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Surface Complexation Modeling of Calcite Zeta Potential Measurements in Brines with Mixed Potential Determining Ions (Ca^{2+} , CO_3^{2-} , Mg^{2+} , SO_4^{2-}) for Characterizing Carbonate Wettability

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ABSTRACT: This study presents experiment and surface complexation modeling (SCM) of synthetic calcite zeta potential in brine with mixed potential determining ions (PDI) under various CO₂ partial pressures. Such SCM, based on systematic zeta potential measurement in mixed brines (Mg²⁺, SO₄²⁻, Ca²⁺ and CO₃²⁻), is currently not available in the literature and is expected to facilitate understanding of the role of electrostatic forces in calcite wettability alteration. We first use a double layer SCM to model experimental zeta potential measurements and then systematically analyze the contribution of charged surface species. Calcite surface charge is investigated as a function of four PDIs and CO₂ partial pressure. We show that our model can accurately predict calcite zeta potential in brine containing a combination of four PDIs and apply it to predict zeta potential in ultra-low and pressurized CO₂ environments for potential application in enhanced oil recovery in carbonate reservoirs. Model prediction reveals that calcite surface will be positively charged in all considered brines in pressurized CO₂ environment (>1atm). The calcite zeta potential is sensitive to CO₂ partial pressure in the various brine in the order of Na₂CO₃ > Na₂SO₄ > NaCl > MgCl₂ > CaCl₂ (Ionic strength=0.1M).

KEYWORDS: Zeta Potential, Surface Complexation Model, Calcite Surface Charge, Wettability Alteration, Enhanced Oil Recovery, Smart Water Flooding

1. Introduction

1.1 Charge of Carbonate for Wettability Study

The injection of “smart water”, which refers to brine with designed ionic composition, can significantly increase oil recovery in a low-cost and effective way for carbonate reservoirs. The majority of carbonate reservoirs are preferentially oil-wet because of the strong affinity between the carbonate rock and the crude oil originating from charge interactions¹. The current working hypothesis is that smart water alters the wettability of carbonate reservoirs to more hydrophilic condition, namely water-wet, which in turn releases crude oil attached to the rock surface, yet the underlying mechanisms regarding how smart water operates remain unclear.^{1–12}

Carbonate surface is usually positively charged in brine as a result of complicated calcite surface reactions whereas crude oil in brine carries negative charges due to the partitioning of dissociated fatty acids at the oil/brine interface.¹³ Because of the electrostatic attraction, crude oil tends to adhere to carbonate rock surface and alter the wettability of carbonate rock to oil-wet conditions. Restoring the wettability of oil-wet carbonate rock to preferentially water-wet can significantly improve the oil recovery by eliminating the capillary entry pressure of injecting brine and increasing the relative permeability of oil.

Electrostatic interaction plays a crucial role in determining the surface wettability.¹⁴ Jackson et al.¹⁵ experimentally demonstrated the strong correlation between carbonate surface wettability and charge interaction among mineral/brine/oil. It is thought that multivalent ions are the potential determining ions (PDIs) that govern the surface charge of the rock^{1,2,5,10}. Most research has focused on divalent ions Ca^{2+} , CO_3^{2-} , Mg^{2+} and SO_4^{2-} which are abundant in most carbonate reservoirs. Divalent ions such as Ca^{2+} and CO_3^{2-} are found in equilibrium with calcite, the main

mineral in carbonate rock, and Mg^{2+} and SO_4^{2-} naturally exist in seawater, which is extensively used as injection fluid. Yet, the exact mechanism of how these four PDIs affect the wettability of calcite remains controversial.^{1,2,11,12,16–18} Investigating how Ca^{2+} , CO_3^{2-} , Mg^{2+} and SO_4^{2-} influence the charge of calcite is needed for understanding wettability alteration induced by “smart water”.

1.2 Zeta Potential Measurement of Carbonate in Brines

Due to the rapid dissolution and precipitation of calcite in brine, it is impractical to measure the surface charge by direct titration methods. Therefore, zeta potential measurements are the most commonly used method to quantify the electrostatic properties of calcite surface in brines. Somasundaran and Agar¹⁹ first reported the zero point of charge (ZPC) of calcite by measuring streaming potential as a function of pH in 1967. Then Thompson and Pownall²⁰ compared two different approaches of changing solution pH, by adding strong acid/base or adding $\text{H}_2\text{CO}_3/\text{Ca}(\text{OH})_2$, and concluded that the calcite potential determining ions are Ca^{2+} and CO_3^{2-} but not H^+ and OH^- . Recently, there is an increasing interest in carbonate zeta potential measurement for wettability alteration study. For example, Strand et al.¹ and Zhang et al.² measured the zeta potential of outcrop chalk in synthetic seawater to demonstrate their proposed mechanism of wettability alteration by surface ion exchange. Mahani et al.³ measured zeta potential of limestone in seawater and formation water in a wide range of pH to help study the wettability alteration by low salinity flooding. Alroudhan et al.⁷ measured the zeta potential of natural limestone in seawater and brines that varied in composition. Kasha et al.¹⁰ measured zeta potential of limestone and Iceland spar aged in stearic acid in solutions with Ca^{2+} , Mg^{2+} and SO_4^{2-} , trying to study the effect of stearic acid adsorption on zeta potential. Alotaibi et al.²¹ measured limestone and dolomite zeta potential in aquifer water and seawater and investigated

the effect of temperature and divalent ions Mg^{2+} , Ca^{2+} , SO_4^{2-} . The mineral surfaces showed negative zeta potential in a wide range of brine compositions at neutral pH (pH=7). Then Alotaibi and Yousef²² measured zeta potential of natural carbonate disk in different electrolyte solutions along with zeta potential of crude oil in these solutions to demonstrate the brine composition effects on oil/rock interaction. Jackson et al.¹⁵ measured the streaming potential of limestone in synthetic seawater and formation brine to demonstrate the importance of charge interaction for enhanced oil recovery by controlled salinity water flooding. Alshakhs and Kovscek²³ took zeta potential measurement of pure calcium carbonate powder in diluted synthetic seawater (SW) and modified diluted SW with extra Mg^{2+} and SO_4^{2-} at various pH condition. The measured zeta potential was used to calculate the electrostatic component of disjoining pressure isotherm for demonstrating the effects of Mg^{2+} and SO_4^{2-} on rock wettability.

