

Use of Electrochemical Quartz Crystal Microbalance in the Study of FeCO_3 Solubility

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ABSTRACT

Carbon dioxide (CO_2) is commonly present in brine from oil and gas wells, creating conditions that trigger steel corrosion with the accompanying formation of iron carbonate (FeCO_3). FeCO_3 present as a corrosion product layer can play a significant role in retarding corrosion, but it can also contribute to the development of localized attack under certain conditions. Before evaluating its protectiveness, it is essential to establish the thermodynamic stability of FeCO_3 under various environmental conditions. In this study, an Electrochemical Quartz Crystal Microbalance (EQCM) was employed to experimentally determine the solubility of FeCO_3 by monitoring in situ mass change on the surface, iron ion concentration, and pH changes in 1 wt.% NaCl solution sparged with CO_2 at three different temperatures (60–80°C). Experimental results were compared to different solubility models: concentration and ionic strength-based (Ma-OT model, 2021) and non-ideal solution speciation model (Pitzer model). The methodology developed in this study provides a basis for future investigations of FeCO_3 solubility under different conditions, while the experimental findings provide a foundation for further research on FeCO_3 precipitation, dissolution, and the protectiveness of corrosion product layers.

Key words: FeCO_3 solubility, Pitzer model, sweet corrosion, Quartz Crystal Microbalance (QCM)

INTRODUCTION

Corrosion of carbon steel infrastructure in the presence of saltwater is ubiquitous in the oil and gas industry. The amount of salt present in water varies, but on average, concentrations exceeding 10 wt.%, which gives rise to non-ideality, are present in almost half of all producing oil and gas wells.¹

Apart from salt and water, particular non-hydrocarbon gases are typically present in oil and gas wells, the most common being the acid gases CO_2 and H_2S . Internal corrosion in the presence of these gases can cause severe damage to hydrocarbon production and pipeline transmission assets. This happens when they dissolve in water, producing weak acids that act as an additional reservoir of H^+ ions, which is one of the primary reactants in the corrosion reaction.²

Precipitation of iron carbonate (FeCO_3) is a significant process that accompanies corrosion of carbon steel in CO_2 conditions. The formation of FeCO_3 can lead to the development of a protective corrosion product layer, which plays a crucial role in retarding corrosion. However, under specific conditions, dissolution of the corrosion product layer can expose bare metal, contributing to the development of

localized attacks. Because of this dual role, the balance between precipitation and dissolution of FeCO_3 governs the corrosion product's protectiveness of the metal surface. One of the crucial factors for predicting this balance is the solubility product, K_{sp, FeCO_3} , which helps corrosion prediction models determine whether the conditions favor the formation or dissolution of FeCO_3 corrosion product layer. Thus, studying the solubility product of iron carbonate under various conditions, such as temperature and ionic strength, is an essential task in understanding and developing the right tools for predicting the protective properties of FeCO_3 .

Formation of a FeCO_3 layer from solution is governed by the following reaction:



FeCO_3 precipitates when the product of activities of Fe^{2+} ions and CO_3^{2-} ions, $a_{\text{Fe}^{2+}_{aq}}$ and $a_{\text{CO}_3^{2-}_{aq}}$, respectively, exceeds the solubility product, K_{sp, FeCO_3} . This non-equilibrium condition is termed as the saturation value, $S(\text{FeCO}_3)$:

$$S(\text{FeCO}_3) = \frac{a_{\text{Fe}^{2+}_{aq}} \times a_{\text{CO}_3^{2-}_{aq}}}{K_{sp, \text{FeCO}_3}} \quad (2)$$

The solubility product depends on temperature and can be determined experimentally or calculated using various models.³⁻⁶ When using concentration-based water chemistry models, where concentrations are used instead of activities (activity coefficients are assumed to be equal to 1), it is essential to correct the solubility product of FeCO_3 for ionic strength to account for non-ideal behavior that concentrations alone cannot capture. When using activity-coefficient based solution speciation models, solubility products are only a function of temperature, since the non-ideal behavior of solution is captured by activity coefficients.

