

SULFATE IN ROCK SAMPLES FROM CARBONATE RESERVOIRS

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ABSTRACT

Sulfate has earlier been reported to alter the wettability of both outcrop and reservoir chalk rocks to more water-wet and improve the oil recovery by increasing the spontaneous imbibition of water.

In the reported study, trim off rock samples from two different oil chalk reservoirs have been analysed for sulfate and elements. Water has also been injected to core plugs from the same chalk reservoirs to determine the concentration of easily accessible sulfate. The sulfate concentrations in the reservoir chinks are compared with the sulfate concentrations in outcrop chinks used as analogous rocks.

Many of the trim off samples from the two chalk fields were found to contain rather high sulfate concentrations. The concentrations of easily accessible sulfate were also determined to be rather high in reservoir core plugs from the two chalk fields. Both in trim off samples and core plugs from the two chalk reservoirs the sulfate concentrations were found to be higher than the sulfate concentrations reported to affect the wettability of chinks.

Since rather high sulfate concentrations have been found in the reservoir chalk rocks, it is recommended to modify the procedures for preparation of reservoir core plugs to establish correct wettability. The core plug preparation procedures should depend on whether the core plugs are contaminated with sulfate or the sulfate is present in the original reservoir rock.

INTRODUCTION

Processes to alter the wettability of fractured carbonate reservoirs to more water-wet and thereby increase the spontaneous imbibition of water have been studied for many years. Methods for wettability alteration of outcrop chinks by changing the composition of the injected water (Strand et al., 2003; Zhang and Austad, 2005; Strand et al., 2006; Tweheyo et al., 2006; Zhang and Austad, 2006; Zhang et al., 2006; Puntervold and Austad, 2007; Zhang and Austad, 2007; Zhang et al., 2007; Yu et al., 2008a; Yu et al., 2008b; Yu et al., 2008c) and by addition of chemicals (e.g. cationic surfactants) (Milter and Austad, 1996; Austad and Milter, 1997; Austad et al., 1998; Standnes and Austad, 2000; Standnes and Austad, 2003; Høgnesen et al., 2004) have been developed. Based on laboratory experiments using Stevns Klint outcrop, potential determining ions, e.g. Ca^{2+} , Mg^{2+} and

SO_4^{2-} , have been reported to be important for the wettability alteration during injection of seawater (Punternold and Austad, 2007). These ions were reported to displace strongly adsorbed carboxylic compounds from chalk surfaces at high temperatures (>90-100°C). Interactions between cationic surfactants and carboxylates have also been reported to alter the wettability of outcrop chalks to more water-wet (Standnes and Austad, 2003). Most of the reported work has been carried out using outcrop chalk rocks as analogous rock to the reservoir rocks. Sulfate has also been reported to alter the wettability of Valhall rock in core experiments (Webb et al., 2005). Stevns Klint chalk outcrop has been reported to contain sulfate concentrations in the range 0.04-0.05 mg/g (Punternold et al., 2007). These concentrations were reported to affect the spontaneous imbibition of water and wettability.

In the work presented in this paper the sulfate concentrations were first determined in trim off samples from two chalk fields, Chalk field A and Chalk field B. The sulfate concentrations were also determined in reservoir core plugs cleaned by toluene and methanol. The concentrations of easily accessible sulfate were determined by injecting water to core plugs followed by analysing the effluents for sulfate. The sulfate concentrations in outcrop chalks used as analogous chalks to the reservoir chalks, were also determined.

EXPERIMENTAL

Artificial Brines

The compositions of artificial formation waters used in the experiments are given in Table 1.

Table 1

Compositions of artificial formation waters

Salt	Chalk field A (FWA) [g/l]	Chalk field B (FWB) [g/l]
NaCl	36.81	57.61
NaHCO ₃	-----	0.78
KCl	0.31	0.40
MgCl ₂ ·6H ₂ O	4.48	1.58
CaCl ₂ ·2H ₂ O	33.25	4.26

Rock Samples

Stevns Klint and Liege chalk outcrops were used as analogous rock to the two reservoir chalk rocks. Liege chalk from Belgium is rather pure and contains only minor amounts of clay and less than 2w% silica (Strand et al, 2007). The permeability is low (2-3mD) and the porosity is high (approx. 40%) for this outcrop chalk. Stevns Klint chalk from a quarry nearby Copenhagen (Denmark) has also a high porosity (45-50%) and low permeability (2-5mD) (Frykman, 2001; Røgen and Fabricius, 2002).

