+}$ ), and sulphate, ( $\text{SO}_4^{2-}$ ). The catalyst for this process was identified to be the sulphate present in SW (Austad et al. 2008b; Zhang et al. 2007), and calcium appeared to be also an important ion that is able to coadsorb on the chalk surface to facilitate the process of wettability alteration. Magnesium ions seemed to be relevant at high temperatures, where it can be exchanged with calcium ions from the chalk surface, making more calcium ions available in the bulk fluid to subsequently impacting positively on the EOR effect (Korsnes et al. 2006). The effect of increased sulphate and calcium concentration on the imbibing brine can be observed in **Fig. 1**.

Further modification of SW composition can boost the oil recovery factor in carbonates. For instance, reducing concentration of NaCl in SW or increasing concentration of the catalyst (sulphate) in the brine (Fathi et al. 2011) is a way to increase oil recovery beyond the wettability alteration potential of SW (**Fig. 2**).

The wettability alteration process in carbonates is also temperature-dependent (Fathi et al. 2011), and it appears that the potential for improved oil recovery is enhanced at higher temperatures. The reason behind this effect is connected to the increased reactivity of ions toward carbonate surfaces at higher temperatures. As the temperature increases, the hydration number of the ions present in water decreases. This change is translated into fewer water molecules surrounding them, allowing more interactions between ions and increasing chemical reactivity (Zavitsas 2005). The temperature effects could impact both the established initial wettability and the wettability alteration processes (Piñerez Torrijos et al. 2019; Strand et al. 2008; Zavitsas 2005).

In a comparative study performed by Zhang et al. (2007), oil recovery by SI tests, using brines with varying  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  concentrations, was evaluated at increasing temperatures from 70 to 100°C and 130°C. It was found that the role of calcium was highly relevant, but that it required the presence of sulphate for being efficient in the wettability alteration process (**Fig. 3**). Note that the four imbibition brines containing varying amounts of sulphate did not produce any oil, above that expected by thermal expansion, until the addition of divalent cations, as indicated in the figure.

The mechanism behind improved oil recovery using smartwater or LS water is still a debate. Smartwater can be LS brine or high-salinity SW as long as its composition can result in higher oil recovery by changing the wettability (Puntervold et al. 2015). A well-known smartwater EOR effect has been observed in natural fractured chalk fields in the North Sea by injecting SW (Austad et al. 2008a; Hermansen et al. 2000). However, Seyyedi et al. (2018) found no extra oil recovery by injecting SW in North Sea quartz-containing reservoir chalk cores from the Ekofisk Formation. In that case, LS water was found to be more effective than SW, and the authors claimed that the presence of a high amount of quartz affects the oil recovery behavior. In a recent study of the initial wettability in three different

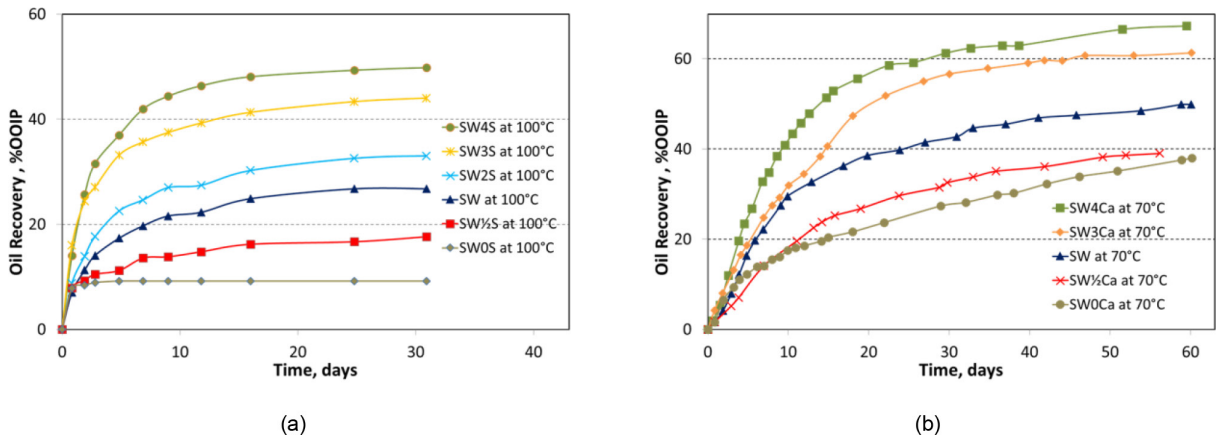


Fig. 1—SI experiments on chalk. (a) Tests at 100°C displaying the EOR effect on SK chalk cores by increasing sulphate concentration. (b) EOR effect at 70°C in chalk cores by increasing calcium concentration (Zhang and Austad 2006).

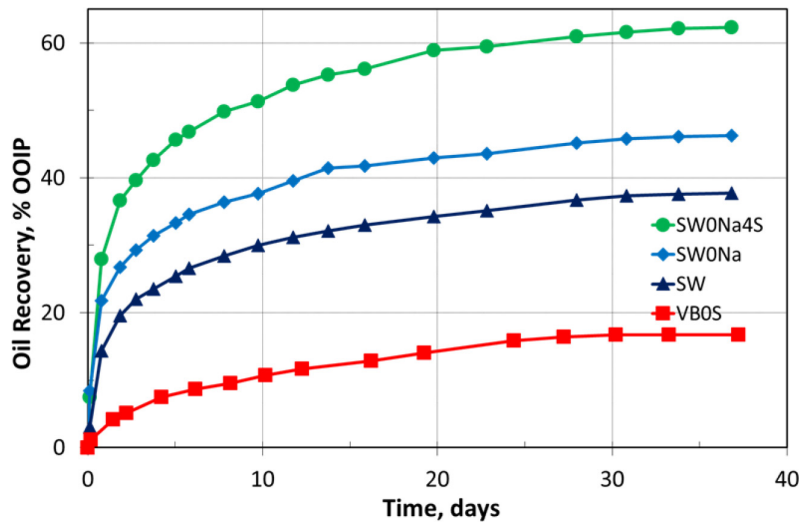


Fig. 2—SI experiments on chalk, EOR effect at 90°C on chalk cores by using VBOS (FW), SW, and two modified SW brines; SW0NaCl and SW0NaCl-4SO4 (Fathi et al. 2011).

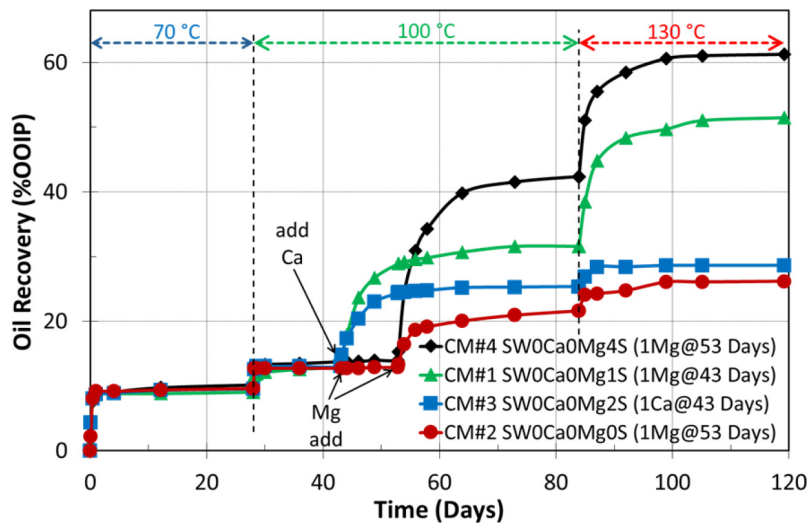


Fig. 3—SI on chalk cores with SW at changing  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  concentrations and temperatures (Zhang et al. 2007).

outcrop cores, pure calcite, sandstone, and silica-containing calcite, it was found that the silica content in the calcite had a significant effect on the generation of initial wettability in the cores (Punternvold et al. 2021). It is not unlikely that presence of noncarbonate minerals in carbonate rock can influence the smartwater EOR effect and the composition of the smartwater. Other studies have shown that even dolomite [ $\text{CaMg}(\text{CO}_3)_2$ ] or dolomitic cores respond differently to SW or modified SW injection compared with chalk/limestone (Punternvold et al. 2018; Romanuka et al. 2012; Shariatpanahi et al. 2016).