Depending on the bulk saturation value, the conditions favorable for the formation of the iron carbonate corrosion product layer can be achieved. If the saturation value is considerably lower than 1, the shift in the equilibrium of the reaction (1) will be to the left, corresponding to non-layer formation conditions or conditions of layer dissolution. When saturation is far higher than 1, the equilibrium of the reaction is shifted to the right, and iron carbonate formation is achieved.⁶ The focus of this study will be on the conditions where the saturation is close to 1, indicating the equilibrium of the system.

Several studies have investigated the solubility product of FeCO_3 . One of the earliest experimental works across different temperatures was done by Greenberg and Tomson.³ They proposed a semi-empirical equation based on the thermodynamic form using temperature in Kelvin (T_K), which is expressed as:

$$\log(K_{sp, \text{FeCO}_3}) = -59.2385 - 0.041377T_K - \frac{2.1963}{T_K} + 24.5724 \log(T_K) \quad (3)$$

Silva, et al., (2002)⁴ proposed a correlation between K_{sp, FeCO_3} and ionic strength based on the measurements in solutions ranging from $I = 0.1$ to 5.5 mol/L at 25°C :

$$\log(K_{sp, \text{FeCO}_3}) = -10 + 2.518I^{0.5} - 0.657I \quad (4)$$

Sun and Nesic (2009)⁶ combined the temperature and ionic strength dependent equation:

$$\log(K_{sp, \text{FeCO}_3}) = -59.3498 - 0.041377T_K - \frac{2.1963}{T_K} + 24.5724 \log(T_K) + 2.518I^{0.5} - 0.657I \quad (5)$$

Ma (2021)⁷ enhanced the expression for K_{sp, FeCO_3} based on the experiments performed by Gao⁸ at different NaCl concentrations at equilibrium conditions (1–25 wt.% NaCl):

$$\log(K_{sp,FeCO_3}) = -59.4 - 0.041377T_k - \frac{2.1963}{T_k} + 24.5724 \log(T_k) + 2.6349I^{0.5} - 1.0027I \quad (6)$$

Experimentally derived by Ma,⁷ $K_{sp,FeCO_3}$ depends on temperature and ionic strength, and can be applied with concentration-based solution speciation models to predict the solubility of iron carbonate. However, when working with non-ideal systems, such as complex brines, only temperature-dependent $K_{sp,FeCO_3}$ should be considered, in which case activity coefficients become necessary. The Pitzer model is one of the solution speciation models that provides a framework to account for non-ideal solution behavior by calculating activity coefficients of species.

The objective of this work is to experimentally validate two models for calculating $K_{sp,FeCO_3}$ – one approach will follow temperature and ionic strength dependence by Ma⁷, along with using concentration-based models to calculate the saturation value. That approach will be compared to temperature-dependent solubility by Greenberg and Tomson³ accompanied by Pitzer model calculations.⁹

EXPERIMENTAL PROCEDURE

Solution preparation

The experiments were performed in a 2-liter sealed glass cell, the schematic of which is presented in Figure 1. A 1 wt.% NaCl solution was prepared by mixing high-grade 99% purity NaCl in deionized (DI) water. The solution was deoxygenated overnight or for at least 2 hours by sparging with high-grade CO₂, this ensured the absence of oxygen in the system. CO₂ was bubbled continuously throughout experiments. Solution pH was measured before the test using a Cole-Palmer[†] pH electrode and pH meter, then adjusted to pH 6.6 to promote the precipitation of FeCO₃ on a working electrode.

The source of Fe²⁺ in this study is iron (II) chloride tetrahydrate FeCl₂·4H₂O, a salt that is injected into the solution at the beginning of the experiment. Since FeCl₂ salt is highly susceptible to oxidation, the preparation process involves deoxygenating 50 mL of DI water using nitrogen, adding the desired amount of crystalline FeCl₂ to this deoxygenated DI water, and continuation of nitrogen sparging for at least 45 minutes to prevent oxygen contamination. After deoxygenation, a calculated volume of this solution was transferred by syringe to inject the required molar amount of ferrous chloride (ferrous ions) into the test electrolyte.

