"Smart Water" for Oil Recovery from Fractured Limestone: A Preliminary Study

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Seawater is characterized as an enhanced oil recovery (EOR) fluid for hot, fractured chalk oil reservoirs because it is able to modify the wetting conditions and improve the displacement of oil. The chemical mechanism for the wettability alteration has been described previously, and it was verified that Ca^{2+}, Mg^{2+}, and SO_4^{2-} played an important role because of their reactivity toward the chalk surface. Chalk, which is purely biogenic $CaCO_3$, consists of fragmentary parts of calcite skeletons produced by plankton algae known as coccolithophorids, and it is believed to have a more reactive surface than ordinary limestone. To validate seawater as an EOR fluid also for limestone and dolomite, the affinities of these ions toward the rock surfaces must be evaluated. The present paper describes some preliminary experimental studies of the affinity of SO_4^{2-}, Ca^{2+}, and Mg^{2+} toward the surface of reservoir limestone cores at temperatures ranging from room temperature to 130 °C. The results confirmed that the ions interacted with the rock surface, and that the established chemical equilibrium was sensitive to the relative concentrations of the ions. It was also observed that the adsorption of Ca^{2+} and Mg^{2+} from a NaCl solution onto the limestone surface was quite similar at room temperature but that Mg^{2+} adsorbed more strongly at higher temperatures. At high temperatures, $T = 130$ °C, Mg^{2+} in seawater was able to substitute Ca^{2+} on the surface but the reactivity was less than for chalk. These findings indicate that seawater will act as an EOR fluid in limestone as well but its potential is probably smaller than for chalk. This was also confirmed by spontaneous imbibition tests performed at 120 °C.

1. Introduction

Initially, in an oil reservoir, a thermodynamic equilibrium has been established between the rock, formation water, and oil through millions of years. In many cases, the wetting condition for oil displacement is not optimal with the available source of injection water. The wetting condition can, however, be improved by modifying the ionic composition of the injected fluid. The waterflood then becomes a tertiary oil recovery method. Examples are: (i) injection of seawater into high-temperature chalk reservoirs, such as Ekofisk and Valhall,[1–4] and (ii) low salinity waterflooding of sandstone reservoirs.[5,6]

Thus, there is no doubt that the injected water is able to change the thermodynamic equilibrium between the different phases in a favorable way during the production time. The change in the equilibrium is mostly linked to the interaction between the injected water and the rock surface. The activation energy or energy barrier for the chemical reactions needed for wettability improvements to take place is crucial. If the reaction rate is too slow, the new equilibrium will not be established during the time frame for the waterflood and improvements of the waterflood will not be achieved. The reservoir temperature plays a very important role here because the activation energy is strongly dependent upon the temperature.[7,8] The activation energy for the wettability modification is related to how strongly the polar oil components are bonded to the mineral surface and the reactivity of the ions present in the injected water. Generally, the bonding energy between polar components in the oil and carbonates is higher than what is observed between oil and minerals, such as clays and silica, present in sandstones.

More than 50% of the oil reserves of the world are located in carbonates, and the average oil recovery from carbonates is generally lower than for sandstone reservoirs. The reason is that the carbonate rock is neutral to preferentially oil-wet and often highly fractured. The carboxylic material in crude oil adsorbs strongly onto the carbonate surface and makes it partly oil-wet. Injection of water is a cheap enhanced oil recovery (EOR) method, but in this case, the water will mainly follow the fractures. Because of the negative capillary pressure in oil-wet rock, water will not imbibe into the matrix blocks to displace the oil. The water will only displace the oil present in the fractures, and less than 5% recovery is therefore expected in some cases when the oil reservoir is highly undersaturated, e.g., $P_{res} \gg P_b$ and contains a large aquifer for pressure support.

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(4) Webb, K. J.; Black, C. J. J.; Tjetland, G. A laboratory study investigating methods for improving oil recovery in carbonates. In International Petroleum Technology Conference, IPTC, Doha, Qatar, 2005.

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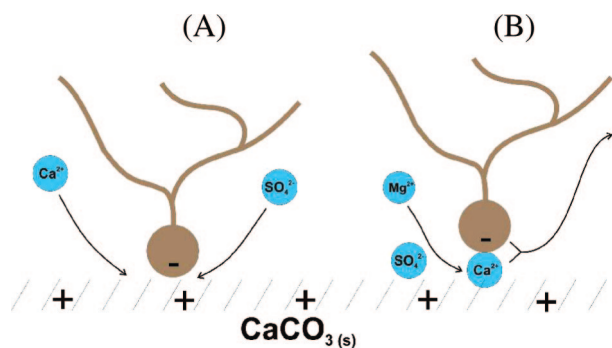(8) Puntervold, T.; Strand, S.; Austad, T. *Energy Fuels* **2007,** *21* (6), 3425–3430.

Figure 1. Schematic model of the suggested mechanism for the wettability alteration induced by seawater. (A) Proposed mechanism when Ca^{2+} and SO_4^{2-} are active. (B) Proposed mechanism when Mg^{2+} and SO_4^{2-} are also active at higher temperatures.[2]

Under these circumstances, it is difficult to create a gas cap by gas injection. Examples are present in the Middle East.

Ekofisk (T_{res} = 130 °C) is an example of a highly fractured chalk field, which is moderately water-wet. Seawater is successfully injected into the formation to maintain the reservoir pressure above the bubble point of the oil and to displace the oil. Recent research at the University of Stavanger[2,9] has shown that seawater contains potential determining ions in a proper concentration ratio to promote wettability modification toward a more water-wet condition, which will enhance the spontaneous imbibition of water into the matrix blocks. The temperature appeared to be a very important parameter for the wettability modification, and increased oil recovery by spontaneous imbibition was observed as the temperature increased. The chemical mechanism for this wettability modification by seawater is now documented and well-understood.[2] The symbiotic interaction between SO_4^{2-}, Ca^{2+}, and Mg^{2+}, which are all components of seawater, will remove some of the carboxylic material from the chalk surface and thereby increase the capillary forces to promote spontaneous imbibition of water into the matrix blocks. The mechanism is schematically shown in Figure 1. Webb et al.[4] have performed spontaneous imbibition studies at complete reservoir conditions on cores from Valhall (T_{res} = 92 °C) and confirmed our laboratory results. Seawater increased the oil recovery by 40% compared to initial brine in a spontaneous imbibition process. When performing a viscous flood with only 1 psi differential pressure, the oil recovery increased from 40 to 60%. Thus, seawater appeared to change the total capillary pressure curve in a positive way for enhanced oil recovery from the chalk fields.