Punternvold et al. (2022) recently found that a tailor-made LS brine, containing 20 mM  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{SO}_4^{2-}$  at a salinity of ~5,000 ppm, was a more efficient imbibition fluid in North Sea reservoir chalk than was SW. This smartwater brine contained all the essential ions to induce wettability alteration, according to the mechanism proposed by Zhang et al. (2007), while at the same time having a reduced salinity, which improves the access of the wettability alteration ions to the chalk surface (Fathi et al. 2011; Punternvold et al. 2015).

Preparation of smartwater for carbonate field applications is a challenge. Efforts have been made to improve SW by using reverse osmosis in combination with nanofiltration. Nevertheless, these methods are highly energy intensive and represent a large investment because they increase capital expenditure and operation expenditure (Ayirala and Yousef 2014). Thereby, there is a need for production of smartwater at low cost that can reduce their impact in operation expenditure and capital expenditure during oil production activities.

Studies by Nair and coworkers at the University of Stavanger used nanofiltration of SW attempting to create a retentate (water containing ions not passing through the membrane) rich in divalent ions and a permeate (water containing ions passing through the membrane) free of divalent ions. The obtained two solutions could be used as main stock (makeup water) for the preparation of smartwater brines (Ravindran 2019). The process required a pressure of 9–18 bar, forcing the SW stream to go through the semipermeable membrane as illustrated in Fig. 4.

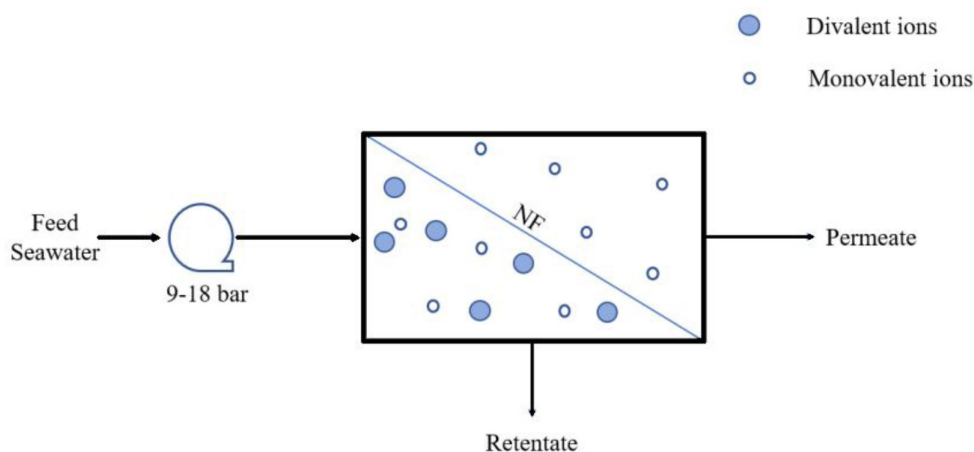


Fig. 4—Schematic of a nanofiltration process with SW as main feed (Ravindran 2019).

The results from the work showed that nanofiltration using SW as main feed was not effective for producing a smartwater enriched in divalent ions and reduced (monovalent ions) salinity. Ion rejection (ions not passing through the membrane) at different pressures quantified by Ravindran (2019) is displayed in Fig. 5.

The rejection of monovalent  $\text{Na}^+$  and  $\text{Cl}^-$  ions was 15–35%, which means that most of these ions passed through the membrane to the permeate, but that a significant amount was present in the retentate. The rejection of calcium increased from 55 to 70% when the pressure increased from 9 to 18 bar. Even though the concentration of monovalent and divalent ions in the permeate could be changed, typically only 5–20% of the feed is allocated to the permeate, resulting in retentates with ion concentrations close to SW.

Preparation of smartwater is a challenge both technically and economically. The best performing smartwater (SW0Na4S) brine described in Fig. 2 precipitates at higher temperature, approximately above 110°C and can thus only be used at temperatures up to approximately 110°C. Moreover, it requires additional chemicals to increase sulphate concentration and expensive filtration processes (such as reverse osmosis, nanofiltration, etc.) to reduce NaCl in the brine. Preparing LS brine also requires expensive filtration, which requires additional energy. Therefore, there is a need for identifying an optimized injection brine that contains the essential ions to induce wettability alteration and is also cheap and easy to prepare.

In this work, PS salts [ $\text{K}_2\text{Ca}_2\text{Mg}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ ] as an EOR additive are evaluated. PS is added to water/brine for preparing smartwater, having a composition containing the essential ions,  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$ , for inducing chemical wettability alteration in chalk. Dissolution of PS in water/brines should provide the potential to determining ions needed for the wettability alteration process in carbonates, and the solution must be stable at high temperature. The performance of PS as an additive will be evaluated based on dissolution tests, chemical surface reactivity tests, and SI tests on restored mixed-wet chalk cores.

## Experimental Work

**Materials. Rock Samples.** Outcrop chalk collected from the SK quarry, near Copenhagen, Denmark, was used in these experiments, and it is known to be a good analog for North Sea chalk oil reservoirs (Frykman 2001). SK chalk consists of 98% pure  $\text{CaCO}_3$  of biogenic origin, mainly coccoliths and fragments of coccoliths which is the building units of this material. Characteristic permeability is between 1 and 10 md, and porosity is relatively high (45–50%). The pore size distribution is presented in Fig. 6, and pore sizes typically range from 0.1 to 1  $\mu\text{m}$ .

Under the scanning electron microscope (SEM), it is possible to see the porous media structure in detail. Coccolithic rings and their fragments as well as the heterogeneity of the chalk surface are clearly visualized in Fig. 7.



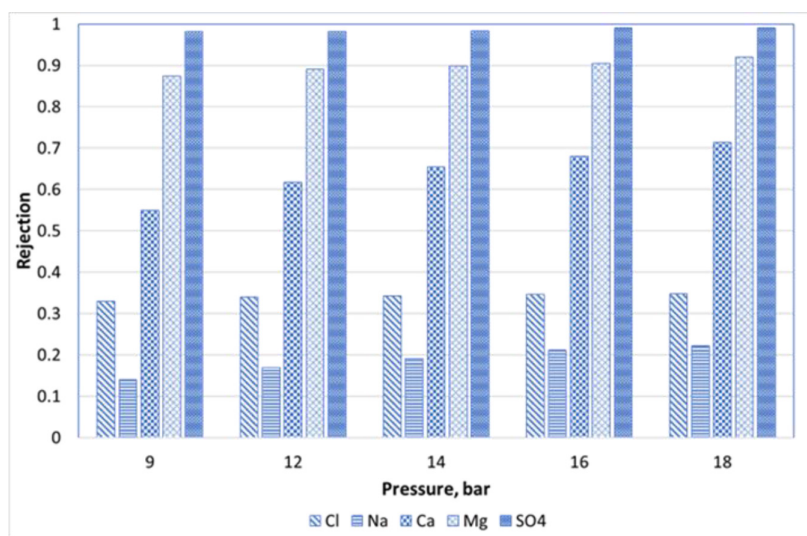


Fig. 5—Ion rejection at different pressures using nano-SW membranes (Ravindran 2019).

