

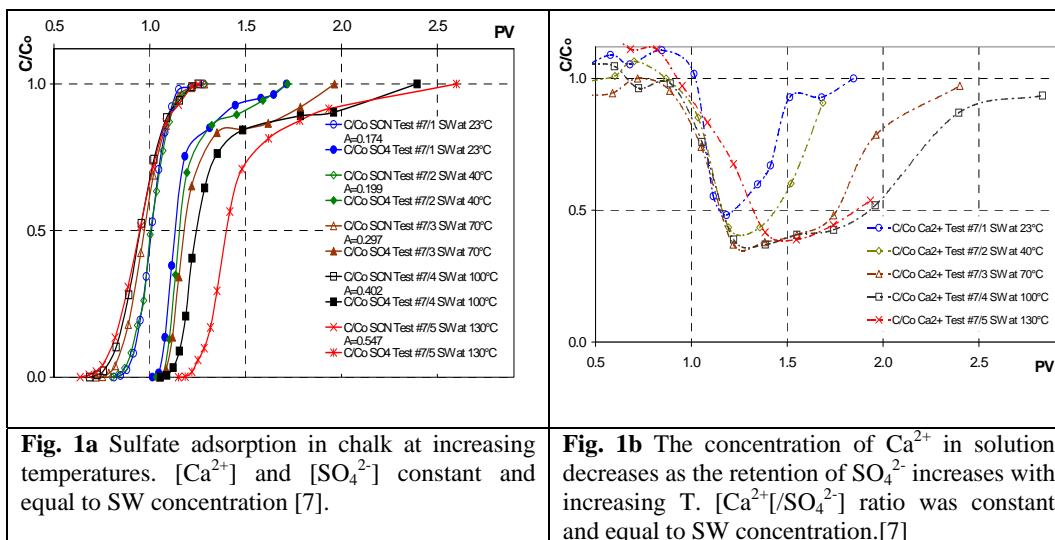
## IS WETTABILITY ALTERATION OF CARBONATES BY SEAWATER CAUSED BY ROCK DISSOLUTION?

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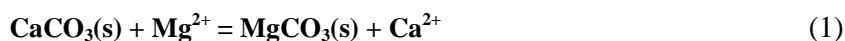
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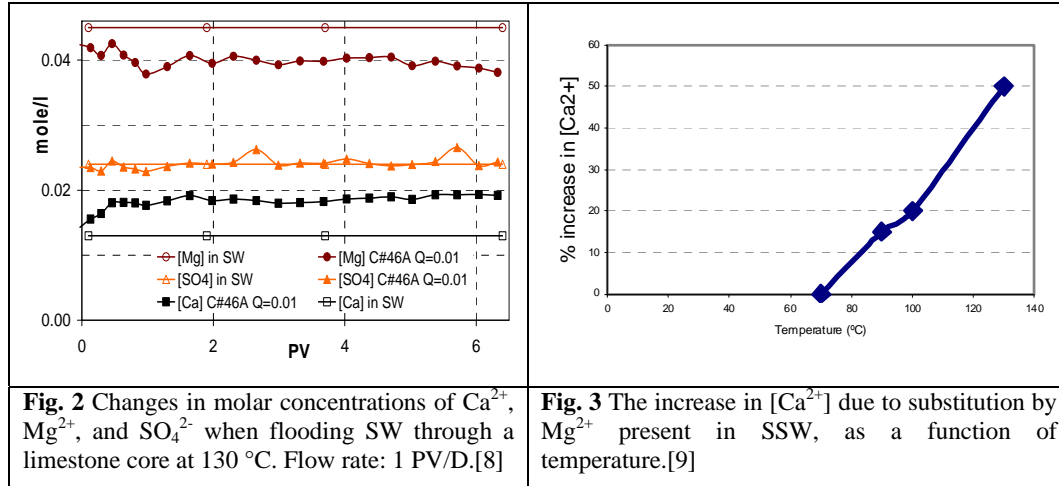
### INTRODUCTION