Though there have been numerous studies regarding the role of calcite surface charge, there remains significant controversies and inconsistencies in reported zeta potential measurements for the purpose of understanding rock wettability^{7,23}. There are several reasons that can lead to this discrepancy in zeta potential reported in literature. First, the natural rocks tested in experiments are highly heterogeneous. Vdovic' et al.^{24,25} showed that natural calcite, which contains trace amount of organic matters, has a completely different surface charge compared to synthetic calcite. The surface charge of natural calcites, such as limestone, chalk, and carbonates, highly depends on the mineral history and source, so the results cannot be easily utilized for modeling or comparison to similar minerals. Second, CO_2 partial pressure is not strictly controlled in most of these studies. However, CO_2 partial pressure can show dramatic impact on the surface potential of calcite by changing carbonate ion concentration in the brine.²⁶ Under reservoir conditions, the CO_2 partial pressure can be higher than 3000psi in the case of miscible CO_2

flooding.²⁷ Third, synthetic seawater is oftentimes used as the aqueous phase. The effect of potential determining ions (PDIs), such as Ca^{2+} , CO_3^{2-} , Mg^{2+} and SO_4^{2-} , on synthetic calcite surface charge under equilibrium condition with CO_2 has not been systematically studied. Here we report the zeta potential of calcite in brines containing PDIs to further fundamental understanding and modeling of calcite wettability alteration.

1.3 Surface Complexation Modeling of Calcite in Brines

The surface complexation model (SCM) is widely used to model the surface charge of minerals. For the case of calcite, SCM can be used in reservoir simulations of “smart water” flooding and low salinity flooding.^{28,29} It can also be used to calculate disjoining pressure isotherm and predict contact angle for the purpose of understanding surface wettability^{14,30,31}.

Van Cappellen et al.³² developed a SCM using the calcite point of zero charge (PZC) to determine model parameters. Pokrovsky et al.³³ modified the model with the same surface reactions based on their FTIR data. Brady et al.³⁴ followed the same SCM and used equilibrium constants of solution analogues to define surface reactions associating with Mg^{2+} and SO_4^{2-} , however they lacked zeta potential measurements to confirm the accuracy of the equilibrium constants. Mahani et al.³⁵ proposed a SCM to fit their zeta potential measurements of natural calcite (Iceland spar, limestone and chalk) in mixed brines with multiple PDIs. Yet the model was not satisfactory in terms of matching the measured data or catching the trend of the curve. The discrepancy is partially because no organic impurity reaction was included in the model to account for the differences between natural calcite and synthetic calcite surfaces. Heberling et al.²⁶ proposed a Stern-model SCM with surface reactions based on electrostatic attraction between charged surface sites and ions in the aqueous phase. In Heberling's work, a series of zeta

potential were measured by adjusting pH of solutions and equilibrating the samples with three different CO₂ partial pressure. Intrinsic reaction equilibrium constants are determined by fitting with zeta potential measurement. However only NaCl was used as brine in all experiments; therefore, Ca²⁺ and CO₃²⁻ were present as a result of calcite dissolution. The role of divalent ions such as Mg²⁺ and SO₄²⁻, which have been proven to be crucial for wettability alteration by “smart water”^{1,2,11} has not been investigated.

Here we present zeta potential measurements of synthetic calcite in mixed brines containing four PDIs and then develop a generalized double layer SCM to model the experimental results. The novelty of this work is to quantify the individual contribution of Ca²⁺, CO₃²⁻, Mg²⁺ and SO₄²⁻ on synthetic calcite surface charge. Moreover, we provide further clarification for the impact of CO₂ partial pressure in calcite system. This is of great importance because CO₂ generally exists in natural reservoirs as a component in produced gas and it can also be introduced as injection gas in the case of miscible CO₂ flooding.

2. Materials and Methods

2.1 Sample Preparation for Zeta Potential Measurement

The synthetic calcite powder ($\geq 99.5\%$, 5 μm in diameter, from Alfa Aesar) was crushed and grounded using a mortar and pestle for 1 hour to make it finer ($\sim 1\mu\text{m}$ in diameter). Brines were prepared with DI water ($18.2\text{M}\Omega\cdot\text{cm}$) and ACS grade electrolytes including NaCl, NaHCO₃, Na₂CO₃•H₂O, CaCl₂•2H₂O, MgCl₂•6H₂O and Na₂SO₄•10H₂O (all $\geq 99.0\%$). All tested brines in this work had the same ionic strength of 0.1M in order to keep the Debye length constant. The concentration of all four PDIs varied in the range of 0 ~ 33 mM in the brine before equilibration.

A mass of 0.6g ground calcite powder and 75 mL brine were mixed to make 0.8%wt. sample. A sonifier (Branson) was used to sonicate the sample for 1 min to facilitate calcite dispersion.

Equilibrium is crucial for repeatability and reproducibility of zeta potential measurements. A home-made gas bubbling system including an air pump or a CO₂ tank and a gas humidifier was set up to bubble gas through the dispersion to equilibrate the sample with atmosphere air (gas phase $10^{-3.4}$ atm CO₂, equivalent to 400ppm CO₂) or pure CO₂ (gas phase 1atm CO₂) until the measured pH reached a calculated reference value predicted by PHREEQC, a widely used geochemistry software developed by US Geological Survey. By this procedure, calcite/brine/CO₂ three phase equilibrium is achieved. Sample equilibration typically occurred over a period of 1-4 days, where samples were weighed on a daily basis and DI water were added when needed to account for water loss due to evaporation. Samples equilibrated with pure CO₂ were sealed from atmosphere by storing in capped bottle before testing and were tested as soon as possible (within 5min after removing pure CO₂ gas source).