Experimental setup

The quartz crystal microbalance (QCM) is a sensitive gravimetric technique that enables real-time monitoring of surface mass gain or loss by measuring changes in resonance frequency of a piezoelectric quartz crystal. The resonance frequency of oscillation will change depending on mass dissolution, deposition/adsorption, medium change, and temperature variations of the quartz crystal. For thin and rigid mass depositions on the QCM surface, Sauerbrey's equation is applicable which relates resonance frequency variations (Δf) with mass change per area ($\frac{\Delta m}{A}$)^{10,11}:

$$\Delta f = -C_f \frac{\Delta m}{A} \quad (7)$$

where C_f is the sensitivity constant (56.6 Hz·cm²·μg⁻¹ for a crystal with resonance frequency of 5 MHz).

[†] Trade name.

The QCM used in this study is the QCM200[†] by Stanford Research Systems,¹² which is connected to the Reference 600 potentiostat by Gamry Instruments^{‡§} and serves as the working electrode. The QCM setup was checked before the test according to the procedure described elsewhere.¹³ The quartz crystal used in this study is a gold-coated etched crystal with a 5 MHz oscillation frequency and an effective surface area of 1.37 cm². A platinum-coated counter electrode and an Ag/AgCl reference electrode through a Luggin capillary were connected along with the working electrode to the potentiostat as a three-electrode system. Temperature was monitored and controlled using a thermocouple attached to a hot plate/stirrer. A condenser was attached to the glass cell to prevent solution evaporation and thus maintain a constant solution concentration.

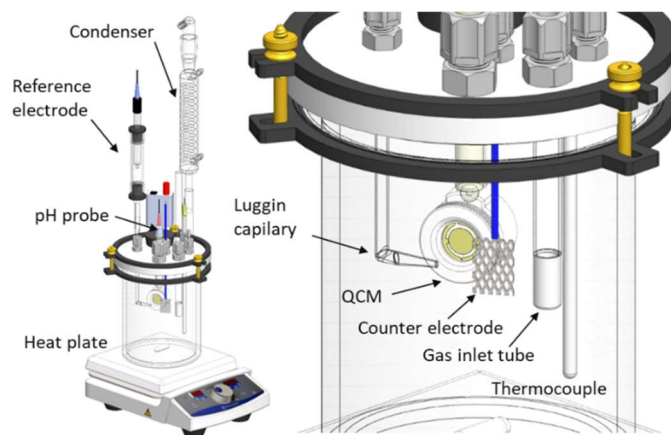


Figure 1. Experimental setup (image by Cody Shafer, Research Engineer ICMT)

Data collection and processing

In situ frequency change was monitored and converted to mass change over time using the Sauerbrey equation.⁹ The pH measurement of the solution was recorded at the same time the solution was sampled for ferrous ion concentration [Fe_{aq}^{2+}] measurement using ultraviolet–visible spectroscopy. UV-vis analysis was conducted using spectrometer by Agilent^{***} and dissolving FerroVer^{**} iron reagent in a 10 mL solution sample. The pH electrode was calibrated and checked in buffer solutions before each measurement (1 – 3 times in 24 hours).

RESULTS and DISCUSSION

Surface analysis

Post-experiment surface analysis was performed to identify the precipitated layer composition. Surface analysis using scanning electron microscopy (SEM) showed crystal formation on the specimen. From SEM, not the whole surface is covered with crystals, probably since surface was exposed to several steps of dissolution caused by pH drops and temperature changes throughout the experiment. Energy dispersive X-ray spectroscopy (EDS) indicated the presence of Fe, C, and O atoms, which can be

[†] Trade name.

[§] Trade name.

^{**} Trade name.

^{***} Trade name

attributed to the iron carbonate layer and was confirmed by X-ray diffraction (XRD) analysis. The presence of gold detected in both EDS and XRD results comes from the QCM substrate used in the experiments.