Chalk is a pure, biogenic material, and it has a much larger surface area compared to limestone. It is therefore expected that the reactivity of the chalk surface toward potential determining ions is higher than that of the limestone surface. An interesting issue is therefore to see if the results obtained for chalk are also applicable to limestone. Limestone is less homogeneous than chalk, both regarding porosity and permeability. The oil components adsorbed onto the surface are, however, of the same type, i.e., carboxylic material, which means that it should be possible to perform wettability modifications in the same way as for chalk by using seawater. Thus, even though the chemical component of both chalk and limestone is $CaCO_3$, the reactivity of the chemical components present in seawater may be different with regard to wettability modification. Some preliminary studies

on brine−rock interactions using reservoir cores from a Middle East limestone reservoir are presented.

2. Experimental Section

2.1. Materials. The properties of the reservoir limestone cores from a field in the Middle East are summarized in Table 1.

The composition of the brines used is listed in Table 2. The terminology is as follows: SW is synthetic seawater; SW0S is SW without SO_4^{2-}; and SW3S is SW with 3 times the SO_4^{2-} concentration in SW. S-brine is the initial formation water of a Middle East limestone oil reservoir. In the chromatographic tracer studies, the brines used were SW-U, which is SW without SO_4^{2-}, and tracer SCN^- (thiocyanate), SW^1/$_2$M, which is SW containing half of the SCN^- and SO_4^{2-} concentrations of SW, and NaCl-M, which contains equal amounts of Ca^{2+}, Mg^{2+}, and tracer SCN^-.

The stock tank oil from the same reservoir was termed S-oil. Because of some precipitation, the oil was filtrated through a 5 μm Millipore filter. The acid and base numbers of the filtrated oil were determined by a modified version[10] of American Society for Testing and Materials (ASTM) D664 and ASTM D2896, to AN = 0.05 and BN = 0.44 mg of KOH/g oil, respectively. The oil density was 0.830 g/cm^3 at 20 °C.

2.2. Core Flooding. *Core Preparation.* The reservoir limestone cores were cleaned at ambient temperature by flooding with water-saturated toluene (at least 5 PV) at a rate of 0.1 mL/min until the effluent was colorless (minimum of 3 PV). Thereafter, the cores were flooded with 3 PV of methanol and finally dried at 110 °C to a constant weight. Prior to use, the cores were evacuated and saturated with the actual fluid. The porosity was determined by the weight difference of wet and dry core.

Adsorption Studies. The affinities of Ca^{2+}, Mg^{2+}, and SO_4^{2-} toward the limestone surface were studied chromatographically by flooding the specific brine solution through the core and determining the retention of the active ions relative to the non-adsorbing tracer, SCN^-. A traditional Hassler core holder was used with a confining pressure of 18 bar. A backpressure valve (7 bar) was used to ensure constant pore pressure and to prevent the fluid from boiling at high temperatures. Samples of the effluent were taken using a fraction collector, and a composition analysis was performed. The flow rate in the chromatographic tests was 0.1 and 0.2 mL/min.

The affinity of SO_4^{2-} toward the limestone surface at room temperature was previously studied by the chromatographic wettability test based on separation of SCN^- and SO_4^{2-}.[11] Between each test, the core was "cleaned" with at least 5 PV of seawater without SO_4^{2-} and SCN^- (SW-U). The water-wet surface is proportional to the area between the effluent curves of the tracer, SCN^-, and SO_4^{2-}.

The relative affinities of Ca^{2+} and Mg^{2+} were studied using NaCl-M, a NaCl-brine with equal amounts of Ca^{2+}, Mg^{2+}, and SCN^-. The tests were conducted at 20, 70, 100, and 130 °C. Before each test, the core was "cleaned" at ambient temperature by flooding 5 PV pure NaCl-brine with the same salinity.

To study possible substitution of Ca^{2+} by Mg^{2+} at the surface, SW was injected very slowly into the core at different temperatures: ambient, 80, 100, and 130 °C. The injection rate was about 1 PV/day for at least 7 days. Before each test, the core was "cleaned" by injecting 5 PV of SW at a rate of 0.1 mL/min at ambient temperature.

2.3. Spontaneous Imbibition. Two limestone cores were initially saturated with S-brine, then flooded with 1.5 PV of S-oil in each direction, and finally centrifuged to S_{wi} in the presence of oil to obtain a low initial water saturation. The initial water saturations in the two cores, S27A and S28A, were 9.1 and 14.8%, respectively. After the cores were aged in the crude oil for 4 weeks at 90 °C, the spontaneous imbibition tests were performed in sealed steel cells

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Table 1. Core Data for Reservoir Limestone Cores

core ID	L (cm)	D (cm)	V_b (cm^3)	Φ (%)	k (mD)	PV (mL)	S_{wr} (%)	OOIP (mL)
2-21	4.91	3.78	55.25	24.7	2.7	13.6		
46A	4.76	3.78	53.42	27.8	2.47	14.8		
20A	4.88	3.78	54.76	26.2	3.03	14.3		
S27A	4.85	3.79	54.72	30.8	53	16.8	9.1	15.3
S28A	4.9	3.8	55.43	31.4	78	17.4	14.8	14.8

Table 2. Composition and Properties of the Brines Used

ions	SW (mol/L)	SW0S (mol/L)	SW3S (mol/L)	S-brine (mol/L)	SW-U (mol/L)	SW^1/$_2$M (mol/L)	NaCl (mol/L)	NaCl-M (mol/L)
HCO$_3^-$	0.002	0.002	0.002	0.003	0.002	0.002	0.000	0.000
Cl$^-$	0.525	0.583	0.408	3.155	0.623	0.574	0.571	0.556
SO$_4^{2-}$	0.024	0.000	0.072	0.002	0.000	0.012	0.000	0.000
SCN$^-$	0.000	0.000	0.000	0.000	0.000	0.012	0.000	0.013
Mg^{2+}	0.045	0.045	0.045	0.134	0.045	0.045	0.000	0.013
Ca^{2+}	0.013	0.013	0.013	0.362	0.013	0.013	0.000	0.013
Na$^+$	0.450	0.460	0.429	2.170	0.500	0.475	0.571	0.504
K$^+$	0.010	0.010	0.010	0.000	0.010	0.022	0.000	0.013
TDS (g/L)	33.39	33.39	33.39	179.87	35.72	35.72	33.39	33.39
IS (mol/L)	0.66	0.64	0.68	3.66	0.68	0.68	0.57	0.59

at 120 °C. The cores were surrounded by the imbibing brine with a backpressure of ∼10 bar. The amount of oil produced, percent of original oil in place (OOIP), was collected in a burette and recorded as a function of time.