Before zeta potential measurements were performed, samples were sonicated by sonifier (Branson) for 1 min to separate calcite particles that may have agglomerated during the equilibration process. It is particularly important to make sure the calcite weight percent is not too high, otherwise calcite particles move as clusters instead of individual particles in electric field, causing inaccuracy of zeta potential measurement. So the calcite particles were allowed to settle down for 1 hour to obtain supernatant with calcite weight percent 0.01%-0.03%. Supernatant (~65mL) was transferred into a new vial for analysis.

Calcite mobility in brine was measured by electrophoretic phase analysis light scattering (PALS) method in a light scattering analyzer (DelsaMax PRO). The zeta potential of the calcite

surface was calculated using the Smoluchowski equation. Each sample was measured 6-10 times to minimize experiment artifacts. Mean value and standard deviation were obtained.

2.2. Quantification of Supernatant Calcite Weight Percent

The calcite weight percent of samples were quantified by measuring light transmittance using UV-Vis spectroscopy. Calibration curve was made by measuring light transmittance of calcite dispersion in 0.1M NaCl brine with various (known) weight percent. Wavelength 560nm was selected for the transmittance measurement which gave a perfect linear calibration curve (see supplementary material). Calcite weight percent of supernatant was in the range of 0.01% ~ 0.03% for all samples. Zeta potential measurement was experimentally proved to be independent of calcite weight percent in this range in preliminary experiment (see supplementary material).

2.3. Surface Complexation Model (SCM)

A generalized double layer model with a surface plane and a diffuse layer was used in this work (Figure 1). Surface potential is equivalent to the potential at the outer Helmholtz plane ($x = x_d$) where all ions are considered being absorbed in the same plane. As described by Borkovec and Westall³⁶, the Poisson-Boltzmann equation is used to establish the relationship of potential and concentration of ions in brine. The equations can be solved for both symmetrical and asymmetrical electrolyte systems.

The unreacted Ca^{+x} atom exposed at the surface of calcite crystal ideally has +1/3 charge instead of +1 charge due to the structure of calcite^{4,26} ($>\text{Ca}^{+1/3}$). As is described by Stipp⁴, the value x is strictly equal to +1/3 only when the bonding between the Ca atom and the O atoms from neighboring CO_3^{2-} is pure ionic bonding, which is not the case. As described in Heberling's work²⁶, we also assumed a value 0.25 ($>\text{Ca}^{+0.25}$) in this work. In an aqueous environment,

unreacted $>\text{Ca}^{+0.25}$ will bond with hydroxyl ion (OH^-) in water and becomes $>\text{CaOH}^{-0.75}$. Therefore, the two major surface sites are $>\text{CaOH}^{-0.75}$ and $>\text{CO}_3\text{H}^{+0.75}$ (site density 4.95nm^{-2}) in this system. As a result of electrostatic interaction, $>\text{CaOH}^{-0.75}$ and $>\text{CO}_3\text{H}^{+0.75}$ can bind with ions of the opposite charge in the aqueous phase and be converted to other charged surface complexes. The surface reactions described in Table 1 are based on electrostatic attraction that are assumed to influence the surface charge of calcite. Intrinsic equilibrium constants, K_1 and K_2 and intrinsic equilibrium ion binding constants, IB_1 to IB_7 , are the nine tunable variables for fitting zeta potential measurements. The intrinsic equilibrium constants are functions of ion activities at the calcite/brine interface and surface species concentrations. The ion activities at the calcite/brine interface and the bulk solution ion activities are different and follow the Boltzmann distribution of ions (Eq. 1)³⁷, where z_i is the charge of ion i (can be positive or negative) and ψ is surface potential:

$$C_i = C_{i,\infty} \exp\left(\frac{-z_i F \psi}{RT}\right) \quad (\text{Eq. 1})$$

All zeta potential measurements were found to be in the range from -20mV to 25mV, where the surface potential can be considered small and the Debye-Huckel equation applies. Measured zeta potentials were converted to surface potential using the Debye-Huckel equation³⁷ (as is shown in Figure 1). The Debye length, κ^{-1} , is considered constant for all solutions with constant ionic strength 0.1M and slipping plane distance d_s is set to 0.33nm based on the slip plane distance – ionic strength relationship in the literature²⁶.

PHREEQC (Version 3.3.7)³⁸, a widely used software developed by USGS for geological system equilibrium calculation, is used for thermodynamic equilibrium calculation. The double layer model with explicit calculation of diffuse layer composition, initially proposed by

Borkovec and Westall, is selected in PHREEQC. Activities in non-ideal solutions are calculated using ion-association and Debye Huckel expressions. By defining surface reactions and the equilibrium constant values, PHREEQC calculates the surface potential at a given equilibrium condition. PEST³⁹ is combined with PHREEQC for optimization of adjustable parameters (K_1 , K_2 , $IB_1 \sim IB_7$) to fit the experimentally determined zeta potential measurements.