In a series of studies, Austad and co-workers [1-5] have documented that seawater at high temperatures is able to modify the wetting conditions of chalk towards more water-wet conditions, and in that way seawater can act as a “Smart” EOR fluid. Through systematic experimental studies, it was verified that  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{SO}_4^{2-}$  were the active ions in the wettability alteration process. Studies by BP at complete reservoir conditions for the Valhall field have confirmed the results [6]. It was documented by Zeta potential measurements that these ions acted as potential determining ions towards chalk, i.e. they were able to adsorb onto the chalk surface and modify the surface charge. The mutual interaction between  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$  at various temperatures is clearly illustrated by **Fig. 1a and b**. Thus, as long as both anionic and cationic potential determining ions are present in solution, the Zeta potential will not change very much as the temperature is increased, but the reactivity of the actual ions increases [7].

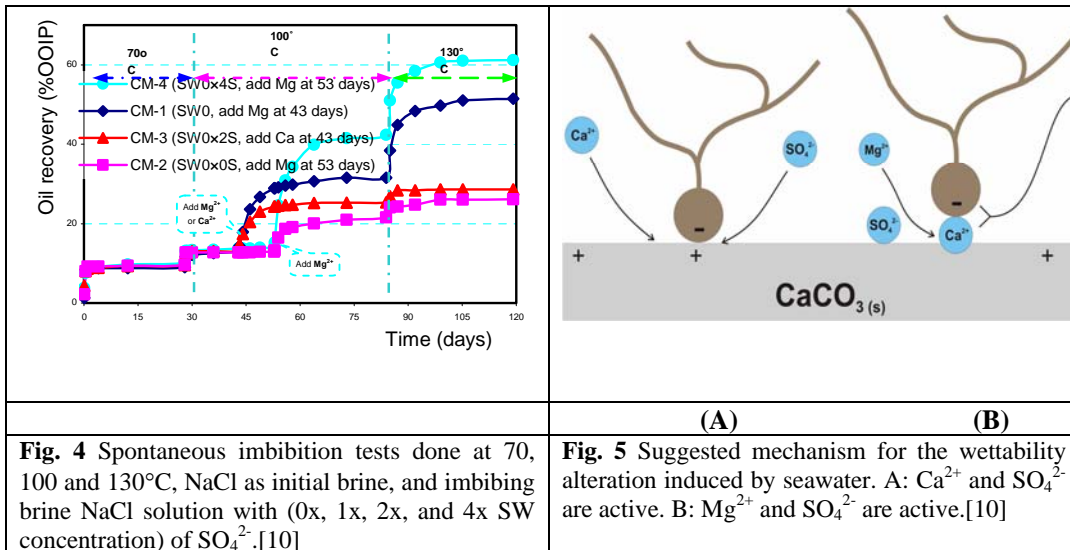


At high temperature,  $\text{Mg}^{2+}$  became much more reactive and even displaced  $\text{Ca}^{2+}$  from the chalk surface lattice. At 130 °C, the decrease in  $[\text{Mg}^{2+}]$  was equal to the increase in  $[\text{Ca}^{2+}]$  by flooding SW slowly (1 PV/D) through a carbonate core, **Fig. 2** [8]. The increase in  $[\text{Ca}^{2+}]$  of SW appeared to correlate linearly with the temperature, **Fig. 3**. No change in surface charge is taking place by this substitution reaction as illustrated by Eq. 1.

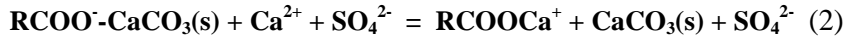




A summary of the impact of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$  and T on the oil recovery from chalk of low water wetness in a spontaneous imbibition process is illustrated by **Fig. 4**. Four chalk cores were prepared using a crude oil with high acid number (AN=2.07 mgKOH/g) and a NaCl brine similar to SW salinity as initial brine [10]. After aging at 90 °C in crude oil for 4 weeks, the cores were imbibed with NaCl brine containing different amounts of  $\text{SO}_4^{2-}$ , (0x, 1x, 2x, and 4x the SW concentration of  $\text{SO}_4^{2-}$ ). No significant increase in oil recovery was detected, neither at 70 °C nor 100 °C, **Fig. 4**.