2.4. Chemical Analysis. The ionic concentrations of Ca^{2+}, Mg^{2+}, SO$_4^{2-}$, and SCN$^-$ were analyzed by an ion-exchange chromatograph, ICS-3000 reagent-free, produced by Dionex Corporation, Sunnyvale, CA. Calibration curves were stored in the computer system. To stay in the linear region of the calibration curve, the effluent samples were diluted 1:10 or 1:20 by distilled water prior to the analyses.

3. Results and Discussion

Carboxylic material present in crude oil is bonded very strongly onto the carbonate surface. It is nearly impossible to use traditional solvents to clean the surface.[12] A chemical reaction under irreversible thermodynamic conditions is needed to remove the material. In a recent study by Masalmeh and Jing,[13] the importance of cleaning the limestone core properly was clearly demonstrated. Proper core cleaning is important to achieve a uniform, water-wet sample that is needed to obtain a reliable drainage P_c curve. This forms the basis for oil in place calculations and for conversion into an imbibition P_c curve. As will be demonstrated below, core flooding with SW at high temperature will improve the water-wet fraction significantly after cleaning the core with water-saturated toluene and methanol.

3.1. Affinity of SO$_4^{2-}$ toward the Carbonate Surface. A chromatographic technique to determine the water-wet surface fraction of chalk has recently been published.[11] The method is based on the separation of a tracer, SCN$^-$, and SO$_4^{2-}$ at the water-wet sites of the chalk surface. The area between the effluent curve of SCN$^-$ and SO$_4^{2-}$ is directly proportional to the water-wet surface. Using a completely water-wet condition as a reference system, the ratio between the two areas will give a wetting index, which describes the water-wet fraction of the actual core surface area. Synthetic seawater spiked with SCN$^-$ to the same concentration as SO$_4^{2-}$, 0.024 mol/L, was used as the chromatographic liquid in chalk. The surface area of limestone is smaller compared to chalk, and therefore, the concentration of SCN$^-$ and SO$_4^{2-}$ was decreased to ^{1}/$_2$ of the

concentrations found in seawater (SW^1/$_2$M). The dispersion of the concentration front of SCN$^-$ and SO$_4^{2-}$ and the area separating the two effluent curves are sensitive to the flow rate, as shown in Figure 2. The core termed 2-21 (Table 1) has a high enough water-wet surface area to separate the effluent tracer, SCN$^-$, and the SO$_4^{2-}$ curve at room temperature. The area for the chromatographic separation increases from 0.112 to 0.173 as the flow rate was increased from 0.1 to 0.2 mL/min. Thus, if the core could be cleaned to a completely water-wet condition, a water-wetting index could be determined. Even though it is difficult to be sure that the cleaning procedure used will create a completely water-wet condition, this chromatographic technique can, however, be used to observe changes in wetting conditions for limestone when exposed to different types of fluids. The test confirmed that sulfate adsorbs onto the limestone surface in the same way as onto chalk, and the adsorption will probably increase with an increasing temperature in the same way as observed for chalk in previous studies.[1]

3.2. Affinity of Ca^{2+} and Mg^{2+} toward the Carbonate Surface. Besides SO$_4^{2-}$, also Ca^{2+} and Mg^{2+} are active in the wettability modification observed in chalk.[2,3] The competitive adsorption of Ca^{2+} and Mg^{2+} onto limestone was studied in NaCl-brine with salinity similar to SW. In the same way as for SO$_4^{2-}$, chromatographic separation between SCN$^-$, Ca^{2+}, and Mg^{2+} was observed on the same core, 2-21. The concentrations of the active species, SCN$^-$, Ca^{2+}, and Mg^{2+}, were the same and equal to 0.013 mol/L, i.e., the same as the Ca^{2+} concentration in SW. The flow rate was 0.1 mL/min. At low temperatures, 20 and 70 °C, the affinity of Ca^{2+} and Mg^{2+} toward the
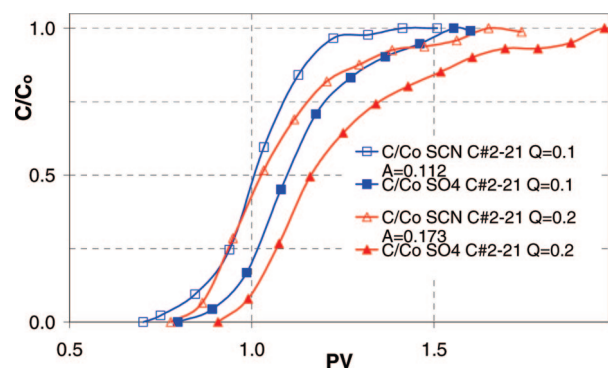
(12) Thomas, M. M.; Clouse, J. A.; Longo, J. M. *Chem. Geol.* **1993**, *109*, 201–213.