Trim off samples and core plugs from the Chalk field A and Chalk field B were analysed.

Analytical Methods

Sulfate analyses were carried out by measuring the turbidity after addition of BaCl_2 to diluted sulfate samples. A sulfate cell test kit (Spectroquant 1.14548.001) based on the ASTM D516-07 method was used. In most cases an external standard method was used, but in some cases a standard addition method was used to confirm that the sample matrix did not affect the results.

Elements in water samples were determined using Inductive Coupled Plasma (ICP).

Crushed Trim Off Samples

Trim off samples from the chalk fields and outcrop chinks were crushed in a mortar. The crushed rock (5g) was mixed with different types of water (30ml). The water was distilled water, 3M HCl (in distilled water) or artificial formation water. An ultrasonic bath was used to mix the crushed rock and water for 45 minutes. The solutions were then filtered through a syringe filter. The sulfate and element concentrations in the water filtrates were then determined.

Crushed Core Plugs

Core plugs from Chalk field A were first cleaned by toluene and methanol. Some core plugs were then crushed and mixed with distilled water or 3 M HCl (in distilled water). The samples were further prepared as for trim off samples. A core plug from Chalk field B was dried to constant weight, before slices of the plug was crushed and further analysed as the trim off samples.

Easily Accessible Sulfate

Core plugs from the chalk fields were cleaned by toluene and methanol. After drying of the core plugs to constant weight, artificial formation water were injected to the core plugs to determine the amount of easily accessible sulfate. The water was injected until sulfate was not detected in the effluent by the Spectroquant method (ASTM D516-07). The effluent samples were analysed for sulfate using the same analytical method and for element using ICP. The concentration of easily accessible sulfate was determined by summarizing the amount of sulfate produced in the effluent samples.

RESULTS**Crushed Rock**Outcrop Chinks

The concentrations of sulfate found in Stevns Klint and Liege outcrop samples are given in Table 2. In samples prepared by distilled water the sulfate concentrations in Liege chalk and Stevns Klint chalk was found to be similar, 0.03 mg/g. Puntervold et al. (2007b) reported slightly higher sulfate concentrations in Stevns Klint core plugs flooded by distilled water, 0.04-0.05 mg/g. For Liege rock the sulfate concentrations in samples prepared by distilled water and 3M HCl were similar. The sulfate concentrations in Stevns Klint samples were by the Spectroquant method found to be higher in samples prepared by HCl than in samples prepared by distilled water. This indicated that some of the sulfate is not easily accessible by mixing with distilled water. One Stevns Klint sample was also analysed for some elements. By assuming that all sulfur in the samples came from sulfate, higher sulfate concentrations

were estimated than determined by the Spectroquant method. This may be due to presence of sulfides in the Stevns Klint samples.

Table 2

Sulfate and elements in crushed outcrop chalk samples and crushed trim off samples from chalk fields.