Figure 1 The schematic of the double layer model. The ψ equals to ψ_0 up to z_d and then decays exponentially with the distance z as governed by Debye-Huckel Equation

Table 1 Surface complexation reactions in the proposed model

surface reaction	intrinsic equilibrium constants
$>CaOH^{-0.75} + H^+ \rightleftharpoons >CaOH_2^{+0.25}$	K_1
$>CO_3H^{+0.75} + OH^- \rightleftharpoons >CO_3^{-0.25} + H_2O$	K_2
$>CaOH^{-0.75} + Ca^{2+} \rightleftharpoons >CaOH \cdots Ca^{+1.25}$	IB_1
$>CaOH^{-0.75} + Mg^{2+} \rightleftharpoons >CaOH \cdots Mg^{+1.25}$	IB_2
$>CO_3H^{+0.75} + CO_3^{2-} \rightleftharpoons >CO_3H \cdots CO_3^{-1.25}$	IB_3
$>CO_3H^{+0.75} + SO_4^{2-} \rightleftharpoons >CO_3H \cdots SO_4^{-1.25}$	IB_4
$>CO_3H^{+0.75} + HCO_3^- \rightleftharpoons >CO_3H \cdots HCO_3^{-0.25}$	IB_5
$>CaOH^{-0.75} + Na^+ \rightleftharpoons >CaOH \cdots Na^{+0.25}$	IB_6
$>CO_3H^{+0.75} + Cl^- \rightleftharpoons >CO_3H \cdots Cl^{-0.25}$	IB_7

3. Results and Discussion

3.1. Zeta Potential Measurement

The zeta potential of calcite in different brines ($I=0.1M$) is shown in Figure 2. The baseline case is calcite in 0.1M NaCl brine because both Na^+ and Cl^- are generally not considered potential-determining ions. Compared to NaCl (middle columns), divalent anions such as CO_3^{2-} and SO_4^{2-} result in the calcite becoming less positively charged and in some cases even negatively charged, while cations Ca^{2+} and Mg^{2+} further increases the positive charge of calcite. Note that for the cases presented, the equilibrium H^+ concentration varies 2~3 order of magnitudes (100 - 1000 times) when the CO_2 partial pressure changes from 400ppm to 1atm; however, the zeta potential is not significantly altered for the NaCl, $CaCl_2$, $MgCl_2$ samples. This is not the case when the solution pH is altered by adding an acid, such as HCl, which shows a dramatic impact on zeta potential since there is a change the relative concentration of the PDIs.

Figure 2 Zeta potential of calcite in different single component brines. Red bars were measured under $P_{CO_2}=10^{-3.4}$ atm (400ppm) whereas black bars were measured under $P_{CO_2}=1$ atm. The ionic strength was $I=0.1M$ for all measurements.

Changes in the calcite zeta potential when mixing the NaCl brine with CaCl₂, MgCl₂, Na₂SO₄ and Na₂CO₃ respectively to different ratios are shown in Figure 3. The ionic strength of brines was kept constant while the concentration of PDIs (Ca²⁺, Mg²⁺, CO₃²⁻, SO₄²⁻) was changed. The horizontal axis on the figures are used to show the initial concentration of a given PDI in the brine solution. However, for the case of Ca²⁺ and CO₃²⁻, the initial concentration and equilibrium concentration can be dramatically different as a result of calcite dissolution.

Varying CO₂ partial pressure from 10^{-3.4}atm to 1atm does not appear to significantly affect the zeta potential of calcite in the tested brines with high Ca²⁺ or Mg²⁺ concentrations. However, for brines containing a high concentration of CO₃²⁻, there is a significant change in the zeta potential of calcite (up to 20mV). Further analysis of the change of zeta potential of calcite and variation of charged species concentration can be analyzed using the SCM.

Figure 3 Zeta potential of calcite in the mixed brines. The ionic strength ($I=0.1\text{M}$) was the same in all measurements. Upper left is NaCl/CaCl₂ brine (to different mixed ratios); upper right is NaCl/MgCl₂ brine; lower left is NaCl/Na₂CO₃ brine; and lower right is NaCl/Na₂SO₄ brine. Red data were measured under $P_{\text{CO}_2}=10^{-3.4}$ atm (400ppm) and black data were measured under $P_{\text{CO}_2}=1$ atm.

3.2. Surface Complexation Modeling (SCM)

A total of 34 experimental measurements of zeta potential were used to fit the 9 adjustable parameters (K_1 , K_2 , $\text{IB}_1\sim\text{IB}_7$). Additionally, two different CO₂ partial pressure environments were tested and the concentration of PDIs was varied in a relatively wide range among all 34 observations to better optimize the fitting parameters. Based on PHREEQC calculations, equilibrium Ca²⁺ concentration ($[\text{Ca}^{2+}]$) ranged from $2 \times 10^{-6}\text{M}$ to $4 \times 10^{-2}\text{M}$, $[\text{CO}_3^{2-}]$ ranged from $6 \times 10^{-7}\text{M}$ to $1 \times 10^{-2}\text{M}$, while $[\text{Mg}^{2+}]$ and $[\text{SO}_4^{2-}]$ ranged from 0 to $3 \times 10^{-2}\text{M}$.

The optimized parameters are listed in Table 2 and compared with experimental observations in Figure 4. The association constants for divalent ions ($IB_1 \sim IB_4$) are at least one order of magnitude higher than those determined for the monovalent ions (K_1 , K_2 , $IB_5 \sim IB_7$), indicating that the divalent ions in the brine are the main factor determining the variation of calcite surface charge. The small values of K_1 and K_2 also indicate that H^+ is not a PDI for calcite. For the ions with the same valence and surface binding sites, it is observed that the binding constants are negatively correlated to the ionic radius. $IB_3 > IB_4$, $\text{radii}(\text{CO}_3^{2-}) < \text{radii}(\text{SO}_4^{2-})$; $IB_5 > IB_7$, $\text{radii}(\text{HCO}_3^-) < \text{radii}(\text{Cl}^-)$; $IB_1 > IB_2$, $\text{radii}(\text{Mg}^{2+}) > \text{radii}(\text{Ca}^{2+})$ (the ionic radius were compared at ambient temperature⁴⁰). The fitted parameters are compared with a similar basic-Stern SCM proposed by Heberling et al²⁶. The major difference is the value of K_2 . In our presented model, K_1 and K_2 are both close to zero, indicating a weak dependence of surface charge to pH. In the original work of Heberling et al²⁶, reaction 2 is expressed as $>\text{CO}_3\text{H}^{+0.75} \rightleftharpoons >\text{CO}_3^{-0.25} + \text{H}^+$, $\log_{10}K = 0.17$. The water dissociation constant is assumed to be 10^{-14} to calculate the K_2 in Table 2. However, if K_2 is as high as 14.17, the majority of major sites $>\text{CO}_3\text{H}^{+0.75}$ will be converted to $>\text{CO}_3^{-0.25}$, which is unlikely.