(13) Masalmeh, S. K.; Jing, X. D. Paper IPTC 11722 presented at the International Petroleum Technology Conference, Dubai, United Arab Emirates, Dec 4–6, 2007.
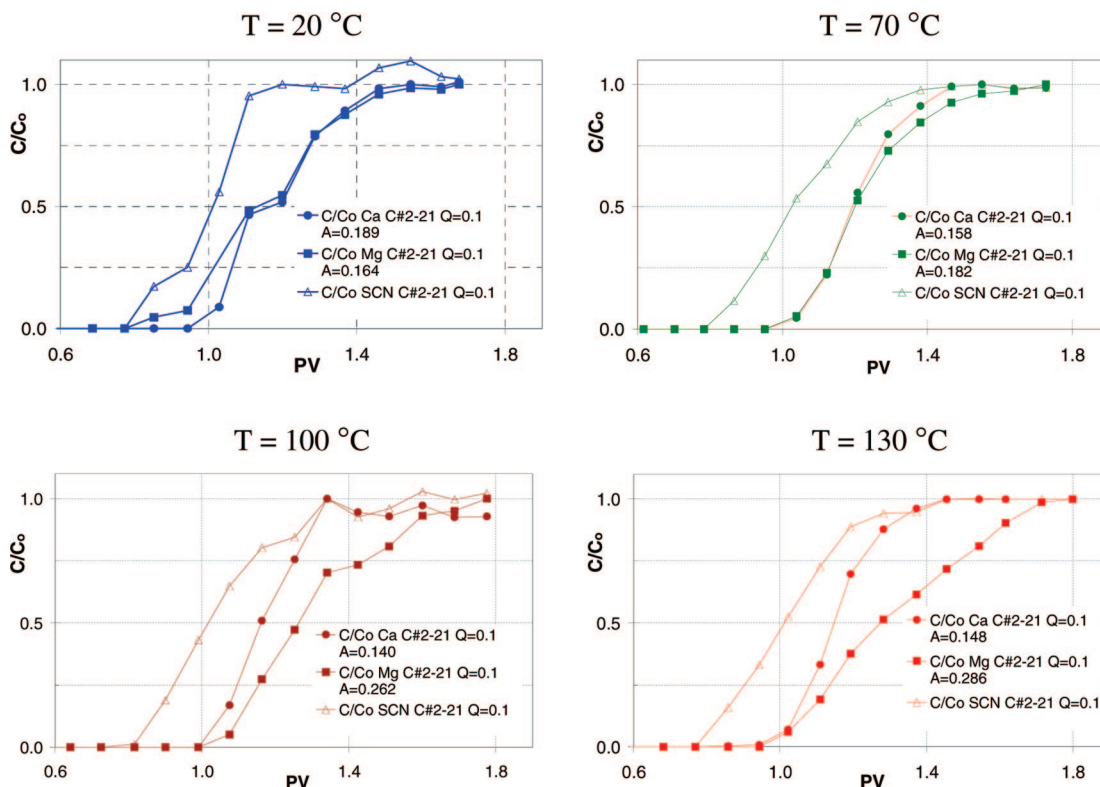

Figure 2. Effluent curves of relative concentration versus the pore volume for SCN$^-$ and SO$_4^{2-}$ using SW^1/$_2$M as the chromatographic fluid. The tests were performed at ambient temperature at two different flow rates, $Q = 0.1$ and 0.2 mL/min, on the core termed 2-21.

Figure 3. Competitive adsorption of Ca^{2+} and Mg^{2+} from NaCl-M brine onto the limestone core termed 2-21 at different temperatures. $[Ca^{2+}] = [Mg^{2+}] = [SCN^-] = 0.013$ mol/L. Flow rate $Q = 0.1$ mL/min.

Table 3. Area between the Ca^{2+} and Mg^{2+} Curves and the Tracer, SCN^-, Curve at Different Temperatures

temperature (°C)	Ca^{2+} adsorption area	Mg^{2+} adsorption area
20	0.19	0.16
70	0.16	0.18
100	0.14	0.26
130	0.15	0.29

carbonate surface was quite similar, but as the temperature increased to 100 and 130 °C, the affinity of Mg^{2+} became stronger than that of Ca^{2+} (Figure 3). This is evident from the areas between the tracer curve and the effluent curves for Ca^{2+} and Mg^{2+} (Table 3). The Mg^{2+} ion is small with a high charge density, and it is therefore more strongly solvated in water than Ca^{2+}. This is also reflected in the hydration energy of the two ions, -459 and -380 kcal/mol for Mg^{2+} and Ca^{2+}, respectively.[14] This means that Mg^{2+} becomes more reactive as the temperature increases because of partial dehydration of the ion.

Similar studies performed on chalk cores showed that Mg^{2+} was even able to substitute Ca^{2+} from the chalk surface at high temperatures (Figure 4). The fact that the concentration of Ca^{2+} increases to a maximum of about 75% higher than the initial concentration and that Mg^{2+} is strongly retarded confirms the substitution reaction. No increase in the concentration of Ca^{2+} was observed in the experiments using limestone reservoir cores even though the flooding rate was $^1/_2$ of the rate used in the chalk experiments. It is therefore concluded that the reactivity of the limestone surface is less than that of the chalk surface, probably because of different biological origin. As will be shown later, Mg^{2+} will substitute Ca^{2+} when SW is flooded very slowly through the limestone core.

Previous experiments with chalk showed that the adsorption of Ca^{2+} onto the chalk surface increased as the concentration
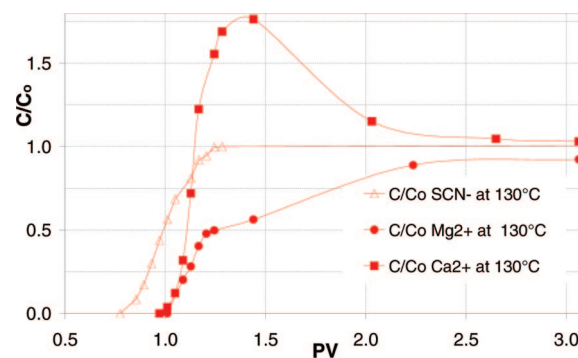
(14) Phillips, C. S. G.; Williams, R. J. P. *Inorganic Chemistry*; Clarendo Press: Gloucestershire, U.K., 1965; Vol. 1, p 160.

Figure 4. Ca^{2+} is substituted by Mg^{2+} at the surface of SK-chalk at 130 °C using NaCl-M brine. $[Ca^{2+}] = [Mg^{2+}] = [SCN^-] = 0.013$ mol/L. Flow rate $Q = 0.2$ mL/min.[2]

of SO_4^{2-} increased. Thus, adsorption of SO_4^{2-} onto chalk decreased the positive charge on the chalk surface, which increased the excess of Ca^{2+} at the surface because of reduced electrostatic repulsion.[1] A similar trend is also expected for limestone.