Thus,  $\text{SO}_4^{2-}$  in the presence of NaCl is not able to change the wettability to improve spontaneous imbibition. If, however, either  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  were present together with  $\text{SO}_4^{2-}$ , improved spontaneous imbibition was observed. A chemical mechanism for wettability alteration, which is in line with experimental observations, was suggested as illustrated in **Fig. 5** [10]. In the case of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  as the wettability modifiers,  $\text{SO}_4^{2-}$  will adsorb onto the positively charged chalk surface, and the positive surface charge is decreased. More  $\text{Ca}^{2+}$  can then be attracted to the surface due to less electrostatic repulsion, **Fig. 1a and b**, and  $\text{Ca}^{2+}$  can react with carboxylic material and displace it from the surface as illustrated by the following reaction:



Thus, the role of  $\text{SO}_4^{2-}$  in this reaction is to act as a catalyst to increase the concentration of  $\text{Ca}^{2+}$  close to the surface. In the case of  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  as the wettability modifiers, we suggest that  $\text{Mg}^{2+}$  is able to displace the  $\text{Ca}^{2+}$  ion, which is connected to the carboxylic group, as well as  $\text{Mg}^{2+}$  is able to displace other  $\text{Ca}^{2+}$  ions from the surface lattice of the chalk. Also this reaction is catalyzed by  $\text{SO}_4^{2-}$ , which is clearly demonstrated by the very small increase in oil recovery for the imbibition test without added sulfate, see **Fig. 4**. This displacement is illustrated by the following reaction:



Recently, two papers were presented by Hiorth et al. at the biannual Wettability Symposium [11] and at the annual SCA Symposium in Abu Dhabi, U.A.E. [12]. In both papers, the authors discussed the impact of ions in solution on the surface charge of chalk. They also discussed the mechanism for wettability alteration of chalk, when seawater was imbibed spontaneously into oil-containing chalk cores of low water-wetness. The discussion was mostly based on chemical modeling of experimental data from Austad and co-workers [1-5], by using a geochemical thermodynamic model. The modeling performed on surface charge properties was in good agreement with previous experimental observations. In addition, geochemical equilibrium modeling was performed to calculate the transformation of chalk into other types of minerals, which the authors termed “dissolution” of chalk. It was argued that “dissolution” of chalk is a possible chemical mechanism for wettability modification of chalk because modeling appeared to show a correlation between dissolved chalk and oil recovery. No experimental documentation of the suggested “dissolution” model was presented, and the conclusions were only based on the chemical modeling.

The objective of this paper is to evaluate published experimental results, to see if a “dissolution” model of the wettability modification mechanism can be supported experimentally.

## DISCUSSION

### Can a thermodynamic model be used to model a kinetic wettability alteration process?

Hiorth et al. have used a thermodynamic geochemical model in their equilibrium calculations on the carbonate–brine systems. To use such a model, the chemical system, chalk and SW, must be at complete geochemical equilibrium. According to Hiorth et al., the model contains a lot of calcium-bearing minerals, e.g. 3 different types of dolomite, huntite, brucite, magnesite, anhydrite, and calcite. Calculations showed that when SW is contacted by chalk at high temperature, 130 °C, a lot of minerals will be supersaturated and also precipitated [12].

In a spontaneous imbibition process into an oil-wet chalk core by wettability modification, the rate of wettability modification must be reflected by the imbibition rate. In order to create positive capillary forces, the wettability alteration must take place at the imbibition front. Depending on the conditions, especially temperature, the time to reach oil production plateau in lab experiments is typically 15 to 30 days. According to a literature study of the formation of dolomite [13], it was concluded that dolomite has never been detected in lab experiments by mixing  $\text{CaCO}_3(\text{s})$  with  $\text{MgCl}_2(\text{aq})$  in this actual temperature range (70-130 °C). It was said that the reaction is probably too slow in order to identify any dolomite, even with very advanced analytical

techniques. In fact, at low temperature, it has been observed that dolomite is transformed into  $\text{CaCO}_3(\text{s})$  in the presence of  $\text{CaCl}_2(\text{aq})$ , which is opposite to the formation of dolomite. Thus, the use of a geochemical model, which includes all the listed minerals, to calculate a chemical equilibrium between  $\text{CaCO}_3(\text{s})$  and SW during a few days of spontaneous imbibition in the actual temperature range of 70-130 °C, is questionable.