Rock	Sample id.	Type	Mixing water*	Concentrations [mg/g rock]							
				SO ₄ ²⁻ **	Al	Ba	Fe	S	Sr	SO ₄ ²⁻ based on S***	
Liege	L1	Dry rock	DW	0.03							
	L2	Dry rock	FWA	0.01							
	L3	Dry rock	HCl	0.03							
Stevens Klint	SK1	Dry rock	DW	0.03	0.000	0.000	0.000	0.013	0.007	0.04	
	SK2	Dry rock	HCl	0.16	0.000	0.009	0.001	0.101	0.914	0.30	
Chalk field A	A1	Trim off	DW	0.39							
			FWA	0.40							
			HCl	0.35 (0.48)							
	A2	Trim off	HCl	0.28 (0.39)							
			A3	Trim off	DW	0.61					
					FWA	0.66					
	A4	Trim off	HCl	0.64							
			DW	0.59	0.000	0.001	0.000	0.192	0.013	0.58	
			HCl	0.67	0.002	0.029	0.083	0.254	1.245	0.76	
Chalk field B	B1	Trim off	DW	0.01	0.000	0.001	0.000	0.012	0.002	0.04	
			DW, dried	0.05							
			HCl	0.01	0.005	0.030	0.232	0.048	0.309	0.14	
	B2	Trim off	DW	0.02	0.000	0.010	0.001	0.012	0.007	0.04	
			DW, dried	0.02							
			HCl	0.06	0.003	0.053	0.529	0.072	0.337	0.22	
	B3	Trim off	HCl, dried	0.22							
			DW	0.47	0.000	0.001	0.001	0.185	0.020	0.55	
			HCl	0.58	0.002	0.044	0.996	0.256	0.493	0.77	

* DW=distilled water, FWA=formation water Chalk field A, HCl=3 M HCl in distilled water

** Spectroquant 1.14548.001 (ASTM D516-07).

External standard method, except results in parentheses by standard addition method

*** SO₄²⁻ estimated assuming all sulfur from sulfate

Reservoir Trim Offs

Trim off samples from Chalk field A were first analysed to confirm that sulfate was not present in the reservoir rock samples. It was therefore a surprise when rather high sulfate concentrations were found in the Chalk field A rock samples, up to 0.67mg/g rock using the Spectroquant method. All these samples were taken from one well. See Table 2. The sulfate concentrations found in the reservoir rock samples are high enough to affect the wettability of outcrop chalks. One sample from Chalk field A was also analysed for elements. By

assuming that also sulfur came from sulfate, the sulfate concentration was estimated to be in the same range as determined by Spectroquant method.

Trim off samples from three different wells were analysed for Chalk field B. Sulfate concentrations up to 0.58mg/g rock were found. In one of the wells, B1, the sulfate concentration was found to be up to 0.05mg/g rock using the Spectroquant method. Dried samples were found to give higher values than the wet samples. This may be due to easier mixing of the crushed dried rock and water solutions. For outcrop chalk, sulfate concentrations of 0.05mg/g rock have been reported to be high enough to affect wettability. For the second well, B2, even higher sulfate concentrations were found, up to 0.22mg/g rock. The sulfate concentrations in the third well (B3) were found to be in the same range as found in the samples from Chalk field A. Some of the samples were also analysed for elements. By assuming that all sulfur came from sulfate, the sulfate concentrations were estimated to be higher than the sulfate concentrations determined using the Spectroquant method. This may be because sulfide minerals are also present in this chalk.

Reservoir Core Plugs

A core plug from Chalk field A was after cleaning with toluene and methanol, dried and analysed in the same way as trim off samples. The sulfate concentration was found to be rather high in this sample. See Table 3. This means that sulfate was not removed during cleaning with toluene and methanol.

A kerosene preserved core plug from Chalk field B was after drying found to contain rather high sulfate concentration, up to 0.35mg/g rock. See Table 3. These samples were taken from within the core to make sure that it was not contaminated by the drilling fluid. When it was assumed that all sulfur came from sulfate, the sulfate concentration was also for this core plug estimated to be higher than the determined by the Spectroquant method. The sulfate concentration was found to be constant across the core plug.

Table 3

Concentrations of sulfate and elements in crushed reservoir chalk plugs.

Chalk field	Sample id.*	Type	Mixing water*	Concentrations [mg/g rock]						
				SO ₄ ²⁻ **	Al	Ba	Fe	S	Sr	SO ₄ ²⁻ based on S***
A	AC1	Solvent cleaned core plug	DW	0.24	0.001	0.002	0.000	0.080	0.010	0.24
			HCl	0.02****	0.012	0.034	0.220	0.142	1.593	0.42
B	BC1	Dried core plug	HCl	0.25	0.053	0.077	1.154	0.203	0.838	0.61
			HCl	0.35	0.138	0.094	1.219	0.240	0.868	0.72