3.3. Slow Injection of SW at Different Temperatures. If Mg^{2+} in SW is able to displace Ca^{2+} from the surface lattice of limestone, similar to what it did for chalk, then Mg^{2+} may also be able to displace Ca^{2+} ions bonded to the carboxylic group of the organic material.[2] Thus, the reactivity of Mg^{2+} in the presence of SO_4^{2-} is related to the wettability modification toward a more water-wet system. Preliminary experiments were therefore performed on the core termed 46A. The core was carefully preflooded with 3PV of SW at a rate of 0.1 mL/min at ambient temperature to remove dissolvable salts. Then, the temperature was increased to the test temperature, and 1.5 PV of SW was flooded at a high rate (1 mL/min), before a 7-day test was initiated at a slow injection rate of 1 PV/day. The test temperature was changed in the following order: 20, 130, 100, and 80 °C. A backpressure of 7 bar was applied to avoid boiling
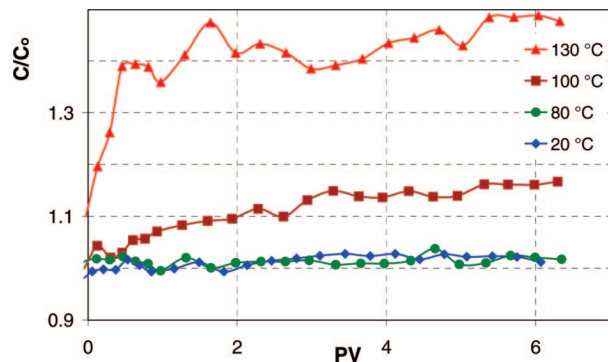
Figure 5. Relative concentration of Ca^{2+} in the effluent at different temperatures, 20–130 °C. Limestone core termed 46A; SW as the flooding fluid. Flow rate: 1.0 PV/day.
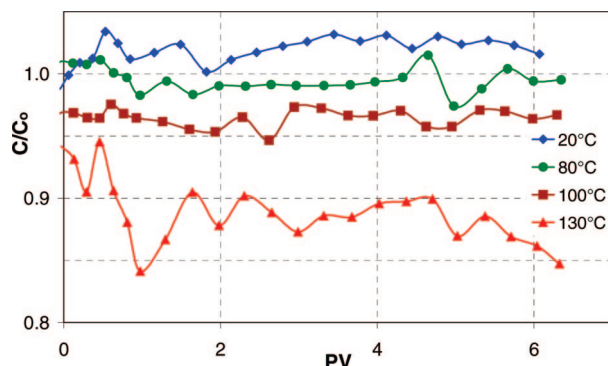

Figure 6. Relative concentration of Mg^{2+} in the effluent at different temperatures, 20–130 °C. Limestone core termed 46A; SW as the flooding fluid; Flow rate: 1.0 PV/day.
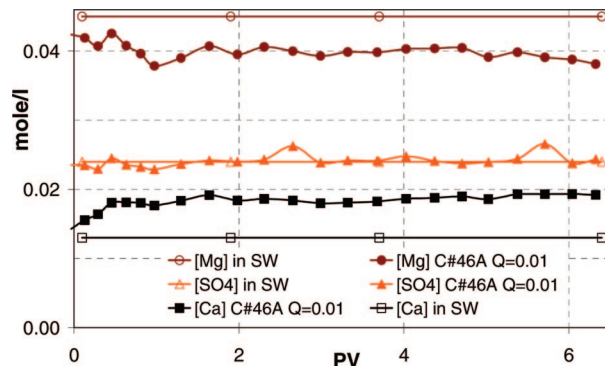

Figure 7. Changes in molar concentrations of Ca^{2+}, Mg^{2+}, and SO_4^{2-} when flooding SW through the 46A limestone core at 130 °C. Flow rate: 1 PV/day.
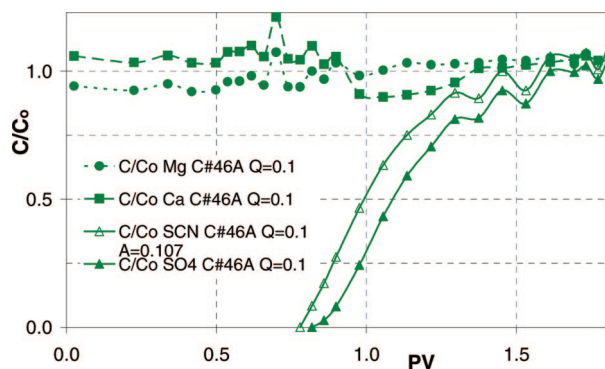

Figure 8. Chromatographic wettability test on core 46A before exposure to SW at high temperature. The core was flooded with $SW^1/_2M$ ([SCN^-] = [SO_4^{2-}] = 0.012 mol/L) at a rate of 0.1 mL/min.

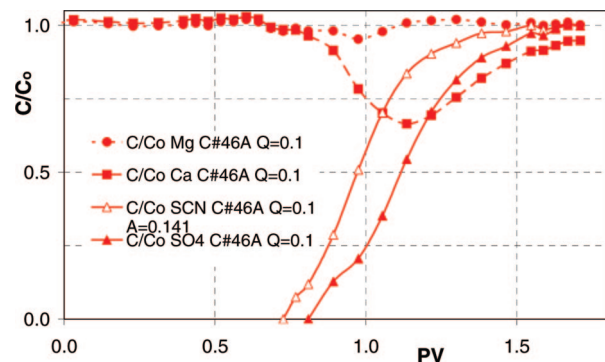**Figure 9.** Chromatographic wettability test on core 46A after exposure to SW at high temperature. The core was flooded with $SW^1/_2M$ ([SCN^-] = [SO_4^{2-}] = 0.012 mol/L) at a rate of 0.1 mL/min.

of the water. Samples of the effluent were collected and analyzed for Ca^{2+}, Mg^{2+}, and SO_4^{2-}. The concentration of SO_4^{2-} did not change for the various temperatures. In the case of Ca^{2+}, the concentration increased when the temperature was above 100 °C (Figure 5). At 130 °C, the concentration of Ca^{2+} increased 40–50% compared to the initial concentration in SW. This is comparable to what was previously observed for chalk.[2,15] At 100 °C, the increase in the concentration of Ca^{2+} was in the range of 15%. Even though there is some scattering in the Mg^{2+} data (Figure 6), it is a fact that the Mg^{2+} concentration decreased at 130 °C. On the mole basis, the decrease in Mg^{2+}, from 0.045 to 0.040 mol/L, is quite similar to the increase in Ca^{2+}, from 0.013 to 0.018 mol/L, which of course indicated a 1:1 substitution (Figure 7). On the basis of these observations and experience from previous work on chalk, it is reasonable to believe that SW is able to improve the water wetness of reservoir limestone at high temperatures. Even a small improvement in water wetness can cause a significant increase in oil recovery by spontaneous imbibition. In a previous study, it was verified that an increase in the water-wet fraction from 0.65 to 0.84, i.e., of 19%, caused an increase in oil recovery by spontaneous imbibition for 5 days from 25 to 60% of OOIP.[8]