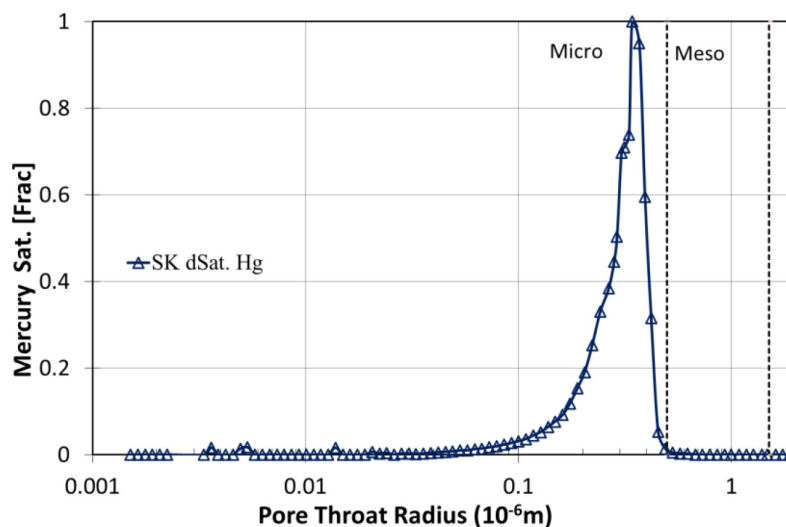


Fig. 6—Pore size distribution for SK chalk determined by mercury injection capillary pressure.

All cores were drilled from the same chalk block in the same direction and cut and shaped to the desired diameter of 3.8 cm and the desired length of 7 cm. All cores were inspected visually, and no fractures and distinct heterogeneities were observed. The properties of the cores used in this work are given in **Table 1**.

The physical properties of the cores were similar to previously published data (Fathi et al. 2010; Hopkins et al. 2016a, 2016b; Zhang et al. 2007).

**PS Salt.** The PS salt provided by ICL Group is also known as polyhalite. The salt is mined from a polyhalite rock layer of the Boulby mine, UK. The rock layer is located 1000 m below the North Sea near the North Yorkshire coast in the UK. The deposition of this polyhalite rock layer occurred 260 million years ago in the Permian period (**Fig. 8**), and only from this source, it is estimated that there are one billion tonnes of PS, making the cost of using PS low (ICL 2022).

The salt was slightly gray in color and was observed to be in range from granulated to powder form. The salt grains had different particle sizes well spread within the samples analyzed. The predominant particle diameter was in the range of 5–30  $\mu\text{m}$ .

No further purification of the raw salt was performed. High-resolution SEM images were taken of the PS salt mineral, and energy dispersive X-ray was used to analyze its composition. The SEM images of PS salts at 5,000 and 10,000 times magnification are shown in **Fig. 9**.

Elemental analysis detecting both cations and anions was carried out for the PS sample. The results are presented below in **Table 2**. The sample composition is dominated by calcium, potassium, and magnesium cations. On the anion side, sulphate was the main component detected in the sample.

**Crude Oil.** A low asphaltenic dead oil with an AN of 2.90 mg KOH/g and a BN of 0.95 mg KOH/g was used as source. The dead oil was diluted with 40 wt% heptane, centrifuged, and filtrated through a 5- $\mu\text{m}$  millipore filter. The prepared base crude oil was named RES40, and the AN and BN were measured to 2.18 and 0.66 mg KOH/g, respectively. The AN and BN of the oil samples were analyzed by potentiometric titration following the procedure by Fan and Buckley (2007). No asphaltenic precipitation was observed during filtration or in the storage phase. A batch of the RES40 oil was treated with silica gel to remove the surface active POC, providing an oil with

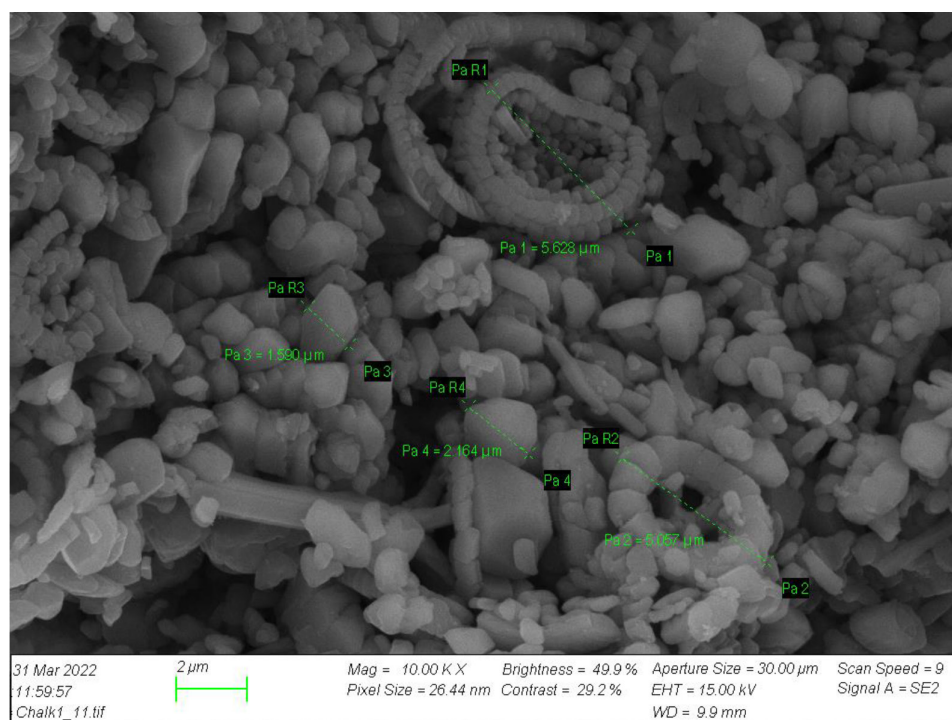


Fig. 7—SEM image of uncleaned SK outcrop chalk at 10,000X magnification.

Core		SK1	SK2	SK3	SK4	SK5	SK6	SK7	SK8	SK9
Length	(cm)	7.1	7.1	7.1	7.2	7.0	6.9	7.1	7.0	7.0
Diameter	(cm)	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8
Pore volume	(mL)	38.6	39.1	39.1	40.1	41.3	38.6	37.9	40.0	37.9
Porosity	(%)	48.6	48.6	48.8	49.2	49.3	49.2	47.4	50.2	47.2
Permeability	(md)	4.1	4.7	3.8	3.8	4.1	4.7	3.8	3.8	4.0
BET (Brunauer, Emmett, and Teller) surface area	(m <sup>2</sup> /g)					2.0				
Used in experiment		SIFW at 90°C	SISW at 90°C	SIDW-PS at 90°C	SISW-PS at 90°C	SIFW at 110°C	SISW at 110°C	SIDW-PS at 110°C	SISW-PS at 110°C	CWT at 25 and 90°C

Table 1—Physical properties of the SK cores.

AN = 0.0 mg KOH/g, named RES40-0 oil. Then, the diluted oil, RES40, and the silica-treated oil, RES40-0, were mixed in the proportion of 1:4 to obtain a crude oil (Oil A) with AN ~0.5 mg KOH/g. The reason for preparing a crude oil with AN ~0.5 mg KOH/g was to prepare slightly water-wet/mixed-wet chalk cores as the initial wettability depends on the AN of the crude oil (Standnes and Austad 2000). The final properties of Oil A were measured to AN = 0.58 mg KOH/g and BN = 0.30 mg KOH/g, with density and viscosity determined to be 0.81 g/cm<sup>3</sup> and 2.4 cp. The properties of the three oils are reported in **Table 3**.