* DW=distilled water, HCl=3 M HCl in distilled water

** Spectroquant 1.14548.001 (ASTM D516-07).

*** SO₄²⁻ estimated assuming all sulfur from sulfate

**** Probably too low result because pH too low in the analysis

Easily Accessible Sulfate

Formation water was injected to reservoir core plugs, and the effluents were analysed for sulfate and elements. Six core plugs from Chalk field A were first cleaned by toluene and methanol before they were dried and artificial formation water was injected. By using the Spectroquant method the sulfate production profiles shown in Figure 1 were determined. After injection of 6 pore volumes, the sulfate concentrations in the effluents were less than the detection limit for the Spectroquant method for all core plugs. The concentrations of easily accessible sulfate were by the same analytical method determined to be in the range 0.38-0.78mg/g rock. See Table 4. This is in the same range as in trim off samples from the same field, 0.28-0.67mg/g rock. By assuming that all sulfur came from sulfate, it was estimated that the concentration of easily accessible sulfate were in the range 0.35-0.62mg/g rock. See Table 4. This is slightly lower than determined by the Spectroquant method, but only samples from the three first pore volumes were analysed by ICP.

Table 4

Concentrations of easily accessible sulfate and elements in core plugs from Chalk field A determined by analysing effluents during injection of artificial formation water. The elements concentrations were determined using samples only from the three first produced pore volumes.

Core plug no.	Absolute permeability brine [mD]	Porosity [%]	Concentrations [mg/g rock]						
			SO ₄ ²⁻ *	Al	Ba	Fe	S	Sr	SO ₄ ²⁻ based on S**
1	3.9	29.2	0.48	0.000	0.001	0.000	0.150	0.008	0.46
2	3.2	34.3	0.39	0.000	0.003	0.000	0.164	0.015	0.49
3	1.4	28.0	0.78	0.000	0.000	0.000	0.205	0.013	0.62
4	2.3	29.0	0.38	0.000	0.011	0.000	0.116	0.012	0.35
5	1.4	28.1	0.43	0.000	0.001	0.000	0.127	0.013	0.38
6	1.6	28.5	0.44	0.000	0.001	0.000	0.135	0.012	0.40

* Spectroquant 1.14548.001 (ASTM D516-07).

** SO₄²⁻ estimated assuming all sulfur from sulfate

From Chalk field B five core plugs from the same well as the trim off sample B3 and the crushed core plug sample BC1, were analysed for easily accessible sulfate. During injection of artificial formation water, the sulfate effluent profiles in Figure 2 were determined using Spectroquant method. It was necessary to inject up to 12 pore volumes water to remove all easily accessible sulfate from these core plugs. The concentrations of easily accessible sulfate were determined to be in the range 0.10-0.20mg/g. See Table 5. In trim off samples from the same well, sulfate concentrations up to 0.58mg/g rock were found. If it is assumed that all sulfur came from sulfate, the sulfate concentrations were estimated to be in the range 0.13-0.31 mg/g. See Table 5. As for the crushed samples, these concentrations are higher than determined by the direct sulfate methods, the Spectroquant method.

The concentrations of easily accessible sulfate in core plugs from Chalk field B were found to be lower than in core plugs from Chalk field A. The sulfate concentrations are for both fields higher than the sulfate concentrations required to alter the wettability of outcrop chalk.

Table 5

Concentrations of easily accessible sulfate and elements in core plugs from Chalk field B determined by analysing effluents during injection of artificial formation water. The elements concentrations were determined using samples only from the three first produced pore volumes.

Core plug no.	Absolute permeability brine [mD]	Porosity [%]	Concentrations [mg/g rock]						
			SO ₄ ²⁻ *	Al	Ba	Fe	S	Sr	SO ₄ ²⁻ based on S**
1	3.5	40.8	0.16	0.003	0.003	0.007	0.103	0.011	0.31
2	0.7	39.0	0.11	0.000	0.002	0.000	0.043	0.007	0.13
3	1.1	37.9	0.14	0.000	0.002	0.000	0.060	0.011	0.18
4	1.2	38.6	0.20	0.000	0.003	0.000	0.075	0.012	0.23
5	1.1	38.9	0.10	0.000	0.000	0.000	0.049	0.009	0.15

* Spectroquant 1.14548.001 (ASTM D516-07).