3.4. Wettability Modification by Hot Seawater. The wetting state of the 46A core was determined by the chromatographic technique before and after the core was used for the high-temperature tests with SW. The wettability tests were performed at room temperature using $SW^1/_2M$. The chromatographic separation between SCN^- and SO_4^{2-} before the core

(15) Korsnes, R. I.; Madland, M. V.; Austad, T. Impact of brine composition on the mechanical strength of chalk at high temperature. In *EUROCK 2006—Multiphysics Coupling and Long Term Behaviour in Rock Mechanics*; Taylor and Francis Group: London, U.K., 2006; ISBN 0 415 41001 0.
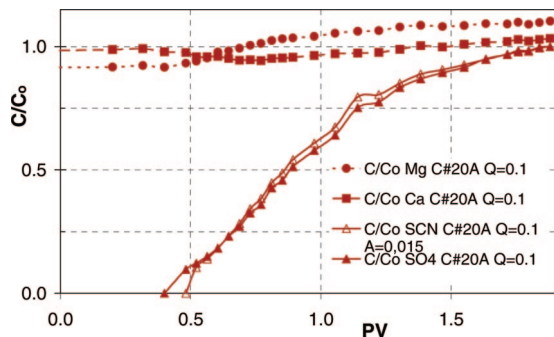
was exposed to SW at high temperatures is shown in Figure 8. The area between the tracer curve and the elution curve for SO_4^{2-}, which is proportional to the water-wet area, was estimated to be 0.107. The fact that the tracer curve passes through the coordinate (1.0, 0.5) indicates that the total pore volume of the core was connected and flooded by the injected fluid. The wettability test of the same core after the core had been exposed to SW at high temperatures (the core was flooded with at least 6 PVs of SW at 130 °C) is shown in Figure 9. The water-wet surface area has been increased because the calculated area between the tracer and sulfate curve was increased to 0.141, which corresponded to an increase in the water wetness of 32%. Increased oil recovery by spontaneous imbibition is expected in line with previous observations.[8]

Carboxylates from the crude are strongly adsorbed onto the carbonate surface, and traditional cleaning of reservoir carbonate cores by using toluene and methanol will not remove all of the

Figure 10. Chromatographic wettability test on core 20A after cleaning with toluene and methanol. The core was flooded with SW^1/$_2$M ([SCN$^-$] = [SO$_4{}^{2-}$] = 0.012 mol/L) at a rate of 0.1 mL/min. The core appeared very oil-wet.
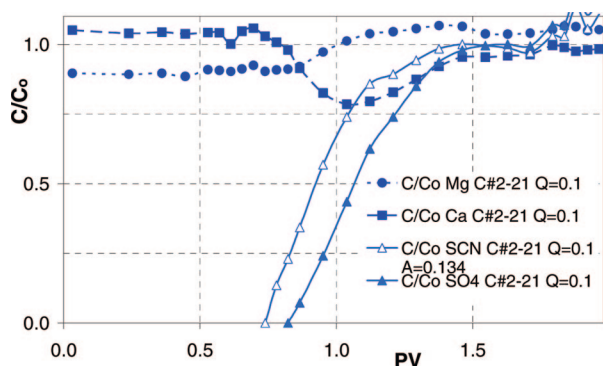

Figure 11. Interactions between surface-active ions (Ca^{2+}, Mg^{2+}, and SO$_4{}^{2-}$) present in SW and the carbonate surface, core 2-21. The core was flooded with SW^1/$_2$M ([SCN$^-$] = [SO$_4{}^{2-}$] = 0.012 mol/L) at a rate of 0.1 mL/min.

adsorbed material. This is clearly illustrated by the wettability test on core 20A, which was cleaned by flooding with toluene and methanol (Figure 10). The tracer and sulfate curve is nearly identical, which indicates a strongly oil-wet condition. There is no water-wet surface for chromatographic separation. Water-saturated toluene is suggested to be the best fluid to remove carboxylates from the carbonate surface.[12] Water will then act as a strong nucleophile and displace some of the carboxylic material from the surface; i.e., the carboxylic material is so strongly bonded to the surface that it has to be reacted away rather than washed away. On the basis of the experimental results and the discussion above, a better way to remove the most strongly bonded organic material is by flooding the carbonate core with seawater at a high temperature, about 130 °C. Because the relative concentration of Mg^{2+} and Ca^{2+} is different in SW and formation water, the core may undergo some changes at the surface; i.e., some Ca^{2+} may be substituted by Mg^{2+} in the surface lattice. Therefore, it is recommended to flood the core with hot distilled water or low salinity brine to dissolve the MgCO$_3$ formed at the surface.[15]

3.5. Interactions between Ca^{2+}, Mg^{2+}, and SO$_4{}^{2-}$ and the Limestone Surface. A picture of the mutual interactions between the potential determining ions Ca^{2+}, Mg^{2+}, and SO$_4{}^{2-}$ in the brine and their affinities toward the limestone surface can be obtained by looking at Figure 11. The core 2-21 was flooded with 3 PV at a rate of 0.1 mL/min with SW without SCN$^-$ and SO$_4{}^{2-}$, SW-U, at room temperature. The salinity was kept constant and equal to SW by adjusting the NaCl concentration. Thereafter, the pore fluid was displaced by SW^1/$_2$M, i.e., SW containing 0.012 mol/L SCN$^-$ and SO$_4{}^{2-}$. The concentration of Ca^{2+}, Mg^{2+}, SCN$^-$, and SO$_4{}^{2-}$ in the effluent was determined and plotted versus injected PV of the SW^1/$_2$M fluid (Figure 11).
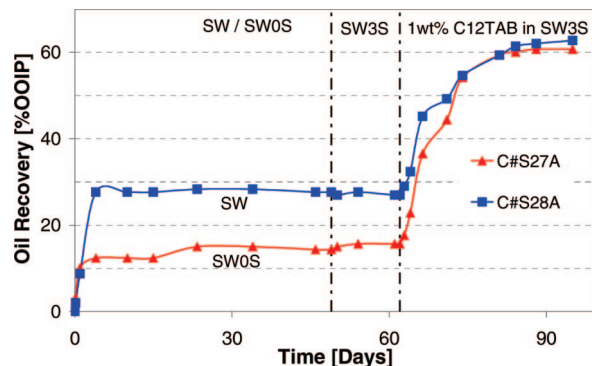

Figure 12. Spontaneous imbibition at 120 °C of SW0S (without SO$_4{}^{2-}$) and SW (with SO$_4{}^{2-}$) into reservoir limestone cores, S27A and S28A.