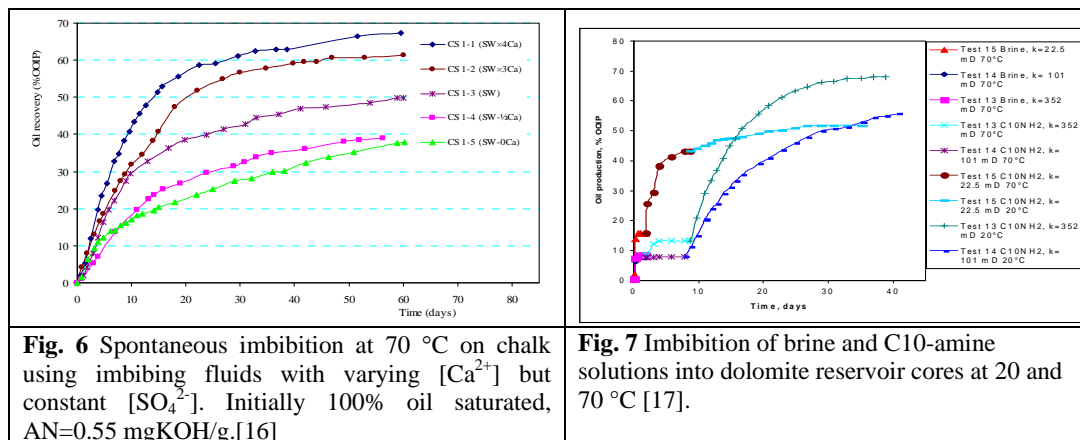
Hiorth et al. calculated the composition by volumetric mixing of initial formation water with imbibed seawater, which they believe is equal to the amount of displaced oil. This will be the composition of the water present in the core after the wettability process is finished, provided that no formation water is displaced. It is, however, well known from laboratory experiments and field observations (Ekofisk) that the connate water is banked up in front of the injected/imbibing fluid and that a significant amount of initial formation water is displaced [14, 15]. Thus, the compositions, which the equilibrium calculations were based on, cannot be correct.

### Is there any experimental evidence supporting a dissolution/precipitation mechanism?

By calculating the new geochemical equilibrium that included various types of calcium-bearing minerals by using the calculated initial brine compositions, Hiorth et al. observed a linear correlation between produced oil and the amount of calcium (in mol/l) that must be released from the chalk to form the new minerals. This quantity was termed “dissolution” of chalk. From a thermodynamic point of view, it could be argued that if calcium containing minerals are precipitated, it will impose dissolution of chalk in order to reestablish equilibrium between the rock and the liquid. Thus, if “dissolution” of chalk is not only taking place at the water-wet sites, but also at the oil-wet sites, adsorbed organic material may be released and new water-wet surface areas will be created, which will enhance oil recovery by spontaneous imbibition.

In the following section a series of experiments, where the composition of the imbibed fluid will affect the dissolution of chalk chemically, is discussed in terms of observed influence on oil recovery.

1. In order to test the impact of  $\text{Ca}^{2+}$  in SW on the wettability modification, the concentration of  $\text{Ca}^{2+}$  was varied from 0 to 4x the concentration found in SW, i.e. from 0 to 0.050 mole/l. No initial water was present in the cores saturated with an oil with  $\text{AN}=0.55$  mgKOH/g. The imbibition tests were performed at 70 °C, **Fig. 6**.



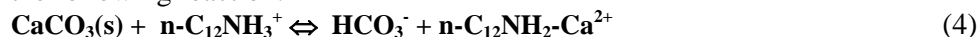
The efficiency of oil production by wettability modification increased as the concentration of  $\text{Ca}^{2+}$  increased [16]. It is a chemical fact, due to the common ion effect, that addition of  $\text{Ca}^{2+}$  to the imbibing fluid will decrease the dissolution of chalk. Thus, a decrease in dissolution of chalk increases oil recovery, which is a contradiction to a dissolution mechanism of wettability alteration.