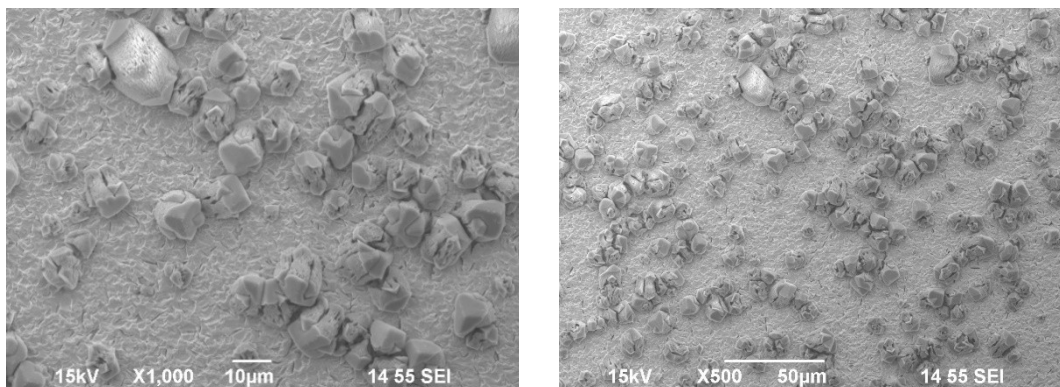


Figure 2. Surface morphologies of the layer formed on a gold QCM surface after the experiment at pH 6.6, 80 °C, 1 wt%. NaCl

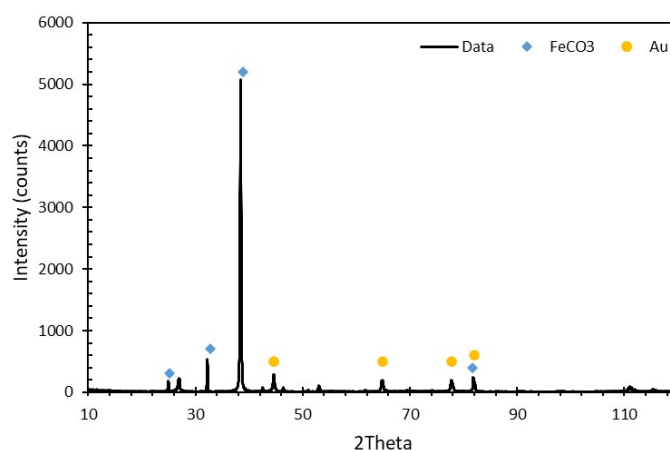


Figure 3. XRD pattern of the layer formed on a gold QCM surface after the experiment at pH 6.6, 80 °C, 1 wt%. NaCl

In situ EQCM response

Figure 4 shows the mass change over time calculated using Sauerbrey's equation, along with the measured pH (Figure 4(a)) and $[Fe_{aq}^{2+}]$ (Figure 4 (b)). It has been shown for these experimental conditions that $FeCO_3$ corrosion product layer behaves as a rigid mass and hence validates the use of Sauerbrey's equation.¹⁴ At the start of the test, the mass increased due to the formation of a $FeCO_3$ layer on the surface. After approximately 25 hours, more ferrous chloride was added to the solution to further increase the mass of iron carbonate precipitated on the surface to ensure even coverage on the surface. Around 40 hours into the experiment, mass change was reaching steady state slowly, and the pH was intentionally lowered to accelerate the approach to equilibrium. It can be seen from the QCM response that the calculated mass change decreased due to the dissolution of the iron carbonate layer from the surface.

The pH was further reduced several times at 80°C until the mass change recorded by QCM was stable, indicating that equilibrium had been achieved. Equilibrium of iron carbonate precipitation and dissolution

processes was assumed when QCM mass change, concentration of ferrous ions $[Fe_{aq}^{2+}]$ and pH measurements did not change considerably over time.