** SO₄²⁻ estimated assuming all sulfur from sulfate

DISCUSSION

The results from determination of sulfate concentrations using the direct sulfate method, Spectroquant method, were found to vary depending on details in the preparation of the samples. The sulfate concentrations determined by assuming that all sulfur came from sulfate, confirmed that sulfate concentrations high enough to affect the wettability were present in the rock samples. Samples from the two chalk fields were taken from wells that were not water flooded with sea water when the wells were cored. The core plugs from these fields were not contaminated during preparation of core plugs. Mud invasion was visually not observed in the core plugs.

Aluminium sulfate was added to the emulsified drilling fluid used in the drilling of the well in Chalk field A. The mole ratio aluminium/sulfate was found to be very low in the rock samples and indicated that invasion of the water phase from the mud has not occurred. Most of the water droplets in emulsified drilling fluids, usually called oil based mud, are larger than 1.0 µm. This is in the same range as the average pore throat sizes in chalk rocks. The risk for invasion of water droplets is therefore low. The risk for invasion of the mud filtrate, the organic phase in oil based mud, is higher, but sulfate is not soluble in the organic phase.

Sulfur containing minerals are found in reservoirs, both sulfides (e.g. pyrite) and sulfates (e.g. gypsum and anhydrite) (Bjørlykke, 1989). The sulfur and sulfate concentrations found in the analyses of samples from Chalk field A and B were rather low. Mineral concentrations in ppm range can not be determined by standard methods. In rock samples from Chalk field A, traces of pyrite were detected by scanning electron microscopy.

Carbonated-associated sulfate (CAS) has been found at ppm levels in many modern and ancient limestones and dolostones (Lyons et al., 2005; Hurtgen et al., 2002). Sulfate substitutes for the carbonate ion in natural and synthetic carbonates (Hurtgen et al., 2002). The amount of sulfate incorporated into calcite is proportional to the log of sulfate concentration in solution and the log rate of crystal growth which can depend on carbonate concentration. The faster crystal precipitation of carbonate and the more sulfate available for carbonate ion substitution, the more sulfate is substituted into the calcite (Hurtgen et al., 2002). Sulfate was present in the marine sedimentation in the North Sea, and it is likely that sulfate has to some degree substituted carbonate during precipitations/crystal growth.

The chalk reservoirs in the North Sea are composed of the skeletal debris of pelagic unicellular algae known as coccolithophorides (Sulak, 1991). Coccospheeres, the calcareous exoskeletons of these algae, are composed of coccoliths, which are composed of coccolith platelets. Coccospheeres can be seen in SEM-images of chalk rocks from the North Sea. The composition of the coccospheeres has probably not changed since the sedimentation. If sulfate was present in the coccospheeres at sedimentation, sulfate is most likely also present in the coccoliths found today. A change of the composition would have damaged the coccospheeres.

Reduction of sulfate to sulfide by bacteria and by thermochemical sulfate reduction can occur (Pedersen et al., 2003). Dissolved sulfate is required for both these reductions. Solid sulfates have been found to not be reactive (Machel et al., 2001). Dissolved sulfate are expected to be more easily accessible than sulfate minerals. Since the structures of the coccoliths are maintained in the chalk rocks, sulfate has probably been preserved inside these structures.

Since sulfate was found in reservoir rock, it is necessary to modify the procedure for preparation of reservoir core plugs to establish correct wettability. If the rock samples are contaminated by sulfate, sulfate should be removed during core preparation. Otherwise too water-wet rock samples can be prepared. If sulfate is present in the original rock samples, sulfate should not be removed during preparation of core plugs. Results from core analyses/floods are used as inputs to evaluation of oil recovery potentials by reservoir simulations. Preparation of core plugs with correct wettability is therefore important to get correct potential estimates. Core plugs that are prepared for enhanced oil recovery studies, e.g. wettability alteration, should also have the correct wettability. Sulfate has also been reported to affect rock mechanic properties (Korsnes et al., 2006a and 2006b). Core plugs for rock mechanic studies should therefore also be prepared with the correct amounts of sulfate.