- In **Fig. 4**, one of the cores was imbibed with a NaCl solution containing  $[\text{Ca}^{2+}] = 0.013$  and  $[\text{SO}_4^{2-}] = 0.048$  mol/l (2x  $\text{SO}_4^{2-}$  concentration found in SW). The imbibing fluid contained ~4 times higher concentration of  $\text{SO}_4^{2-}$  compared to  $\text{Ca}^{2+}$ . Because no  $\text{Mg}^{2+}$  was present, the solution was at the saturation point at 100 °C regarding precipitation of  $\text{CaSO}_4(\text{s})$  [10]. A sudden increase in oil recovery was noticed when  $\text{Ca}^{2+}$  was added to the system. Chemically, the addition of  $\text{Ca}^{2+}$  ions will suppress the dissolution of chalk, but the oil recovery was improved. Due to precipitation of  $\text{CaSO}_4(\text{s})$ ,  $[\text{Ca}^{2+}]$  was reduced and consequently no increase in oil recovery was noticed by increasing the temperature to 130 °C.
- In the other tests shown in **Fig 4**, the imbibing fluids consisted of a NaCl solution with various concentrations of  $\text{SO}_4^{2-}$ .  $\text{Mg}^{2+}$  was added to the system, at a similar concentration to what is found in SW, 0.045 mol/l. The oil recovery increased with increasing content of  $\text{SO}_4^{2-}$  in the brines at 100 and 130 °C. It has been experimentally verified that  $\text{Mg}^{2+}$  displaces  $\text{Ca}^{2+}$  in a substitution reaction on the chalk surface, **Figs. 2 and 3**. This process is not a dissolution process, but a surface reaction where  $\text{Ca}^{2+}$  is exchanged with  $\text{Mg}^{2+}$ , probably in the surface lattice. Thus in-situ generation of  $\text{Ca}^{2+}$  will decrease dissolution of chalk, however, the oil recovery increased due to improved wetting condition.
- According to the geochemical modeling by Hiorth et al., the final equilibrium between  $\text{MgCl}_2$  dissolved in a NaCl solution in equilibrium with chalk at 130 °C should lead to transformation of chalk into various types of dolomite, supersaturated and precipitated, which then should create wettability alteration and increased the oil recovery. According to **Fig. 4**, only a very small increase in oil recovery was observed at 100 °C, and no improvements in spontaneous imbibition were observed at 130 °C for the system containing only  $\text{Mg}^{2+}$  and no  $\text{SO}_4^{2-}$ . There appears to be no correlation between the modeled dissolution/transformation of chalk and improved oil recovery.
- In the same way as quaternary ammonium surfactants like C12TAB can act as wettability modifier in carbonates, primary ammonium surfactants,  $\text{C}_{12}\text{-NH}_3^+$  have also been shown to improve oil recovery by wettability alteration by spontaneous imbibition [17]. The corresponding amine will affect the solubility of  $\text{CaCO}_3(\text{s})$  drastically as the temperature increases, **Table 1**.

**Table 1** Solubility test for  $\text{CaCO}_3(\text{s})$  determined by the ICP-AES technique [17]

Chalk powder suspended in	Temp. °C	Amount of chalk powder, g	Calcium concentration in the water, mg/l	Amount dissolved calculated as mg $\text{CaCO}_3$	% $\text{CaCO}_3$ dissolved
Distilled water (DW)	20	1.0126	32.2	4.0	0.4
Distilled water	90	1.0043	11.3	1.4	0.14
1.0 wt.% C10-amine in DW	20	1.0105	86	10.8	1.07
1.0 wt.% C10-amine in DW	90	1.0079	186	23.3	2.31

At high temperatures, the primary ammonium surfactant will dissolve the chalk by the following reaction:



The surfactant will dissolve the carbonate, and the spontaneous imbibition is stopped, as demonstrated for the dolomite cores of 101 and 352 mD in **Fig. 7**. Thus, dissolution of  $\text{CaCO}_3(\text{s})$  will take place at the already water-wet sites without affecting the wetting conditions of the rock significantly.

## CONCLUSION

There is no published experimental work by Austad et al. supporting a dissolution mechanism for wettability modification of carbonates when exposed to SW at high temperature. In fact, a dissolution mechanism is in contradiction to experimental facts.