To further test the equilibrium solubility of $FeCO_3$, the temperature was first reduced to 70°C and then to 60°C, with solution speciation continuously monitored throughout the process until the equilibrium was reached for each temperature. It should be noted that QCM is an excellent temperature sensor too, so changing the temperatures would lead to a false response in mass change which is what we can see in Figure 4 – small blimps at temperature change points. However, since AT-cut crystals were being used, which are known to have good temperature stability in this range, plus the net mass change from experimental conditions versus the little deviation we expect due to temperature changes, the effect of temperature on QCM response can be ignored.¹¹ At least two points of solution pH and $[Fe_{aq}^{2+}]$ indicating equilibrium were used to calculate saturation of $FeCO_3$.

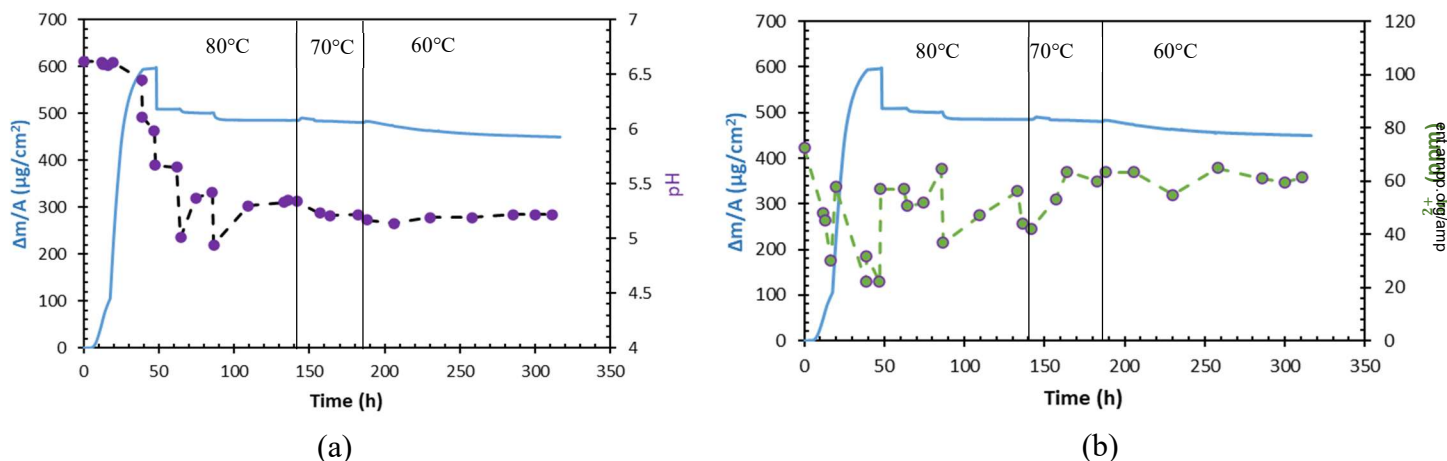


Figure 4. a) QCM mass change (left y-axis) and pH of the solution (right y-axis) over time and b) QCM mass change (left y-axis) and iron ion concentration $[Fe_{aq}^{2+}]$ (right y-axis) over time in 1 wt.% NaCl, CO_2 sparged solution at 1 bar total pressure over the temperatures 60 – 80 °C

MODEL VALIDATION

Concentration-based models

The chemistry of an aqueous solution is affected by the species present. Table 1 presents the chemical reactions occurring in the solution in the presence of dissolved CO_2 gas, along with the equilibrium constant relations for these reactions. When working with solution speciation, it is essential to determine the concentrations and activities of species dissolved in the solution. Two types of models are discussed in this paper: concentration and ionic strength-based models, and activity coefficient-based models. The former type of model assumes the activity coefficient of species to be 1; thus, it is mostly used for dilute solutions. However, this type of model can include an ionic strength term to account for non-ideality, as seen in a high concentration of NaCl.