The concentration of Ca^{2+} in the pore fluid was very close to the initial concentration, while the concentration of Mg^{2+} decreased significantly compared to the initial condition. In both cases, the concentration remained constant until the breakthrough of SO$_4{}^{2-}$. Then, the concentration of Ca^{2+} decreased drastically, and the concentration of Mg^{2+} increased close to the initial concentration found in SW. Thus, the presence of SO$_4{}^{2-}$ in the pore fluid caused an immediate dynamic activity in the system. Remember that the affinities of Ca^{2+} and Mg^{2+} toward the limestone surface in a NaCl solution at 20 °C were quite similar when both ions were present at equal concentrations, as confirmed by Figure 3. In SW, [Mg^{2+}] ≈ 4[Ca^{2+}] and therefore Mg^{2+} overrides Ca^{2+} in the adsorption onto the carbonate surface even though Mg^{2+} is more strongly hydrated than Ca^{2+} as discussed earlier. In the presence of SO$_4{}^{2-}$, the situation is changed. The concentration of Ca^{2+} decreases because of adsorption onto the carbonate surface, and the concentration of Mg^{2+} increases because of desorption from the carbonate surface. The dynamics in the composition prevail as long as there is a gradient in the concentration of SO$_4{}^{2-}$. A new equilibrium is established, and the concentration of ions in the effluent becomes equal to the concentration in the injected fluid. The reason for the change in the concentrations of Ca^{2+} and Mg^{2+} in the presence of SO$_4{}^{2-}$ is explained in the following way: (i) SO$_4{}^{2-}$ adsorbs onto the positively charged carbonate surface, and the positive charge density is decreased. The adsorption of Ca^{2+} onto the surface is then enhanced because of smaller electrostatic repulsion between the surface and Ca^{2+}.[1] (ii) At the same time, SO$_4{}^{2-}$ forms an ion pair with Mg^{2+} in the aqueous phase:

$$[Mg^{2+} \cdots SO_4{}^{2-}] = Mg^{2+} + SO_4{}^{2-}$$
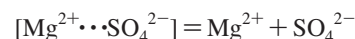
This ion-pair lowers the activity of Mg^{2+} in solution, and Mg^{2+} is then desorbed from the carbonate surface.

The interaction between SW and limestone is quite identical to previous studies using chalk as carbonate rock.[1,16] According to the results from the chalk study, as the temperature is increased, the observed effects at room temperature are enhanced because the adsorption of SO$_4{}^{2-}$ onto the carbonate surface increases and the ion-pair formation between Mg^{2+} and SO$_4{}^{2-}$ becomes stronger.[1,17] At very high temperatures, 130 °C, another type of interaction is activated. Mg^{2+} becomes more reactive because of dehydration, and it is able to substitute Ca^{2+} in the surface lattice of limestone as discussed previously (Figures 5 and 6).

(16) Zhang, P.; Austad, T. *Colloids Surf., A* **2006**, *279*, 179–187.
(17) Carlberg, B. L.; Matthews, R. R. Solubility of calcium sulfate in brine. In Oilfield Chemistry Symposium of the Society of Petroleum Engineers of AIME, Denver, CO, 1973.
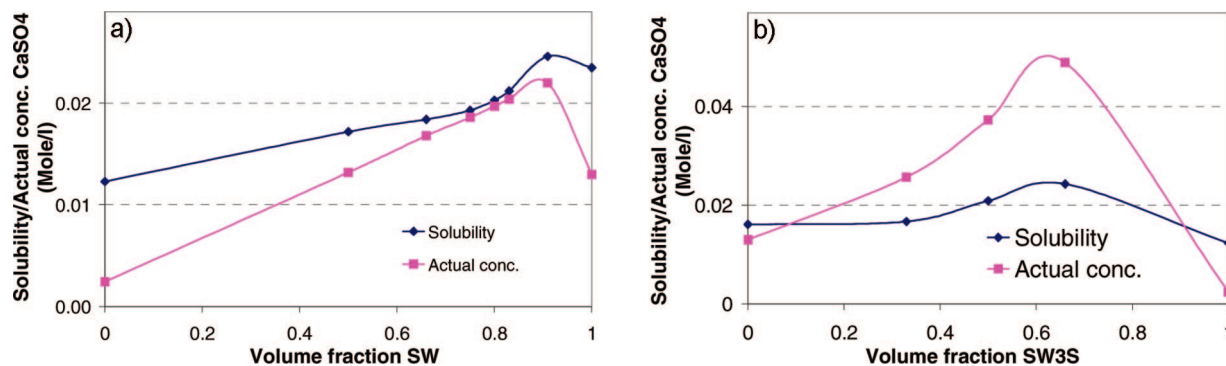
Figure 13. (a and b) Solubility of CaSO$_4$ when SW and SW3S were mixed with formation brine, S-brine, at 125 °C. The calculations were made according to the method described by Carlberg and Matthews.[17]

All of the chemical interactions between the active components in SW (Ca^{2+}, Mg^{2+}, and SO$_4^{2-}$) and the chalk surface, which were identified as important reactions for the observed wettability modification in chalk, are also present in reservoir limestone cores. Thus, there is a reason to believe that seawater will act as an EOR fluid for limestone and possibly also for dolomite.