**Brines.** SW and FW used in these experiments were made by mixing distilled water (DW) with reagent-grade salts. The SW composition is based on the SW composition from the North Sea. The FW composition is based on an FW from a North Sea chalk reservoir (Valhall formation brine without sulphate - VBOS). SW and FW were mixed overnight by magnetic rotation and filtered through a 0.22- $\mu$ m millipore filter. The PS brines, DW-PS, and SW-PS were made by mixing DW and SW with 5.00 g PS per liter solution, respectively. The solutions were mixed for 6 days with a magnetic stirrer before filtration through a 0.22- $\mu$ m millipore filter. Very similar amounts of PS salt were dissolved independently of the aqueous solution used, i.e., SW or DW. Thus, the solubility of the salt in different brines is high, and more than 95% of the PS added was dissolved. The ion compositions of the filtered brines were analyzed by ion chromatography. The brine composition of DW-PS and SW-PS after 6 days of mixing is given in **Table 4**. The filters along with insoluble particles from the salts were dried, and the residue was quantified by weight and analyzed with SEM and energy dispersive X-ray. Small variations in ion composition of the prepared brines were observed from one batch to another as the PS is a naturally occurring salt, taken from a mine. To minimize variations in the concentrations, stock solutions of 20 L for both DW-PS and SW-PS were prepared and used throughout this experimental work.

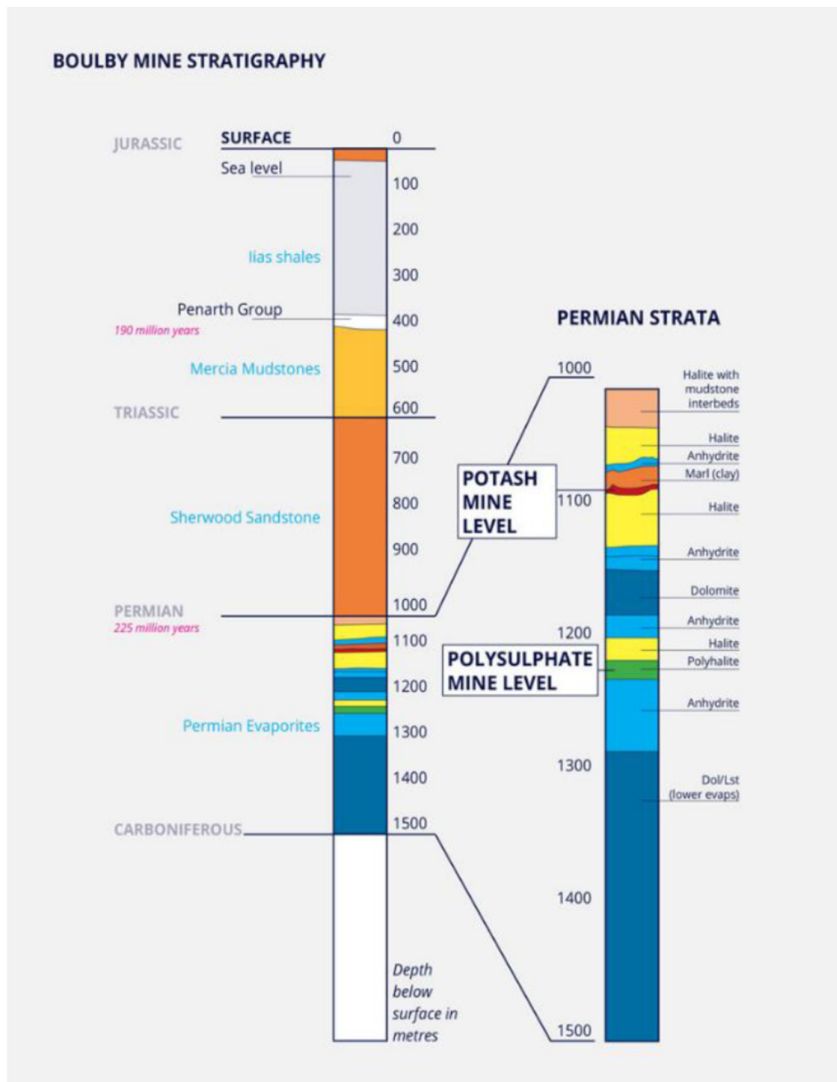


Fig. 8—Stratigraphy of the Boulby mine where PS is found in the Permian strata 1200 m below the surface level (ICL 2022).

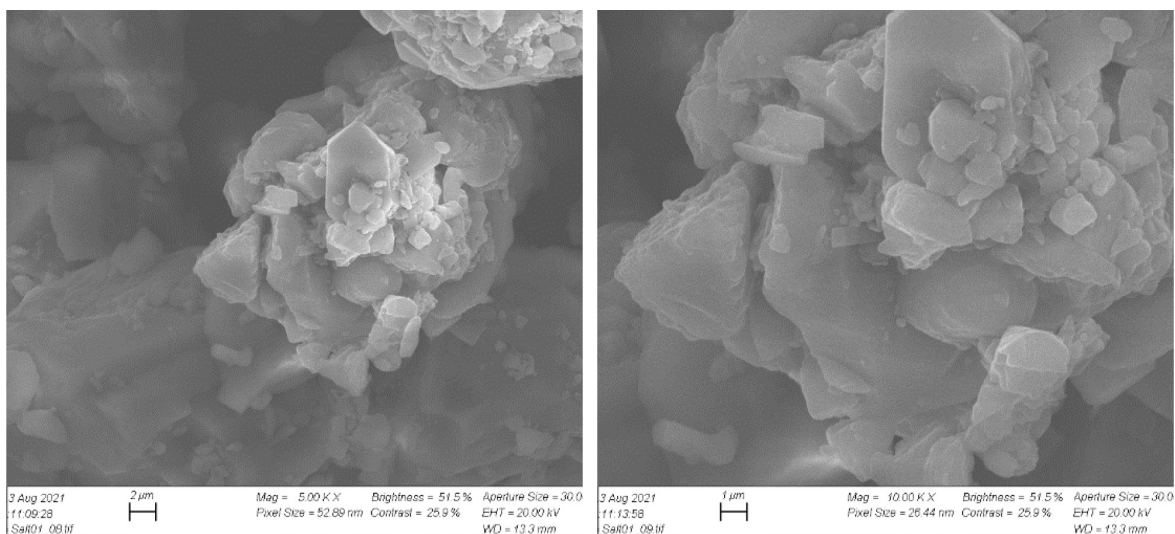


Fig. 9—SEM images of a PS sample at (left) 5,000X magnification and (right) 10,000X magnification.

Cations		Anions	
Element	Atomic Weight %	Element	Atomic Weight %
Sodium	9.3	Sulfur	85.4
Magnesium	21.9	Chloride	14.6
Aluminum	3.2		
Silica	3.3		
Potassium	25.5		
Calcium	36.9		

Table 2—Elementary composition by atomic weight % of cations and anions in PS.

Oil	AN (mg KOH/g)	BN (mg KOH/g)	$\rho_{20^{\circ}\text{C}}$ (g/ $\text{cm}^3$ )	$\mu_{20^{\circ}\text{C}}$ (mPa·s)
RES40	2.18	0.66	0.81	2.4
RES40-0	0.0	0.05	0.81	2.1
Oil A	0.58	0.30	0.81	2.4

Table 3—Oil properties.