Table 1. Chemical reactions in CO₂ environment and corresponding equilibrium constants

Chemical equilibria reactions in CO ₂ environment	Equilibrium constants
$\text{CO}_{2(g)} \rightleftharpoons \text{CO}_{2(aq)}$	$K_{\text{sol}} = \frac{a_{\text{CO}_2}}{p_{\text{CO}_2}}$
$\text{CO}_{2(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_2\text{CO}_{3(aq)}$	$K_{\text{hyd}} = \frac{a_{\text{H}_2\text{CO}_3}}{a_{\text{CO}_2}}$
$\text{H}_2\text{CO}_{3(aq)} \rightleftharpoons \text{H}^+_{(aq)} + \text{HCO}_3^-_{(aq)}$	$K_{\text{ca}} = \frac{a_{\text{H}^+} a_{\text{HCO}_3^-}}{a_{\text{H}_2\text{CO}_3}}$
$\text{HCO}_3^-_{(aq)} \rightleftharpoons \text{H}^+_{(aq)} + \text{CO}_3^{2-}_{(aq)}$	$K_{\text{bi}} = \frac{a_{\text{H}^+} a_{\text{CO}_3^{2-}}}{a_{\text{HCO}_3^-}}$
$\text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}^+_{(aq)} + \text{OH}^-_{(aq)}$	$K_{\text{wa}} = a_{\text{H}^+} a_{\text{OH}^-}$

One of the first empirical concentration-based models to predict water chemistry in aqueous solution containing dissolved CO₂ was proposed by Oddo and Tomson.¹⁵ They developed expressions to find equilibrium constants for the dissolution of carbon dioxide, the dissociation of carbonic acid, and the dissociation of bicarbonate anions. Non-ideality in these equations is handled by the ionic strength term:

$$I = \frac{1}{2} \sum_j c_j z_j^2 \quad (8)$$

where I is ionic strength in mol/L, c_j is the anion or cation concentrations in mol/L, and z_j is charge of the species in the solution.

The expressions for K_{hyd} and K_{wa} were developed by Palmer and van Eldik¹⁶ and Kharaka, et al.,¹⁷ respectively. The expressions for the equilibrium constants are presented in Table 2.

Table 2. Equilibrium constants developed for the concentration-based water chemistry model

Equilibrium Constant	Source
$K_{\text{sol}} = \frac{14.5}{1.00258} \times 10^{-(2.27+5.65 \times 10^{-3} T_f - 8.06 \times 10^{-6} T_f^2 + 0.075 I)}$ molar/bar	Oddo and Tomson ¹⁵
$K_{\text{ca}} = 387.6 \times 10^{-(6.41 - 1.594 \times 10^{-3} T_f + 8.52 \times 10^{-6} T_f^2 - 3.07 \times 10^{-5} p - 0.4772 \times I^{1/2} + 0.1180 I)}$ molar	Oddo and Tomson ¹⁵
$K_{\text{bi}} = 10^{-(10.61 - 4.97 \times 10^{-3} T_f + 1.331 \times 10^{-5} T_f^2 - 2.624 \times 10^{-5} p - 1.166 \times I^{1/2} + 0.3466 I)}$ molar	Oddo and Tomson ¹⁵
$K_{\text{hyd}} = 2.58 \times 10^{-3}$ at 25°C	Palmer and van Eldik ¹⁶
$K_{\text{wa}} = 10^{-(29.3868 - 0.0737549 \times T_K + 7.47881 \times 10^{-5} T_K^2)}$ molar/bar	Kharaka, et al ¹⁷

where, T_f is the temperature in Fahrenheit, T_K is the temperature in K, p is the CO₂ partial pressure in psi.

Comparison with the experimental data has shown that the Oddo and Tomson model performance is not accurate for high ionic strength solutions, and equilibrium constants should be reviewed.^{5,8} Ma⁵ revised the equilibrium constant for carbonic acid dissociation and empirically adjusted it based on the change of ionic strength of solution. This adjustment improved the comparison to laboratory data at higher chloride concentrated solutions for temperatures from 5 °C to 80 °C. The “Ma-OT” solution speciation model, Equation (9), will be used in this paper along with $K_{sp,FeCO_3}$ to compare to the experimentally found solubility.

$$K_{ca} = 387.6 \times 10^{-(6.6216 - 1.594 \times 10^{-3} T_f + 8.52 \times 10^{-6} T_f^2 - 3.07 \times 10^{-5} p - 0.7379 \times I^{\frac{1}{2}})} \quad (9)$$

Activity coefficient-based model (Pitzer model)

Concentration based models are easy to use and work well for a large range of conditions, but are expected to have greater inaccuracies in extreme conditions (concentrated brines, high temperature, pressure) as compared to activity coefficient-based models. Activity coefficient-based models are more advanced and theoretically based than concentration-based models. The calculation of activity coefficients is performed based on the potential energy of interaction of charged species in the solution.