Table 2 Parameterization of Surface Complexation Modeling

parameter ($\log_{10}K$)	value	literature(Heberling ²⁶)	surface reactions
K_1	0.30	-0.17	$>CaOH^{-0.75} + H^+ \rightleftharpoons >CaOH_2^{+0.25}$
K_2	0.50	14.17	$>CO_3H^{+0.75} + OH^- \rightleftharpoons >CO_3^{-0.25} + H_2O$
IB_1	1.74	1.68	$>CaOH^{-0.75} + Ca^{2+} \rightleftharpoons >CaOH \cdots Ca^{+1.25}$
IB_2	1.62	-	$>CaOH^{-0.75} + Mg^{2+} \rightleftharpoons >CaOH \cdots Mg^{+1.25}$
IB_3	2.23	3.26	$>CO_3H^{+0.75} + CO_3^{2-} \rightleftharpoons >CO_3H \cdots CO_3^{-1.25}$
IB_4	1.00	-	$>CO_3H^{+0.75} + SO_4^{2-} \rightleftharpoons >CO_3H \cdots SO_4^{-1.25}$
IB_5	0.09	0.04	$>CO_3H^{+0.75} + HCO_3^- \rightleftharpoons >CO_3H \cdots HCO_3^{-0.25}$
IB_6	0.14	0.56	$>CaOH^{-0.75} + Na^+ \rightleftharpoons >CaOH \cdots Na^{+0.25}$
IB_7	-0.64	-0.05	$>CO_3H^{+0.75} + Cl^- \rightleftharpoons >CO_3H \cdots Cl^{-0.25}$

Figure 4 Comparison between measured calcite zeta potential and the surface complexation modeling in the mixed brines. Upper left is NaCl/CaCl₂ brine; upper right is NaCl/MgCl₂ brine; lower left is NaCl/Na₂CO₃ brine; and lower right is NaCl/Na₂SO₄

brine. Red data were measured under $P_{CO_2}=10^{-3.4}$ atm (400ppm) and black data were measured under $P_{CO_2}=1$ atm.

Because the calcite zeta potential is determined by surface speciation, the analysis of surface species contribution can provide better insights on the observed zeta potential trends. We introduce the contribution of a surface charged species i $contribution(i)$ to quantify the surface species contribution. It is defined as the product of its surface concentration and the molar fraction of this species, as shown in Eq. 2.

$$\begin{aligned} contribution(i) &= frac(i) \cdot z_i \\ frac(i) &= \frac{[surface\ specie\ i]}{[>CaOH^{-0.75}]_0} \quad (cationic\ surface\ species) \\ frac(i) &= \frac{[surface\ specie\ i]}{[>CO_3H^{+0.75}]_0} \quad (anionic\ surface\ species) \end{aligned} \quad Eq. (2)$$

In the previous literature, the surface concentration was used to compare and analyze different species' contribution. However, such comparison and analysis suffer two major drawbacks: (1) the surface concentration failed to include the effect of valency of the species. Given the same surface concentration, surface species of different valences contribute differently to the surface charge. (2) The practice of using surface concentration for comparison is not convenient. Because the surface concentrations span several orders of magnitude for different species, it is hard to compare in normal scale. However, when plotted the surface concentration in log-scale, the contribution, in turn, seems to be equally important for many different species. The definition of $contribution(i)$ overcomes the two drawbacks. It normalizes the contribution of different species within the range of 0~1, which allows the analysis to be clearer and more intuitive.

The major surface sites of calcite surface are $>\text{CO}_3\text{H}^{+0.75}$ and $>\text{CaOH}^{-0.75}$. Under all brine conditions tested, the calculation shows that their contribution outweigh all other species: contribution ($>\text{CO}_3\text{H}^{+0.75}$) ranges from 0.68 to 0.72 and contribution ($>\text{CaOH}^{-0.75}$) ranges from -0.72 to -0.63, while contribution of all other species is within ± 0.16 . This indicates that only a small portion of the major sites are converted to a charged surface complex. Instead of analyzing $>\text{CO}_3\text{H}^{+0.75}$ and $>\text{CaOH}^{-0.75}$ contribution individually, the algebraic sum of $>\text{CO}_3\text{H}^{+0.75}$ and $>\text{CaOH}^{-0.75}$ contributions are used for analysis. The variation of charged species contribution and zeta potential under two different P_{CO_2} in different brines are shown in Figure 5 – Figure 8. The net charge of the calcite surface, which directly correlates to zeta potential, is calculated by summing up contributions of all charged species.

The surface species contribution analysis also sheds light upon the mechanism of carbonate wettability alteration in the presence of PDIs. As shown in Figure 5, the $>\text{CaOH}\dots\text{Ca}^{+1.25}$ contribution increases when the initial SO_4^{2-} concentration is higher. This observation provides additional proof to the hypothesis proposed by Strand et al.¹ and Zhang et al.² that the presence of SO_4^{2-} can lower the surface charge of calcite and facilitate the free Ca^{2+} in solution to bind and release the surface carboxylic acid. However, the experimental results also reveal another possible explanation for the calcite wettability alteration. It is observed that the positively charged synthetic calcite surface can be tuned to carry negative charge by simply increasing the amount of SO_4^{2-} in the brine. When the calcite surface becomes negatively charged, the carboxylic acid will be repelled from the surface by electrostatic forces. In other words, the SO_4^{2-} itself can induce the wettability alteration without the aid of Mg^{2+} . Further investigation of wettability alteration by contact angle measurement and spontaneous imbibition will be required to verify this hypothesis.