Ion (mM)/ Properties	SW	FW	DW-PS	SW-PS	DW0T	DW1T
[Na <sup>+</sup> ]	450.1	997.0	6.3	466.2	6.3	6.3
[K <sup>+</sup> ]	10.1	5.0	17.4	28.2	17.4	17.4
[Li <sup>+</sup> ]	-	-	-	-	-	24.0
[Ca <sup>2+</sup> ]	13.0	29.0	15.2	29.6	15.2	15.2
[Mg <sup>2+</sup> ]	44.5	8.0	5.8	47.9	5.8	5.8
[Cl <sup>-</sup> ]	525.1	1066.0	9.2	528.5	65.7	33.2
[HCO <sub>3</sub> <sup>-</sup> ]	2.0	9.0	-	-	-	-
[SO <sub>4</sub> <sup>2-</sup> ]	24.0	0.0	31.5	55.9	-	31.5
TDS (g/L)	33.38	62.83	4.9	38.14	-	-
Density (g/cm <sup>3</sup> )	1.02	1.04	1.0	1.02	1.0	1.0
Bulk pH	7.8	7.3	7.5	8.1	7.8	7.8

Table 4—Properties of brines.

DW0T and DW1T brines were used for the surface reactivity tests. DW1T was actually DW-PS mixed with 1.0 g/L of LiCl that worked as a tracer, and DW0T was prepared with reagent-grade salts to have similar composition as DW-PS but depleted in SO<sub>4</sub><sup>2-</sup>. All brine compositions are listed in **Table 4**.

**Surface Reactivity.** The surface reactivity of chalk cores in the presence of DW-PS was studied at different temperatures (25 and 90°C) using the chromatographic wettability test developed for evaluating the wettability and the reactivity of potential determining ions such as sulphate, calcium, and magnesium with the carbonate surface (Strand et al. 2006a, 2006b). The test is performed using a coreflooding setup. First, the core was conditioned by flooding 5–6 pore volumes (PV) with DW0T, a brine having similar concentration of ions as DW-PS but depleted in sulphate. Then the core was flooded with DW1T (DW-PS brine with a small amount of Li<sup>+</sup> ions as tracer). The tracer has no affinity for the chalk surface and therefore follows the displacement front. On the other hand, sulphate has affinity for the water-wet chalk surface and is thus eluted with a delay compared with the tracer. IC analysis of the effluents during the coreflooding will determine the tracer and sulphate concentrations. The relative amount of water-wet area or the reactivity of sulphate toward water-wet chalk minerals will be determined by the delay in sulphate elution compared with the elution of the tracer.

**Core Restoration. Initial Water Saturation ( $S_{wi}$ ).** All cores were initially cleaned by flooding 5 PV of DW at room temperature to remove easily dissolvable salts, especially sulphate salts (Punternold et al. 2007a). The cores were then dried at 90°C to a constant weight. The initial FW saturation ( $S_{wi}$ ) of 10% was established using the desiccator technique, then the core was stored in a sealed container for 3 days to allow an even ion distribution within (Springer et al. 2003).

**Oil Exposure and Aging.** The cores with  $S_{wi} = 10\%$  were vacuumed before saturation with Oil A. One PV of Oil A was flooded initially from both sides to saturate the core followed by 1.5 PV crude oil flooded in both directions at 50°C. A total of 4 PV was flooded to saturate the cores. Finally, the cores were wrapped in Teflon<sup>TM</sup> tape to avoid unrepresentative adsorption of POC on the outer surface, and then the cores were aged in the same oil for 2 weeks at 90°C to achieve a homogeneous core wetting.



**Oil Recovery by SI.** SI experiments were performed on the restored cores to evaluate the initial core wettability and the performance of different brines as EOR fluids. The imbibition experiments were performed at 90 and 110°C at a backpressure of 10 bar using FW, SW, DW-PS, and SW-PS as the imbibing brines. The volume of oil produced was calculated as %OOIP vs. time. The experimental setup is depicted in the following Fig. 10.

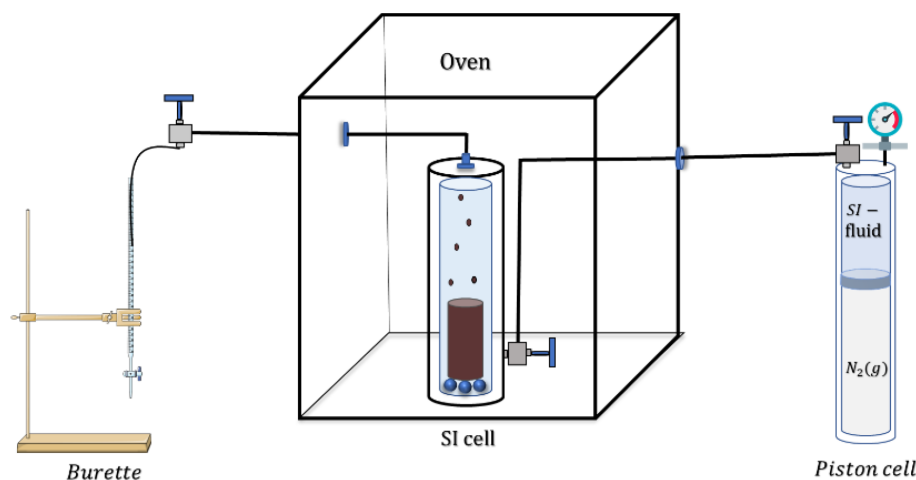


Fig. 10—Schematic of the setup used for the SI experiment.

## Results and Discussion

**Dissolution of PS Salts in DW and SW.** The ion composition after dissolving 5.00 g of PS in 1 L of DW showed a sulphate concentration of 31.5 mM, slightly higher than the concentration of sulphate in SW, 24 mM (Table 4). The calcium concentration was 15.2 mM and magnesium 5.8 mM. In comparison with SW, the largest difference was observed for the magnesium which is 44.5 mM in SW. The PS salt also contains a significant amount of potassium which when dissolved in DW gave a concentration of 14.4 mM. The total salinity of DW-PS was 4,885 ppm, with a rather low concentration of sodium, 6.3 mM, and chloride, 9.2 mM. The insoluble part of the PS after filtration was 0.115 g, which means that the solid residue represents only 2.3% of the total PS salt added to DW.

After dissolving 5.00 g PS salt in 1 L of SW, the concentration of sulphate in SW-PS was 55.9 mM (Table 4). This represents an increase of 31.9 mM compared with SW, 24.0 mM. Calcium concentration was 29.6 mM, which represents an increase of 16.6 mM compared with the concentration of calcium in SW, 13.0 mM. Magnesium concentration was 47.9 mM, confirming an increase of 3.4 mM after PS exposure. Potassium concentration increased from 10.1 mM in SW to 28.2 mM in SW-PS, which represents an increase of 18.1 mM. The total salinity of the SW-PS brine was 38,140 ppm, which is an increase of 4,760 ppm compared with the salinity of SW. The solid residue after filtration was only 0.200 g, which represents only 4.0% of the PS added to SW.

It appears that in both brines, DW-PS and SW-PS, the concentrations of the determining ions calcium, sulphate, and magnesium are sufficient to trigger smartwater EOR effects. However, the concentrations of these ions are larger in the SW-PS solution, due to the original presence of these ions in SW.

It was observed that almost similar amounts of PS salt were dissolved independently of the aqueous solution used, i.e., SW or DW. More than a 95% of the salt was dissolved in the mixing processes. This might be due to the elementary composition of the salt (Table 2).

**Residue Analyses.** After filtration with the 0.22- $\mu$ m millipore filter, the residue was dried and analyzed by SEM and energy dispersive X-ray. The SEM images of the residue from the dissolution of PS in DW and SW are presented in Fig. 11.