The activity coefficient of species γ_i can be determined from its chemical potential μ_i :

$$\mu_i = \mu_i^0 + RT \ln(a_i) = \mu_i^0 + RT \ln\left(\frac{m_i}{m_i^0}\right) + RT \ln(\gamma_i) \quad (10)$$

where μ_i^0 is the standard chemical potential in a standard state (J/mol), R is the universal gas constant (J/(mol·K)), T is the temperature (K), a_i is the activity of a species (mol/(kg of H₂O)), $\frac{m_i}{m_i^0}$ is the relation of molalities of species i to the standard molality which is 1 mol/(kg of H₂O).

The last term on the right-hand side of the equation (10) represents the deviation from non-ideality and can be called the “excess Gibbs free energy change” term, G_i^E . Therefore, if Gibbs excess free energy of the solution is known, the activity coefficient can be found:

$$\ln(\gamma_i) = \left(\frac{\partial G_i^E / RT}{\partial n_i} \right)_{T, P, n_j} \quad (11)$$

Non-ideal water speciation models focus on calculating the activity coefficient of species through the excess Gibbs free energy term. Pitzer^{9,18,19} presented the following expression for the Gibbs free excess energy for the solvent containing n_w kg of solvent, m_i, m_j, m_k moles per kg of H₂O of species:

$$\frac{G_i^E}{RT} = n_w M_w f(I) + n_w M_w \sum_i \sum_j m_i m_j \lambda_{ij}(I) + n_w M_w \sum_i \sum_j \sum_k m_i m_j m_k \mu_{ijk} \quad (12)$$

The first term on the right-hand side has the Debye-Hückel term $f(I)$ which is the function of ionic strength^{20,21}, the second parameter on the right-hand side of the equation has the term $\lambda_{ij}(I)$ which is used to account for the interaction between two species, while the parameter μ_{ijk} is a triple interaction parameter between three species. Step-by-step derivation of the expression can be found in the original publication.⁹ The derivative of the $\frac{G_i^E}{RT}$ term will give the expression for the activity coefficient of each of the species. The Pitzer model will be used herein along with the expression for $K_{sp,FeCO_3}$ by Greenberg and Tomson.^{3,9}

Comparison of solution speciation models to experimental results

Experimentally determined equilibrium saturation values at different temperatures were compared using two models, where concentrations and/or activities of species were calculated for each condition.

1. The Ma-OT model: the empirical $K_{sp,FeCO_3}(T, I)$ model in Equation (6) combined with an ideal concentration and ionic strength-based water chemistry model in Table 2 and Equation (9), and
2. The non-ideal Pitzer model: the temperature-dependent $K_{sp,FeCO_3}(T)$ model in Equation (3) coupled with the Pitzer model.

Figure 5 shows the calculated saturation values using both the Ma-OT model⁵ and the non-ideal Pitzer model at experimental equilibrium (when pH of the solution and $[Fe^{2+}]$ remained constant over time). Solution pH and $[Fe^{2+}]$ were monitored throughout the whole test several times a day (Figure 4), however, the graph shows only the conditions when the equilibrium was reached based on the solution speciation values and QCM response. The resulting saturation values fall within the range of 0.5 to 1, indicating that the models calculating the saturation value of $FeCO_3$ perform well under these conditions. Since the electrode was polarized during the entire experiment, the surface pH was recalculated using an expression formulated by Nesic and Madani Sani for calculation of cathodic limiting current density²² and used to determine the solution speciation in the Pitzer model. Both models show good agreement with experimental results at different temperatures in these low-concentration solutions.