Another interesting observation is that the CO_2 partial pressure can affect the zeta potential by changing the initial Ca^{2+} concentration in solution. Increasing CO_2 partial pressure will lower the CO_3^{2-} concentration, resulting in a higher Ca^{2+} concentration and therefore increasing the zeta potential. Consequently, if the reservoir is pressurized with a high CO_2 content, the correspondingly high Ca^{2+} concentration will make it more difficult for the carbonate surface to become negatively charged.

Figure 5 Contribution analysis of charged surface species for calcite in the mixed brines of $\text{NaCl}/\text{Na}_2\text{SO}_4$ ($I=0.1\text{M}$). The surface species that make the major contribution are highlighted.

Based on our model, in the mixed brine of $\text{NaCl}/\text{Na}_2\text{CO}_3$, the dominant charged species vary as a function of CO_2 partial pressure, as shown in Figure 6. When $P_{\text{CO}_2}=10^{-3.4}\text{atm}$, increasing

$[>\text{CO}_3\text{H}\dots\text{CO}_3^{-1.25}]$ is the major reason why the calcite zeta potential becomes more negative when the initial CO_3^{2-} concentration increases. However, when $P_{\text{CO}_2}=1\text{atm}$, the rise of $[>\text{CaOH}\dots\text{HCO}_3^{-0.25}]$ and drop of $[>\text{CO}_3\text{H}\dots\text{Ca}^{+1.25}]$ are responsible for the variation of zeta potential. Because of the high CO_2 partial pressure, a large portion of CO_3^{2-} is converted to HCO_3^- in equilibrium. So $>\text{CO}_3\text{H}\dots\text{CO}_3^{-1.25}$ is not one of the dominant species under such CO_2 partial pressure. The CO_2 partial pressure shows a dramatic effect on calcite charge in CO_3^{2-} concentrated brines because the equilibrium CO_2 phase can significantly vary the equilibrium $[\text{CO}_3^{2-}]$ from initial CO_3^{2-} concentration. In the case of $P_{\text{CO}_2}=1\text{atm}$, equilibrium $[\text{CO}_3^{2-}]$ is so low that the charge of the calcite surface is a result of Ca^{2+} adsorption.

Figure 6 Contribution analysis of charged surface species for calcite in the mixed brines of $\text{NaCl}/\text{Na}_2\text{CO}_3$ ($I=0.1\text{M}$). The surface species that make the major contribution are highlighted.

Figure 7 shows the variation of contributions of charged surface species in the brines of $\text{CaCl}_2/\text{NaCl}$. For both cases of $P_{\text{CO}_2}=10^{-3.4}\text{atm}$ and $P_{\text{CO}_2}=1\text{atm}$, $[>\text{CaOH}\dots\text{Ca}^{+1.25}]$ dominates the surface charge variation when initial Ca^{2+} concentration increases. Furthermore, calcite zeta potentials are almost the same if the initial Ca^{2+} concentration is high but are somewhat different if the initial Ca^{2+} concentration is low. This is because P_{CO_2} affects equilibrium $[\text{Ca}^{2+}]$ as a function of the initial Ca^{2+} concentration. Increasing P_{CO_2} can raise equilibrium $[\text{Ca}^{2+}]$ by converting CO_3^{2-} into HCO_3^- , causing a shifting in the calcite dissolution equilibrium. Such impact is negligible when the initial Ca^{2+} concentration is high (close to 0.033M) because the CO_3^{2-} concentration is low even before equilibration. Based on PHREEQC calculations, when the brine is $I=0.1\text{M}$ NaCl (no initial Ca^{2+} before equilibrium), the equilibrium $[\text{Ca}^{2+}] = 8.1 \times 10^{-4}\text{M}$ at $P_{\text{CO}_2}=10^{-3.4}\text{atm}$ versus the equilibrium $[\text{Ca}^{2+}]$ is $1.1 \times 10^{-2}\text{M}$ at $P_{\text{CO}_2}=1\text{atm}$.

Figure 7 Contribution analysis of charged surface species for calcite in the mixed brines of NaCl/CaCl₂ (I=0.1M). The surface species that make the major contribution are highlighted.

Mg²⁺ as a PDI shows positive impact on the calcite surface charge by forming positively charged surface complex $>\text{CaOH}\dots\text{Mg}^{+1.25}$ (Figure 8). This effect is similar to Ca²⁺ shown in Figure 7 except that in I=0.1M MgCl₂ solution the calcite zeta potential is 2~3mV lower than that in I=0.1M CaCl₂ solution for both CO₂ partial pressures. Unlike Ca²⁺, which indirectly participates in the equilibrium of CO₃²⁻ due to a constant CaCO₃ solubility product, increasing the Mg²⁺ concentration does not impact bulk solution CO₃²⁻ concentration. Thus in I=0.1M MgCl₂ solution, $[>\text{CO}_3\text{H}\dots\text{CO}_3^{-1.25}]$ and $[>\text{CO}_3\text{H}\dots\text{HCO}_3^{-0.25}]$ are higher than those in I=0.1M CaCl₂ solution, resulting in the relatively lower zeta potential. Moreover, at $P_{\text{CO}_2}=1\text{atm}$, we observe a decrease of $>\text{CaOH}\dots\text{Ca}^{+1.25}$ contribution as Mg²⁺ concentration increases. Increasing

Mg^{2+} concentration makes calcite surface more positively charged, resulting in stronger electrostatic repulsion between Ca^{2+} and calcite surface. So $[\text{Ca}^{2+}]$ near calcite/brine interface decreases when Mg^{2+} concentration increases, even though bulk Ca^{2+} concentration is nearly constant.

Figure 8 Contribution analysis of charged surface species for calcite in the mixed brines of NaCl/MgCl₂ (I=0.1M). The surface species that make the major contribution are highlighted.