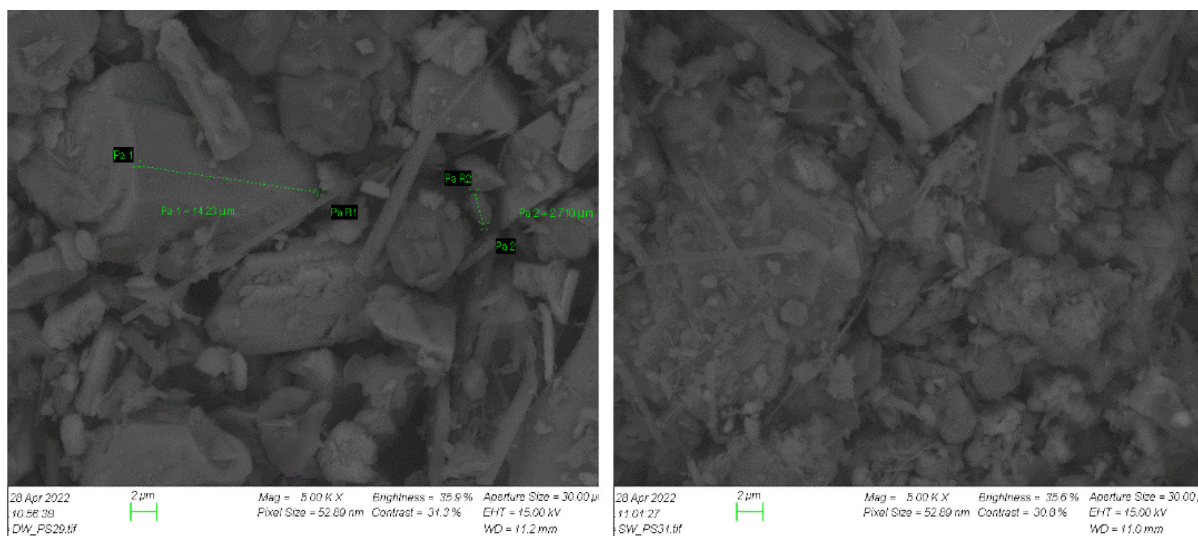
The particle sizes of the residue range from 0.2 up to 30  $\mu$ m. Different grain shapes were observed under the microscope. Irregular grains were the most common, but also elongated crystals appeared to be a part of the residue in both samples. However, more small particles appeared present in the SW residue, and the particle surfaces also appeared more worn in the presence of SW.

Elemental analysis of the residues was carried out on both samples, and the results are given in Table 5.

The insoluble residue was dominated by calcium, sodium, and magnesium cations. On the anion side, sulphate was the main component detected. The DW residue was richer in calcium and sulfur than the SW residue. On the other hand, the SW residue contained more silica and aluminum. These results suggest that the dissolution in SW may have been more effective.

**Surface Reactivity.** The chromatographic surface reactivity test was performed at both 23 and 90°C using a 100% water saturated SK chalk core SK9. The chromatographic separation between the lithium tracer and sulphate is presented in Fig. 12.

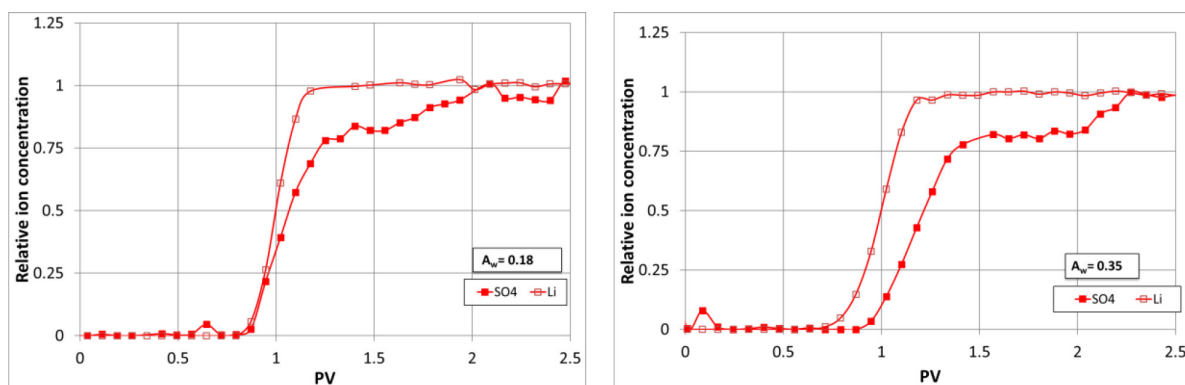
The delayed elution of sulphate ions confirms that the sulphate ions gained from PS interact with the chalk surface, and the sulphate reactivity increases with increasing temperature. The first lithium tracer is observed in the effluent after 0.8 PV injected and reaches injection concentration after 1.4 PV. The increase in sulphate concentration is significantly delayed, especially for the test performed at 90°C. At 23°C, the injection concentration of sulphate was reached after 2.0 PV, while after 2.2 PV at 90°C. The separation area ( $A_w$ ) between lithium tracer and sulphate was quantified by the trapezoidal method and increased from 0.18 at 23°C to 0.35 at 90°C, confirming that the sulphate adsorbs on the CaCO<sub>3</sub> surface, and that the adsorption is temperature-dependent. The increased reactivity of the sulphate ions at high temperatures could be explained by dehydration, breaking the hydrogen bond structures between water molecules surrounding the sulphate ion in solution. The results from the surface reactivity test are summarized in Table 6.



**Fig. 11**—SEM images at a magnification of 5,000X of PS residue after filtration with 0.22- $\mu\text{m}$  millipore filter. (Left) DW residue and (right) SW residue.

Element	DW Residue	SW Residue
	Atomic Weight %	Atomic Weight %
Sodium	7.0	9.3
Magnesium	11.8	37.5
Aluminum	0.4	1.9
Silica	4.3	14.5
Potassium	0.5	1.5
Calcium	42.4	23.9
Sulfur	33.6	11.4

**Table 5**—Cation analyses for DW and SW residues after filtration.



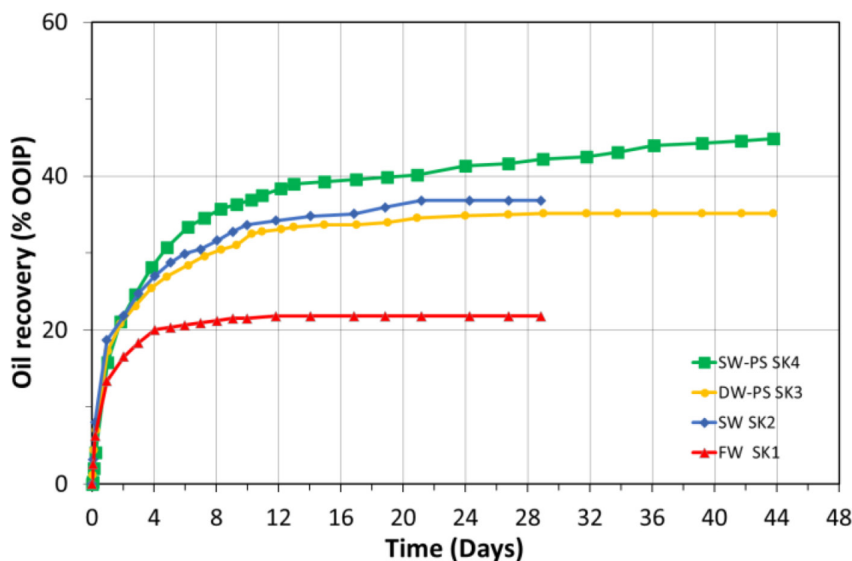
**Fig. 12**—Chromatographic separation between sulphate and lithium ions in SK outcrop chalk core SK9 (left) at 23°C and (right) at 90°C, flooding DW0T followed by DW1T at an injection rate of 0.2 mL/min.

Temperature	23°C	90°C
Chromatographic separation observed	Yes	Yes
Area of chromatographic separation, $A_w$	0.18	0.35

**Table 6**—Data from the surface reactivity tests.

In summary, a chromatographic separation between sulphate and lithium reveals the potential of the DW-PS as a possible wettability modifier in carbonates. Thus, increased wettability alteration and increased oil mobilization when this brine is used as smartwater (Strand et al. 2006b) can be expected. The increased chromatographic separation at higher temperatures confirms higher reactivity at elevated temperatures, which increases the EOR potential at high reservoir temperatures.