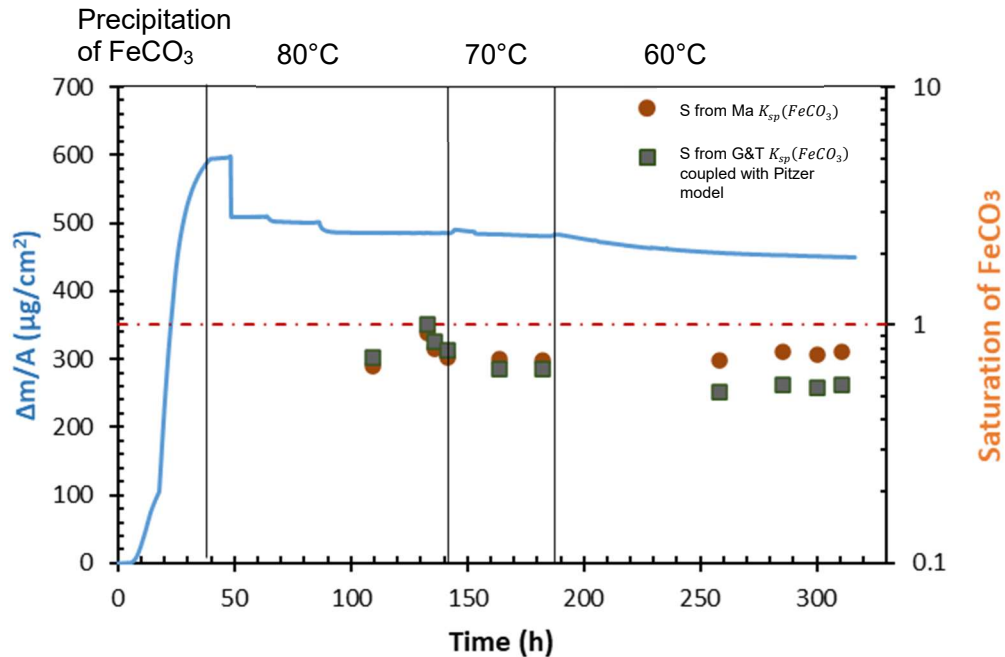


Figure 5. QCM mass change (left y-axis) and Saturation (right y-axis) calculated using Ma model⁷ coupled with Ma-OT (circles), and Greenberg and Tomson (G&T) coupled with Pitzer model^{3,9} (squares) over time at 1 wt.% NaCl, CO₂ sparged, 1 bar total pressure over the temperatures 60 – 80 °C.

Slight deviations between models and experimental data can be attributed to several factors. First, uncertainties in the experimental derivation of the $K_{sp,FeCO_3}$ values, like pH measurements, temperature deviations, ferrous ion concentration calibration, and measurements, can introduce discrepancies. Second, empirical and Pitzer models are limited to the range of conditions from which they are derived, which could also introduce some deviations from the experimental results. However, despite minor deviations, both models perform well in the studied conditions, as the $FeCO_3$ solubility behavior was accurately captured by the models in dilute solutions over the temperature range of 60–80 °C. To fully assess the model's capabilities, the experimental matrix will be expanded to a higher NaCl concentrations, introducing further non-ideality to the system and validating it against both models in future research. For that, QCM has been a valuable tool to assess the solubility of $FeCO_3$ in real time in combination with solution speciation measurement.

CONCLUSIONS

- In situ QCM successfully captured $FeCO_3$ solubility in real-time. pH and ferrous ion concentration were monitored simultaneously with mass changes to calculate solubility.
- Experimentally obtained solubility data at the equilibrium were compared to the empirical $K_{sp,FeCO_3}(T, I)$ model by Ma coupled with the Ma-OT water chemistry model ⁷, and $K_{sp,FeCO_3}(T)$ expression by Greenberg and Tomson ³ coupled with the non-ideal Pitzer model.⁹ Both models showed relatively close results compared to experiments at the studied conditions in a dilute system.
- Future investigation includes performing experiments at higher NaCl concentration and validating models in the non-ideal conditions.

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