In order to verify the validity and robustness of our model, an additional experiment condition was conducted but not included in the SCM model fitting to verify the validity of the parameters. A I=0.1M MgCl₂ solution and I=0.1M Na₂SO₄ solution were mixed together at varying ratios to obtain brines with different concentration of Mg^{2+} and SO_4^{2-} but the same ionic strength as 0.1M. Because Ca^{2+} and CO_3^{2-} always exist in the brine from calcite dissociation, the tested brines have

four PDIs present. The sample were equilibrated at atmospheric condition (400 ppm CO₂). The measured zeta potential is compared with our model prediction in Figure 9. The SCM successfully predicts the zeta potential of calcite in brines with all four PDIs, confirming the reliability of the model.

Figure 9 Model prediction and experimental measurement of calcite zeta potential in the mixed brine of MgCl₂/Na₂SO₄ (I=0.1M, $P_{CO_2} = 10^{-3.4}$ atm). These data were not included in the model parameter fitting.

Additionally, the impact of CO₂ partial pressure on calcite zeta potential for CO₂ is important to consider since in applications such as miscible CO₂ flooding, the CO₂ partial pressure can go to 3000 psi (10^{2.3} atm). The zeta potential of calcite in I=0.1M different electrolyte solutions as a function of CO₂ partial pressure is calculated using the presented model, shown in Figure 10. Ionic strength of equilibrium solution can deviate dramatically from 0.1M when $P_{CO_2} > 10$ atm, as

significant amount of CO_2 dissolved in the brine. At these conditions, the Debye length and slip plane distance are recalculated when converting surface potential to zeta potential.

The trend shows different characteristics in low P_{CO_2} (<1atm) region and high P_{CO_2} region. In the low P_{CO_2} region, the sensitivity of calcite zeta potential in different brines to gas phase CO_2 is in the sequence of $\text{Na}_2\text{CO}_3 > \text{Na}_2\text{SO}_4 > \text{NaCl} > \text{MgCl}_2 > \text{CaCl}_2$ (all $I=0.1\text{M}$). Due to the high initial concentration of Ca^{2+} in $I=0.1\text{M}$ CaCl_2 solution, equilibrium $[\text{Ca}^{2+}]$ will be in a high level and equilibrium $[\text{CO}_3^{2-}]$ will be low invariant of the CO_2 partial pressure. In this case, $[\text{CaOH} \dots \text{Ca}^{+1.25}]$ is the major contribution to surface charge and is not sensitive to the variation of CO_2 partial pressure. In $I=0.1\text{M}$ Na_2CO_3 solution, the situation is different because the major species CaCO_3^{2-} is strongly dependent on CO_3^{2-} concentration. For the rest cases of MgCl_2 , NaCl and Na_2SO_4 solution, the impact of CO_2 partial pressure obviously depends on the significance of $\text{CaOH} \dots \text{Ca}^{+1.25}$ and $\text{CaCO}_3^{1.25}$ contributions in the brine. For example, when $P_{\text{CO}_2}=1\text{atm}$, contribution of $\text{CaOH} \dots \text{Ca}^{+1.25}$ is 0.124 in $I=0.1\text{M}$ Na_2SO_4 solution, while in $I=0.1\text{M}$ NaCl it is 0.042 and it is 0.025 in $I=0.1\text{M}$ MgCl_2 solution. However, in the high CO_2 partial pressure region (>1atm), the calcite zeta potential in different brines tends to converge to around 10mV as the CO_2 partial pressure keep increases.

Figure 10 Model prediction of calcite zeta potential in I=0.1M different electrolyte solutions as a function of CO₂ partial pressure.

Species contribution analysis for calcite in I=0.1M NaCl is performed to understand the effect of P_{CO_2} , shown in Figure 11. When P_{CO_2} is low (<0.01atm), both net charge and the contribution of all surface species vary in a relatively small range. However, as P_{CO_2} increases, $>CaOH...Ca^{+1.25}$ and $>CO_3H...HCO_3^{-0.25}$ contributions have a dramatic rise simultaneously. At the same time, $>CaOH^{-0.75}$ becomes more abundant than $>CO_3H^{+0.75}$ ($P_{CO_2} > 0.25atm$) and contributes to the decrease of calcite zeta potential. The change in $>CaOH...Ca^{+1.25}$, $>CO_3H...HCO_3^{-0.25}$ and $>CaOH^{-0.75}$ contributions almost cancel each other out, resulting in the net charge of calcite only varying slightly when CO₂ partial pressure changes.

Figure 11 Contribution analysis of charged surface species for calcite in I=0.1M NaCl under different CO₂ partial pressure. The surface species making the major contributions are highlighted.

4. Conclusions

The zeta potential of synthetic calcite in brines containing different PDIs (Mg^{2+} , SO_4^{2-} , Ca^{2+} , CO_3^{2-}) under $10^{-3.4}$ atm (400ppm) CO_2 and 1atm CO_2 were measured. The role of four major divalent ions that either naturally exist in carbonate reservoirs (Ca^{2+} , CO_3^{2-}) or enriched in seawater (Mg^{2+} , SO_4^{2-}) were investigated. The zeta potential of calcite can shift from positive to negative value when increasing the content of CO_3^{2-} or SO_4^{2-} in $P_{\text{CO}_2}=10^{-3.4}$ atm. However, when the system is equilibrated with 1atm CO_2 , even if the brine is Na_2CO_3 or Na_2SO_4 ($I=0.1\text{M}$) solution, the zeta potential of synthetic calcite does not become negative.

A new surface complexation model was proposed based on a generalized double layer model. Our model assumes that surface potential is equal to the potential at the substrate side of the diffuse layer. This model includes the effect of four divalent PDIs in carbonate reservoir thus can be useful for application of carbonate wettability alteration study. Compared to the previous SCM proposed by van Cappellen et al.³², Pokrovsky et al.³³ and Brady et al.³⁴, our model parameters are derived from direct zeta potential measurements and therefore are more realistic. Compared to the SCM proposed by Heberling et al.²⁶, our model has included two additional yet very crucial PDIs: Mg^{2+} and SO_4^{2-} and enhanced the robustness of the predictability to a wider range of ion concentrations. We confirm that the binding constants for divalent ions are at least one order of magnitude higher than those for monovalent ions, confirming the importance of divalent ions in determining calcite surface charge.