CONCLUSIONS

Rather high sulfate concentrations have been found in rock samples from two chalk reservoirs, both in trim off samples and core plugs.

The sulfate concentrations are higher than the level reported to give alteration of wettability to more water-wet of outcrop chalks.

The concentrations of easily accessible sulfate in core plugs were also rather high for both chalk fields.

It is necessary to modify the procedures for preparation of carbonate core plugs. The modification will depend on whether the sulfate source is a contamination or the original reservoir rock.

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REFERENCES

- Austad, T., and Milner, J. 1997. "Spontaneous imbibition of water into low permeable chalk at different wettabilities using surfactants," SPE37236, Int. Symp. Oilfield Chem., Houston, TX, USA.
- Austad, T., Matre, B., Milner, J., Sævareid, A., and Øyno, L., "Chemical flooding of oil reservoirs 8. Spontaneous oil expulsion from oil- and waterwet low permeable chalk material by imbibition of aqueous surfactant solutions," *Colloids and Surfaces A: Physicochemical and Eng. Aspects*, (1998) **137**, 117-129.
- Bjørlykke, K., *Sedimentation and Petroleum Geology*, 0-387-17691-8 Springer-Verlag New York Berlin Heidelberg, (1989), 363.
- Frykman, P., "Spatial Variability in Petrophysical Properties in Upper Maastrichtian Chalk Outcrops at Stevns Klint, Denmark," *Marine and Petroleum Geology*, (2001) **18**, 1041-1062.
- Hurtgen, M.T., Arthur, M.A., Suits, N.S., and Kaufman, A.J., "The sulphur isotopic composition of Neoproterozoic seawater sulfate: implications for a snowball earth?," *Earth and Planetary Science Letters*, (2002) **203**, 413-429.
- Høgenesen, E. J., Standnes, D. C., and Austad, T., "Scaling spontaneous imbibition of aqueous surfactant solutions into preferential oil-wet carbonates," *Energy and Fuels*, (2004), **18**, pp. 1665-1675.
- Korsnes, R.I., Strand, S., Hoff, Ø., Pedersen, T., Madland, M.V., and Austad, T., "Does the chemical interaction between seawater and chalk affect the mechanical properties of chalk?," *Eurock 2006, Multiphysics Coupling and Long Term Behaviour in Rock Mechanics*, Eds. Cottheim, A.V., Charlier, R., Thimus, J.F. and Tshibangu, J.P., Taylor & Francis, London, (2006a), 427-434.
- Korsnes, R.I., Madland, M.V., and Austad, T., "Impact of Brine Composition on the Mechanical Strength of Chalk at High Temperature," *Eurock 2006, Multiphysics Coupling and Long Term Behaviour in Rock Mechanics*, Eds. Cottheim, A.V., Charlier, R., Thimus, J.F. and Tshibangu, J.P., Taylor & Francis, London, (2006b), 133-140.
- Lyons, T.W., Hurtgen, M.T., and Gill, B.C.2005. "New insight into the utility of carbonate-associated sulfate," Goldschmidt Conf. Abstracts.