## REFERENCES

1. Zhang, P., *Water-based EOR in fractured chalk - Wettability and chemical additives*. 2006, University of Stavanger, Norway. ISBN: 82-7644-293-5: PhD Thesis.
2. Høgnesen, E.J., *EOR in fractured oil-wet chalk - Spontaneous imbibition of water by wettability alteration*. 2005, University of Stavanger: Dr. Ing. Thesis.
3. Puntervold, T., *Waterflooding of carbonate reservoirs - EOR by wettability alteration*. 2008, University of Stavanger, Norway. ISBN 978-82-7644-347-9: PhD Thesis.
4. Standnes, D.C., *Enhanced oil recovery from oil-wet carbonate rock by spontaneous imbibition of aqueous surfactant solutions*. 2001, NTNU, Norway: Dr. Ing. Thesis.
5. Strand, S., *Wettability alteration in chalk - A study of surface chemistry*. 2005, University of Stavanger: Dr. Ing. Thesis.
6. Webb, K.J., C.J.J. Black, and G. Tjetland, *A laboratory study investigating methods for improving oil recovery in carbonates*, in *International Petroleum Technology Conference*. 2005, IPTC: Doha, Qatar.
7. Strand, S., E.J. Høgnesen, and T. Austad, *Wettability alteration of carbonates - Effects of potential determining ions ( $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$ ) and temperature*. *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 2006. **275**: p. 1-10.
8. Strand, S., T. Austad, T. Puntervold, E.J. Høgnesen, M. Olsen, and S.M.F. Barstad, *"Smart water" for oil recovery from fractured limestone - A preliminary study*. *Energy & Fuels*, 2008. **22**: p. 3126-3133.
9. Puntervold, T. and T. Austad, *Injection of seawater and mixtures with produced water into North Sea chalk formation: Impact of fluid-rock interactions on wettability and scale formation*. *Journal of Petroleum Science and Engineering*, 2008. **63**: p. 23-33.
10. Zhang, P., M.T. Tweheyo, and T. Austad, *Wettability alteration and improved oil recovery by spontaneous imbibition of seawater into chalk: Impact of the potential determining ions:  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$* . *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 2007. **301**: p. 199-208.
11. Hiorth, A., L.M. Cathles, J. Kolnes, O. Vikane, A. Lohne, and M.V. Madland, *Chemical modelling of wettability change in carbonate rocks*. Paper presented at the 10th International Symposium on Reservoir Wettability held in Abu Dhabi, U. A. E., 27-28 Oct, 2008.
12. Hiorth, A., L.M. Cathles, J. Kolnes, O. Vikane, A. Lohne, and M.V. Madland, *A chemical model for the seawater- $\text{CO}_2$ -carbonate system - Aqueous and surface chemistry*. Paper SCA2008-18 presented at the International Symposium of the Society of Core Analysts, Abu Dhabi, U. A. E., 29 Oct - 2 Nov, 2008.
13. Deelman, J.C., *Low-temperature formation of dolomite and magnesite*. Compact disc publications Geology series, Eindhoven, The Netherlands, ISBN 90-809803 - 1 - 5, 2003.
14. Korsbech, U., H.K. Aage, B.L. Andersen, K. Hedegaard, and N. Springer, *Measuring and modeling the displacement of connate water in chalk core plugs during water injection*. *SPE Reservoir Eval. & Eng.*, 2006. **June**.
15. Nielsen, C.M., D. Olsen, and N. Bech, *Imbibition process in fractured chalk core plugs with connate water mobilization*. Paper SPE 63226 presented at the SPE Annual Tech. Conference and Exhibition, Dallas, Texas, 1-4 October., 2000.
16. Zhang, P., M.T. Tweheyo, and T. Austad, *Wettability alteration and improved oil recovery in chalk: The effect of calcium in the presence of sulfate*. *Energy & Fuels*, 2006. **20**: p. 2056-2062.
17. Standnes, D.C. and T. Austad, *Nontoxic low-cost amines as wettability alteration chemicals in carbonates*. *Journal of Petroleum Science and Engineering*, 2003. **39**(3-4): p. 431-446.