**Effect of PS on Oil Recovery. PS at 90°C.** Four equally restored cores were used in this study at 90°C. SI tests were performed to evaluate the restored core wettability and oil mobilization potential by using different imbibition brines. Core SK1 was exposed to FW as the imbibing brine. FW will not facilitate any chemical-induced wettability alteration as long as FW is used as the initial brine. The oil production during SI with FW will give the wettability and baseline oil production from the restored core. Core SK2 was imbibed with SW as imbibing brine. SW is known to behave as a smartwater for mixed-wet cores and is commonly used as injection brines for pressure support for offshore reservoirs. The other two imbibing brines tested were DW-PS and SW-PS. These brines are used to evaluate the effect of PS to improve the oil mobilization by wettability alteration. Core SK3 was imbibed with DW-PS while core SK4 was imbibed with SW-PS. The oil recovery results at 90°C are presented in Fig. 13.



**Fig. 13—Oil recovery tests at 90°C by SI of equally restored cores with  $S_{wi} = 10\%$  and exposed to Oil A. Core SK1 was exposed to FW as the imbibing brine, SK2 to SW, SK3 to DW-PS, and SK4 to SW-PS.**

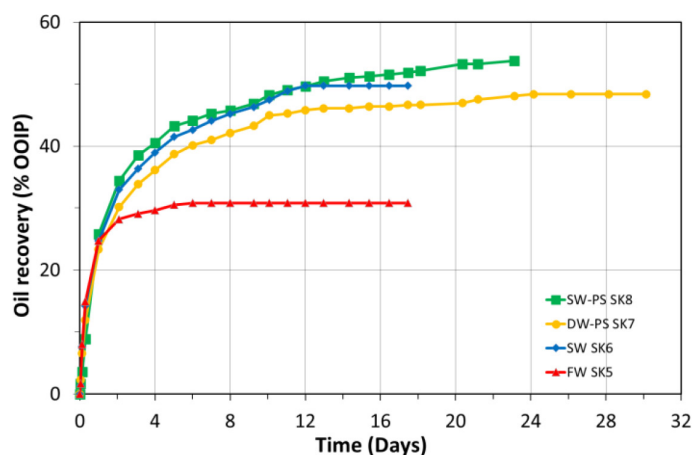
The production plateau for core SK1 reached the ultimate recovery plateau of 22 %OOIP after 12 days using FW as the imbibing brine. The moderate imbibition of FW confirms that the restored SK chalk cores behave slightly water-wet.

SI as an oil recovery method is a practical way of quantifying the wettability of porous systems as both the imbibition rate and ultimate recovery give relevant information that describes the core's wettability (Anderson 1986). A core can be considered to be water-wet, to some degree, if water can imbibe into the oil saturated core. Previously, Puntervold et al. (2021) showed that a similarly prepared SK chalk core, but saturated with oil having no POCs, imbibed FW to 75 %OOIP. This was considered to be the oil recovered from a strongly water-wet core as there were no POCs in the oil. In contrast, an oil-wet core should not imbibe water and an example of a reservoir core of intermediate to oil-wet condition is described by Puntervold et al. (2022) where there was no oil produced by SI of FW.

The restored core SK2 was imbibed with SW. Both the speed of imbibition and the ultimate oil recovery plateau of 37 %OOIP after 21 days is a substantial improvement compared with FW. This confirms that SW induces a wettability alteration in the chalk core during the test, resulting in a significantly more water-wet state (Austad et al. 2008b; Fathi et al. 2010). Wettability alteration also took place with the imbibing brines containing PS. Core SK3 imbibed with DW-PS reached an ultimate production plateau of 35 %OOIP after 28 days, which is very close to the ultimate oil recovery obtained for SW. When using SW-PS as imbibing brine, the ultimate recovery and speed of imbibition of core SK4 were the highest seen. An ultimate oil recovery of 45 %OOIP was reached after 44 days, providing an extra 8 %OOIP compared with SW. These results show that SW as displacement fluid can be improved by the addition of PS salts before injection. PS can also be added to fresh surface and aquifer water to be as efficient as SW in wettability alteration of chalk. Addition of PS to the injection water increases the concentrations of  $SO_4^{2-}$  and  $Ca^{2+}$  ions needed to induce an efficient wettability alteration, as suggested in the model proposed by Zhang et al. (2007).

**PS at 110°C.** SI of the restored core SK5 with FW as imbibing brine provides the baseline of oil production and wettability at 110°C, because no chemical-induced wettability alteration will take place when FW is used both as initial brine during core restoration and as the imbibition brine. SW was used as the imbibing brine on core SK6 as a reference for a smartwater. To evaluate the effect of PS as a smartwater additive, DW-PS and SW-PS brines were used as imbibing brines in core SK7 and core SK8, respectively. The results from the SI oil recovery tests at 110°C are given in Fig. 14.

The oil recovery results follow the same trend as that observed at 90°C, with the lowest oil recovery with FW and highest oil recovery with SW-PS brine. The recovery plateau with FW on core SK5 reached a recovery plateau of 31 %OOIP after 5 days. Without wettability alteration, the baseline oil production with FW confirms slightly water-wet conditions in core SK5, in-line with the experiment performed on core SK1 at 90°C. When SW was used as the imbibing brine in core SK6, the oil recovery increased from 31 %OOIP with FW to 50 %OOIP with SW, which is an increase of 19 %OOIP, confirming a change in core wettability giving both increased speed of imbibition and significant higher oil mobilization. For the imbibing brines with PS, the recovery plateau with DW-PS on core SK7 was 49% after 24 days, while SW-PS gave the highest ultimate oil recovery of 54 %OOIP after 23 days on core SK8, when the experiment ceased out due to scaling in the inlet line. By adding PS to freshwater, DW-PS, a brine with smartwater properties equal to SW was made. 18 %OOIP



**Fig. 14—Oil recovery by SI at 110°C in secondary mode in similarly restored outcrop cores using FW (core SK5), SW (core SK6), DW-PS (core SK7), and SW-PS (core SK8) as imbibition brines.**

extra oil compared with that by FW imbibition was mobilized from core SK7 using DW-PS as the imbibing brine. PS added to SW significantly increased both the  $\text{Ca}^{2+}$  (29.6 mM) and  $\text{SO}_4^{2-}$  concentrations (55.9 mM) in the SW-PS brine, resulting in the most efficient smartwater brine, mobilizing 23 %OOIP extra oil, which is 4 %OOIP more than that achieved with SW.

**Temperature Effect.** It was observed that the speed of imbibition significantly increased when the temperature increased from 90 to 110°C, which also gave a significant increase in the ultimate oil recovery. The chemical reactivity of sulphate and calcium ions present in the smartwater brines increases with increasing temperature, which results in a significant increase in the ultimate oil mobilization from heterogeneous pore systems. Increased ion reactivity was observed with increasing temperature during the surface reactivity tests performed with the PS brine DW-PS (Fig. 12), clearly indicating that temperature will influence the recovery potential for PS brines. These results are in-line with previous reported findings (Strand et al. 2006a). Higher oil recovery at higher temperature can also be connected to the surface reactivity shown in Fig. 12. The surface reactivity tests showed that the sulphate from the PS salts reacted with the carbonate minerals, and that this process was increased at higher temperatures. Thus, the oil recovery was higher at 110°C. The ultimate oil recovery results shown in the SI tests at 90 and 110°C (Figs. 13 and 14) are systemized in Table 7.