- Machel, H.G., "Bacterial and thermochemical sulfate reduction in diagenetic settings – old and new insights," *Sedimentary Geology*, (2001) **140**, 143-175.
- Milner, J., and Austad, T., "Chemical flooding of oil reservoirs 7. Oil expulsion by spontaneous imbibition of brine with and without surfactant in mixed-wet, low permeability chalk material," *Colloids and Surfaces A: Physicochemical and Eng. Aspects*, (1996) **117**, Issues 1-2, October 15, 109-115.
- Pedersen, M., Nielsen, J.K., Boyce, A.J., and Fallick, A.E., "Timing and genesis of base-metal mineralisation on black shales of the Upper Permian Ravnelfeld Formation, Wegener Halvø, East Greenland," *Mineralium Deposits*, (2003) **38**, 108-123.
- Punternvold, T., Strand, S., and Austad, T., "New method to prepare outcrop cores for wettability and oil recovery studies at low initial water saturation", *Energy Fuels*, (2007) **21** (6), 3425-3430.
- Punternvold, T., and Austad, T. 2007. "Injection of Seawater and Mixtures with Produced Water into North Sea Chalk Formation: Impact on Wettability, Scale Formation and Rock Mechanics Caused by Fluid-Rock Interaction," SPE 111237, 2007 SPE/EAGE Reservoir Characterization and Simulation Symp., Abu Dhabi, UAE.
- Røgen, B. and Fabricius, I.L., "Influence of Clay and Silica on Permeability and Capillary Entry Pressure of Chalk Reservoirs in the North Sea," *Petr. Geoscience*, (2002) **8**, 287-293.
- Standnes, D.C., and Austad, T., "Wettability alteration in carbonates interaction between cationic surfactant and carboxylates as a key factor in wettability alteration from oil-wet to water-wet conditions," *Colloids and Surfaces A: Physicochem. Eng. Aspects*, (2003) **216**, 243-259.
- Standnes, D.C., and Austad, T., "Wettability alteration in chalk. 2. Mechanism for wettability alteration from oil-wet to water-wet using surfactants," *J. Petr. Sci. Eng.*, (2000) **28**, 123-143.
- Strand, S., Hjulser, M.L., Torsvik, R., Madland, M.V., and Austad, T., "Wettability of chalk: impact of silical, clay content and mechanical properties," *Petr. Geoscience*, (2007) **13** (1), 69-80.
- Strand, S., Høgnesen, E.J., and Austad, T., "Wettability alteration of carbonates – Effects of potential determining ions (Ca^{2+} and SO_4^{2-}) and temperature," *Colloids and Surfaces A: Physicochem. Eng. Aspects*, (2006) **275**, Issues 1-3, 1-10.
- Strand, S., Standnes, D.C., and Austad, T., "Spontaneous imbibition of aqueous surfactant solutions into neutral to oil-wet carbonate cores: Effects of brine salinity and composition," *Energy & Fuels*, (2003) **17**, pp 1133-1144.
- Sulak, R.M., "Ekofisk field: The first 20 years," *JPT*, (1991) October.
- Tweheyo, M.T., Zhang, P., and Austad, T. 2006. "The Effects of Temperature and Potential Determining Ions Present in Seawater on Oil Recovery From Fractured Carbonates," SPE 99438, 2006 SPE/DOE Symp. IOR, Tulsa, Oklahoma, U.S.A..
- Webb, K.J., Black, C.J.J., and Tjetland, G. 2005. "A Laboratory Study Investigating Methods for Improved Oil Recovery in Carbonates," Paper IPTC 10506, Int. Petr. Tech. Conf., Doha, Qatar.

- Zhang, P., and Austad, T. 2005. "The Relative Effects of Acid Number and Temperature on Chalk Wettability," SPE 92999, SPE Int. Symp. Oilfield Chem., Houston, Texas, USA.
- Zhang, P. and Austad, T., "Wettability and Oil recovery from Carbonates: Effects of Temperature and Potential Determining Ions," *Colloids and Surfaces A: Physicochemical and Eng. Aspects*, (2006) **279**, Issues 1-3, 179-187.
- Zhang, P., Tweheyo, M.T., and Austad T., "Wettability Alteration and Improved Oil Recovery in Chalk: The Effect of Calcium in the Presence of Sulfate," *Energy and Fuels*, (2006) **20**, no. 5, 2056-2062.
- Zhang, P., Tweheyo, M.T., and Austad, T., "Wettability alteration and improved oil recovery by seawater injection in chalk: Impact of divalent cations (Ca^{2+} and Mg^{2+})," *Colloids and Surfaces A: Physicochemical and Eng. Aspects*, (2007) **301**(1), 199-208.
- Yu, L., Evje, S., Fjelde, I., Kleppe, H., Kårstad, T., and Skjæveland, S. M., "Modeling of wettability alteration processes in carbonate oil reservoirs," *Network and Heterogeneous Media*, (2008a) **3**(1): 149-189.
- Yu, L., Evje, S., Fjelde, I., Kleppe, H., Kårstad, T., and Skjæveland, S. M. 2008b "Analysis of the wettability alteration process during seawater imbibition into preferentially oil-wet chalk cores," SPE 113304, 2008 SPE IOR Symp., Tulsa, Oklahoma, USA.
- Yu, L., Evje, S., Fjelde, I., and Skjæveland, S. M. 2008c. "Wettability alteration by spontaneous imbibition of sulphate containing water onto chalk core with different boundary conditions," SCA2008-A14, *Int. Symp. SCA, Abu Dhabi, UAE*.