3.6. Oil Displacement by Spontaneous Imbibition. SO$_4^{2-}$, in the presence of Ca^{2+} or Mg^{2+}, is a necessary component to promote a wettability alteration of the chalk surface.[2] Two cores, S27A and S28A, were saturated with S-brine, flooded with filtrated S-oil, centrifuged to S_{wr}, aged, and immersed into two different brines, i.e., SW without SO$_4^{2-}$ (SW0S) and SW (with SO$_4^{2-}$). The salinity of SW0S was kept equal to the salinity of SW by adjusting the NaCl concentration. The initial water saturations for the two cores, S27A and S28A, were 9.1 and 14.8%, respectively. The permeability of the two cores was in the same range but significantly higher than for the previous limestone cores (Table 1). The spontaneous imbibition experiment was performed in steel cells at 120 °C with a backpressure of 10 bar. The oil recovery from the core exposed to SW without SO$_4^{2-}$ only reached 15% of OOIP (Figure 12). The oil recovery may mostly be related to thermal expansion and some inhomogeneities in the wetting state close to the carbonate surface, as discussed previously by Standnes and Austad.[18] The core S28A exposed to SW produced about 15% more oil. Thus, in line with the previous discussion concerning the interaction between potential determining ions in SW and the limestone surface, SW appeared to act as a wettability modifier, which means that it is an EOR fluid also for limestone.

Previous spontaneous imbibition studies on chalk have revealed that the oil recovery improved when the concentration of SO$_4^{2-}$ increased.[1,2,16] Therefore, the concentration of SO$_4^{2-}$ was increased to 3 times the concentration in SW, but no additional increase in oil recovery from the limestone core was detected (Figure 12). The salinity of the initial brine was very high, i.e., 5.3 times the SW salinity. Calculations at 125 °C based on the method described by Carlberg and Matthews showed that CaSO$_4$ was close to precipitation if the volume fraction of SW was in the range of 0.7−0.8 (Figure 13a). For the imbibing fluid containing 3 times the SO$_4^{2-}$ concentration in SW, precipitation of CaSO$_4$ was expected at nearly all mixing ratios (Figure 13b). It is reasonable to believe that spontaneous imbibition of the brine with a high sulfate concentration is prohibited by precipitation of CaSO$_4$ in the pore system when mixed with formation brine. It is, however, very interesting to observe that adding 1.0 wt % of the cationic surfactant dodecyl-

trimethyl-ammonium bromide, C$_{12}$TAB, increased the recovery to more than 60% of OOIP for both cores, despite the compatibility problem. The high oil recovery confirmed that the porous network was interconnected in both cores, and the difference in spontaneous imbibition by SW with and without SO$_4^{2-}$ cannot be explained by different rock properties. Cationic surfactants of this type will act as wettability modifiers in chalk[19] and dolomite[20] even at low temperatures when SO$_4^{2-}$ is present in the imbibing fluid. An explanation for the high oil recovery in the presence of the surfactant can be that, when the imbibition process is initiated, the concentration of sulfate may decrease at the imbibing water front because of adsorption onto the carbonate rock and that the imbibing water displaces the initial formation water as well as the oil.[21] Thus, the high saline formation water is displaced and replaced by seawater and not mixed with it in the pores. This explanation is, of course, mostly a hypothesis, and further work is needed to verify the impact of incompatibility between the imbibing fluid and the formation water on the flooding process.

4. Conclusions

Seawater acts as an EOR fluid in chalk at high temperatures because it is able to improve the water wetness of the rock. The chemical mechanism has been studied in detail, and the interaction between Ca^{2+}, Mg^{2+}, and SO$_4^{2-}$ in seawater and the chalk surface played an important role.[2] The question that was addressed in this paper was "Will the same interactions between seawater and reservoir limestone cores take place even though the surface area as well as the reactivity of the limestone surface is believed to be lower than for chalk?" In general, the type of interactions between SW and limestone were similar to chalk, and the main conclusions drawn were as follows: (i) The chromatographic wettability test based on separation between the tracer, SCN$^-$, and SO$_4^{2-}$ at the water-wet surface sites is also applicable to limestone; i.e., SO$_4^{2-}$ is adsorbed onto the surface. (ii) In a NaCl solution at room temperature, Ca^{2+} and Mg^{2+} appeared to have similar affinity toward the limestone surface. At higher temperatures, the affinity of Mg^{2+} was superior to that of Ca^{2+}. (iii) In seawater, the relative interaction between Ca^{2+} and Mg^{2+} toward limestone is dictated by the presence of SO$_4^{2-}$. Ca^{2+} appeared to adsorb more strongly than Mg^{2+} because of the ion-pair formation between Mg^{2+} and

(18) Standnes, D. C.; Austad, T. *J. Pet. Sci. Eng.* **2000**, *28* (3), 111–121.

(19) Standnes, D. C.; Austad, T. *J. Pet. Sci. Eng.* **2000**, *28* (3), 123–143.

(20) Standnes, D. C.; Nogaret, L. A. D.; Chen, H.-L.; Austad, T. *Energy Fuels* **2002**, *16* (6), 1557–1564.

(21) Nielsen, C. M.; Olsen, D.; Bech, N. Paper SPE 63226 presented at the SPE Annual Technology Conference and Exhibition, Dallas, TX, Oct 1−4, 2000.

SO_4^{2-} and the strong adsorption of SO_4^{2-} onto the rock. (iv) The water wetness of a reservoir limestone core cleaned by toluene and methanol can be improved by flooding the core with seawater at high temperature, 130 °C. Seawater can then act both as a cleaning agent and as a wettability modifier. (v) The oil recovery at 120 °C by spontaneous imbibition was about 15% higher when the limestone core was imbibed with seawater compared to seawater without SO_4^{2-} present, confirming that seawater will act as an EOR fluid/"smart water" also in limestone at certain conditions.

Nomenclature

A = adsorption area
AN = acid number (mg of KOH/g)
BN = base number (mg of KOH/g)
D = core diameter (cm)
IS = ionic strength

k = permeability (mD)
L = core length (cm)
NaCl-M = NaCl brine containing equal amounts of Ca^{2+}, Mg^{2+}, and tracer SCN^-
OOIP = original oil in place (mL)
PV = pore volume
Q = flow rate (mL/min)
S-brine = initial formation brine
SK = Stevns Klint
S_{wi} = initial water saturation (%)
S_{wr} = residual water saturation (%)
SW = synthetic seawater
$SW^{1}/_2M$ = synthetic seawater where the concentration of SCN^- and SO_4^{2-} is 0.012 mol/L
SW0S = synthetic seawater without SO_4^{2-}
SW3S = synthetic seawater with 3 times the SO_4^{2-} concentration compared to seawater
SW-U = synthetic seawater without SO_4^{2-} and SCN^-
TDS = total dissolved solids (g/L)
T_{res} = reservoir temperature
V_b = bulk volume (cm^3)
wt % = weight percent
Φ = porosity (%)