Imbibition Fluid	OOIP % T = 90°C	$\Delta$ OOIP % Relative to FW T = 90°C	OOIP % T = 110°C	$\Delta$ OOIP % Relative to FW T = 110°C
FW	22	-	31	-
SW	37	15	50	19
DW-PS	35	13	48	17
SW-PS	45	23	54	23

Table 7—Summary of oil recovery.

Significant higher oil mobilization was observed at 110°C for brines capable of inducing wettability alteration, i.e., SW, DW-PS, and SW-PS. For SW the  $\Delta$ OOIP % relative to FW increased from 15% OOIP at 90°C to 19 %OOIP at 110°C, and for DW-PS  $\Delta$ OOIP % increased from 13 %OOIP at 90°C to 17 %OOIP at 110°C (Table 7). For SW-PS, the  $\Delta$ OOIP % of 23 %OOIP at 90°C did not increase when the temperature increased to 110°C, most likely due to  $\text{CaSO}_4$  precipitation, which will reduce the effective concentration of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  needed for the wettability alteration.

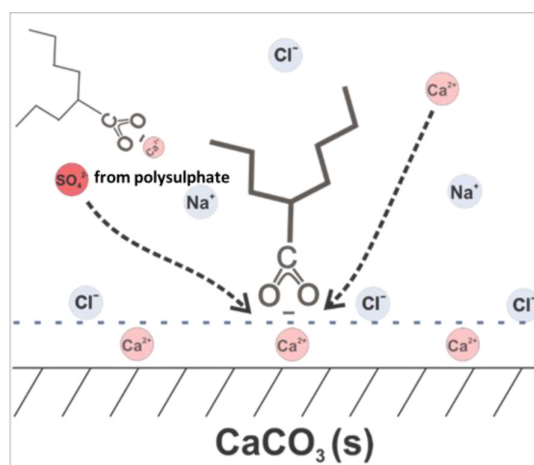
**Is PS an Alternative Additive for Smartwater Preparation?** From the experimental results at 90 and 110°C, it is possible to conclude that the brines prepared with the PS salt are validated as wettability modifiers; and hence, that PS salt could be used to produce smartwater giving significant EOR effects.

The mechanistic understanding of how PS contributes to the smartwater EOR mechanism for carbonates is believed to agree with the previously proposed mechanism by Zhang et al. (2007). Here, the adsorption of  $\text{SO}_4^{2-}$  ions, now provided by the PS salts, on the rock surface will reduce the positive surface charge facilitating a coadsorption of  $\text{Ca}^{2+}$ , which is a common ion to  $\text{CaCO}_3$ . Then, a reaction between  $\text{Ca}^{2+}$  and the adsorbed acidic components on the surface, which are largely represented by dissociated carboxylic acids ( $\text{RCOO}^-$ ), takes place, triggering the desorption of the organic molecule, in turn changing the wettability as illustrated in Fig. 15.

It is important to point out that also temperature will influence this process.  $\text{Mg}^{2+}$  ions at high temperature become more reactive due to dehydration. Experiments have confirmed that  $\text{Mg}^{2+}$  can interact with the calcite surfaces and release more  $\text{Ca}^{2+}$  ions into the surrounding environment, speeding up the process of wettability alteration (Zhang et al. 2007). The influence of  $\text{Mg}^{2+}$  ions on the wettability alteration process at high temperature was observed in Fig. 3. At high temperatures, the  $\text{Mg}^{2+}$  ions will complex with  $\text{SO}_4^{2-}$  ions reducing or preventing anhydrite ( $\text{CaSO}_4$ ) precipitation, which will lower the active concentration of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  ions that are needed in the wettability alteration process.

Injection brines containing PS outperformed FW as injection brine. At 90°C, the oil mobilization was improved by 61% with DW-PS and by 105% with SW-PS. Furthermore, no salt precipitation or scaling was observed in the injection or production lines during the SI tests at 90°C. Thus, the best performing brine in this set of experiments was the SW-PS brine. At 110°C, the increment in oil mobilization





**Fig. 15—A modified schematic illustration of the smartwater wettability alteration mechanism in carbonates involving PS salts. The active ions are  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$ . After Zhang et al. (2007).**

relative to FW was 57% for DW-PS and 74% for SW-PS. Increased temperature and high concentration of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  in the injection brines could result in  $\text{CaSO}_4$  precipitation, as observed in the injection line after 23 days for core SK8. Referring to the composition of SW-PS, it is only  $\text{CaSO}_4$  that can precipitate at higher temperature.  $\text{CaSO}_4$  precipitation is the most common precipitation problem in the oil industry and is a function of temperature and salinity (Carlberg 1973). Puntervold et al. (2009) showed  $\text{CaSO}_4$  precipitates at higher temperature using simulation and experiments.  $\text{CaSO}_4$  precipitation could explain the similar performance of SW-PS at 110 and 90°C.

The potential to use PS as an additive exists, and yes, it can be an implementable EOR alternative. If PS should be used as a smartwater additive for a given carbonate reservoir system, the amount of PS added needs to be optimized based on reservoir temperature, bottomhole temperature in injection wells, and the ion composition of the makeup water.

It is important to note that the oil recovery observed with DW-PS was very similar to that observed with SW. This opens the possibility of using PS salt in onshore carbonate fields where access to SW as smartwater is limited. The results with SW-PS showed that increased sulphate and calcium concentrations can lead to higher recoveries. Thus, it would be important to maximize the ion content, while at the same time staying below their  $\text{CaCO}_4$  precipitation threshold. Field implementation will require laboratory testing to identify those precipitation thresholds for specific brines prepared with different water sources.

Another benefit of using the PS salt is linked to improvement of current water management strategies. For example, PS salts can be applied to minimize the use of expensive filtration systems, i.e., reverse osmosis or nanofiltration when specific water compositions are required. In case of field operation, most injection waters are pretreated for solid removal before injection. Typically, sand filter, membrane filter, or gravity separation is used for solid removal depending on space and weight limitations of the platform, especially offshore. These filtering processes are cheap and already installed on the platform, thus no extra capital expenditure should be expected related to the treatment of PS brines.

## Conclusion

A study for evaluating the potential of PS brines as a new additive for smartwater processes in carbonates has been carried out. The study combined chemical characterization and wettability studies by chromatographic and SI tests. The rock material used was SK outcrop chalk, which is commonly used for parametric studies and wettability studies in carbonates. SI tests were performed at 90 and 110°C, using FW, SW, DW-PS, and SW-PS as imbibing brines, with the latter two containing the PS salt. The conclusions derived from this work are presented below.

- The chromatographic wettability tests suggested that there was potential for wettability alteration by using a PS-based brine.
- The chromatographic separation area increased from 0.18 to 0.35 by increasing the temperature from 25 to 90°C, confirming an increased reactivity of sulphate as the temperature was elevated.
- The PS salt was easily dissolved in SW and DW. The solubility of the PS salt in different brines appeared to be rather high, with more than a 95% of the salts used being fully dissolved at a concentration of 5 g/L.
- During the SI tests, FW recovered 22 and 31 %OOIP at 90 and 110°C, respectively. These results set the lowest oil production baseline since no wettability alteration was induced in these tests.
- Wettability alteration was confirmed by using DW-PS and SW-PS as they recovered more oil than that observed with FW. At 90°C, the improvement in oil production with DW-PS was 61% and for SW-PS 105% relative to FW. At 110°C, the incremental oil for DW-PS in relation to FW was 57%, and for SW-PS it was 74%.
- Precipitation was observed at 110°C with the SW-PS brine, occurring in the inlet line of the SI cell. However, the ultimate oil recovery with SW-PS brine was the highest observed, 54 %OOIP.
- The performance of DW-PS at both 110 and 90°C was very similar to that observed with SW, providing an opportunity to obtain an injection brine with wettability alteration efficiency similar to SW for onshore fields where there is limited or restricted access to SW.

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