To our best knowledge, it is the first time that we discovered the negative correlation between the surface binding equilibrium constants and the hydrated ionic radius for ions of the same charge in a calcite surface complexation model. We have also proposed a new definition to quantify the contribution of charged specie. The use of the newly proposed quantity *contribution(i)* is clearer and more intuitive than surface concentration when comparing the

different ion's contribution to the overall surface charge. According to our surface species contribution analysis, it is revealed that increasing SO_4^{2-} content in the solution can effectively facilitate the adsorption of Ca^{2+} due to electrostatic interactions. High SO_4^{2-} concentration can effectively reduce the positively charged surface species concentration and make the surface negatively charged. Therefore, high SO_4^{2-} concentration can lead to the detachment of carboxylic acids as a result of electrostatic repulsion. Consequently, the mechanism of carbonate wettability alteration cannot simply be concluded from the charge interaction measurements. SO_4^{2-} can induce wettability alteration by either facilitating Ca^{2+} surface adsorption or changing the calcite surface to be negatively charged by itself.

We also highlight the role of CO_2 partial pressure in the study of wettability alteration in carbonate reservoirs. The species that make the major contributions to the calcite surface charge vary under different CO_2 partial pressures and the effect of CO_2 partial pressure is not monotonic.

We also used our model to predict the zeta potential of calcite in high CO_2 partial pressure up to 500atm (~7000psi) for possible applications in research of miscible CO_2 flooding. Prediction reveals that the sensitivity of calcite zeta potential to P_{CO_2} differs in different electrolyte solutions in the order of $\text{Na}_2\text{CO}_3 > \text{Na}_2\text{SO}_4 > \text{NaCl} > \text{MgCl}_2 > \text{CaCl}_2$ ($I=0.1\text{M}$). However, in high P_{CO_2} conditions ($>1\text{atm}$), the synthetic calcite surface remains positively charged in all considered brine solutions.

We plan to extend the current SCM to take into account the trace amount of organic impurities on the natural carbonate surface so that the model can predict both synthetic and natural calcite surface charge. We also plan to extrapolate our SCM to predict calcite surface charge in high temperature conditions.

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Table 1 Surface complexation reactions in the proposed model

surface reactions	intrinsic equilibrium constants
$>CaOH^{-0.75} + H^+ \rightleftharpoons >CaOH_2^{+0.25}$	K_1
$>CO_3H^{+0.75} + OH^- \rightleftharpoons >CO_3^{-0.25} + H_2O$	K_2
$>CaOH^{-0.75} + Ca^{2+} \rightleftharpoons >CaOH \dots Ca^{+1.25}$	IB_1
$>CaOH^{-0.75} + Mg^{2+} \rightleftharpoons >CaOH \dots Mg^{+1.25}$	IB_2
$>CO_3H^{+0.75} + CO_3^{2-} \rightleftharpoons >CO_3H \dots CO_3^{-1.25}$	IB_3
$>CO_3H^{+0.75} + SO_4^{2-} \rightleftharpoons >CO_3H \dots SO_4^{-1.25}$	IB_4
$>CO_3H^{+0.75} + HCO_3^- \rightleftharpoons >CO_3H \dots HCO_3^{-0.25}$	IB_5
$>CaOH^{-0.75} + Na^+ \rightleftharpoons >CaOH \dots Na^{+0.25}$	IB_6
$>CO_3H^{+0.75} + Cl^- \rightleftharpoons >CO_3H \dots Cl^{-0.25}$	IB_7

Table 2 Parameterization of Surface Complexation Modeling

parameter ($\log_{10}K$)	value	literature ²⁶	intrinsic equilibrium constants
K_1	0.30	-0.17	$>CaOH^{-0.75} + H^+ \rightleftharpoons >CaOH_2^{+0.25}$
K_2	0.50	14.17	$>CO_3H^{+0.75} + OH^- \rightleftharpoons >CO_3^{-0.25} + H_2O$
IB_1	1.74	1.68	$>CaOH^{-0.75} + Ca^{2+} \rightleftharpoons >CaOH \dots Ca^{+1.25}$
IB_2	1.62	-	$>CaOH^{-0.75} + Mg^{2+} \rightleftharpoons >CaOH \dots Mg^{+1.25}$
IB_3	2.23	3.26	$>CO_3H^{+0.75} + CO_3^{2-} \rightleftharpoons >CO_3H \dots CO_3^{-1.25}$
IB_4	1.00	-	$>CO_3H^{+0.75} + SO_4^{2-} \rightleftharpoons >CO_3H \dots SO_4^{-1.25}$
IB_5	0.09	0.04	$>CO_3H^{+0.75} + HCO_3^- \rightleftharpoons >CO_3H \dots HCO_3^{-0.25}$
IB_6	0.14	0.56	$>CaOH^{-0.75} + Na^+ \rightleftharpoons >CaOH \dots Na^{+0.25}$
IB_7	-0.64	-0.05	$>CO_3H^{+0.75} + Cl^- \rightleftharpoons >CO_3H \dots Cl^{-0.25}$

Equation 1.

$$C_i = C_{i,x=\infty} \exp\left(\frac{-z_i F \psi}{RT}\right)$$

Equation 2.

$$\text{contribution}(i) = \text{frac}(i) \cdot z_i$$

$$\text{frac}(i) = \frac{[\text{surface specie } i]}{[> \text{CaOH}^{-0.75}]_0} \quad (\text{cationic surface species})$$

$$\text{frac}(i) = \frac{[\text{surface specie } i]}{[> \text{CO}_3\text{H}^{+0.75}]_0} \quad (\text{anionic surface species})$$