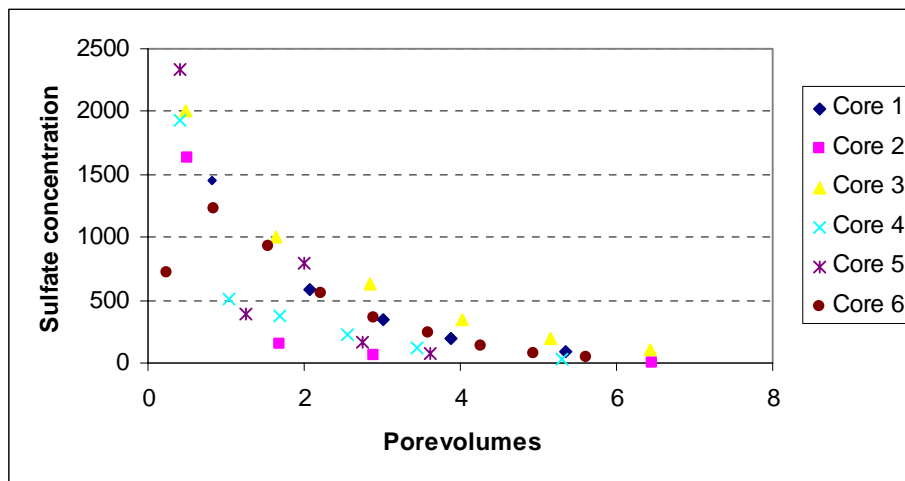


Figure 1

Sulfate effluent profiles when artificial formation water was injected to toluene/methanol cleaned core plugs from Chalk field A.

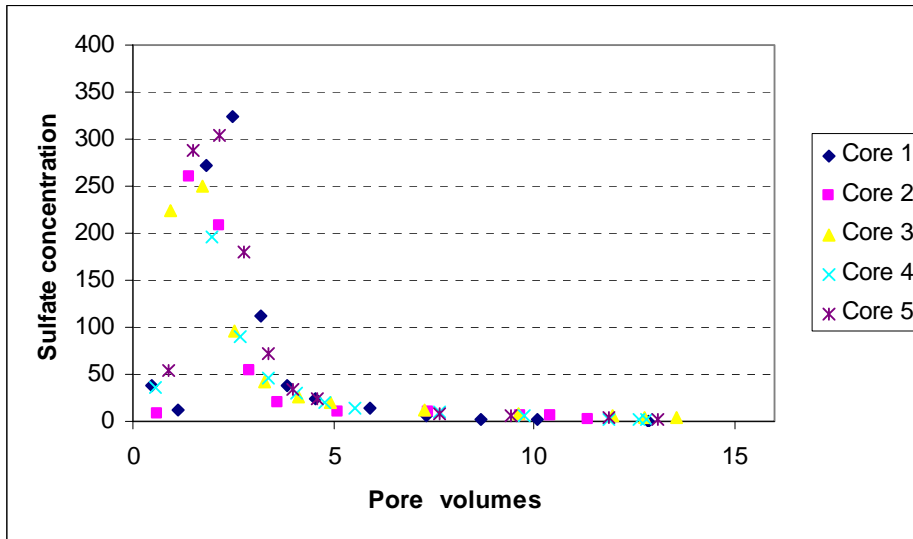


Figure 2

Sulfate effluent profiles when artificial formation water was injected to toluene/methanol cleaned core plugs from Chalk field B.