

A Quantitative Study of FeCO₃ Solubility in Non-ideal Solutions

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ABSTRACT

The effect of NaCl concentration (non-ideality) was investigated on the solubility of FeCO₃ layer. After a layer of FeCO₃ was formed on a gold coated crystal, NaCl was incrementally added into the solution and the mass change of the FeCO₃ layer was measured with an Electrochemical Quartz Crystal Microbalance (EQCM). It was found that the mass of the precipitated FeCO₃ layer did not change with increasing NaCl concentration even though the saturation value of FeCO₃ (S_{FeCO_3}) was far below 1 and dissolution of FeCO₃ was expected. It was hypothesized that the calculation of S_{FeCO_3} was incorrect due to inaccurate equations for dissociation equilibrium constants or solubility product constant (K_{sp}). Therefore, the equations for dissociation equilibrium constants taken from Oddo & Tomson 1982 and the K_{sp} equation borrowed from Sun et al. 2009 were revisited. New equations were proposed for carbonic acid first dissociation equilibrium constant (K_{ca}) and K_{sp} .

$$K_{ca} = 387.6 \times 10^{-(6.527 - 1.594 \times 10^{-3} T_f + 8.52 \times 10^{-6} T_f^2 - 3.07 \times 10^{-5} P - 0.7173 I^{0.5})}$$

$$K_{sp} = 10^{-(58.98 + 0.041377 T_K + \frac{2.1963}{T_K} - 24.5724 \log T_K - 1.5223 I^{0.5} + 0.5594 I)}$$

The predicted pH and S_{FeCO_3} values at low pressures over a temperature range of 30°C to 80°C and an ionic strength range of 0 to 4.95 M were in good agreement with the experimental results. The new equations could justify the observations for the effect of NaCl concentration on FeCO₃ solubility.

Keywords: Iron carbonate layer, FeCO₃ solubility, non-ideal solutions, ionic strength, salt concentration, water chemistry model

INTRODUCTION

Iron carbonate (FeCO₃) formed on the internal surface of oil and gas pipelines plays an important role in protecting these pipelines from further corrosion. Whether precipitation of FeCO₃ is thermodynamically favorable is determined by a parameter called saturation of FeCO₃, S_{FeCO_3} . In CO₂ corrosion, ferrous ions, coming from the dissolution of the steel matrix, combine with carbonate ions to form FeCO₃. Precipitation of FeCO₃ occurs when S_{FeCO_3} is larger than one. If the precipitated FeCO₃ covers the steel surface evenly, it can form a compact and protective layer. This acts as a diffusion barrier hindering the mass transfer of corrosive species to the surface, which enhances the resistance of mild steel to further uniform CO₂

corrosion. S_{FeCO_3} is inversely proportional to the $FeCO_3$ solubility limit constant, K_{sp} . Therefore, it is important to be able to calculate K_{sp} accurately, which is a function of temperature and ionic strength. There are several studies that investigated the effect of temperature¹⁻³ and ionic strength⁴ on K_{sp} . When Sun, *et al.*⁵ reviewed literature associated with $FeCO_3$ solubility, they found studies of K_{sp} at room temperature and very low ionic strength, studies of solubility limit dependence on temperature, as well as studies of solubility limit dependence on ionic strength. Sun *et al.* combined the equations from Greenberg and Tomson² for temperature[†] and Silva *et al.*⁴ for ionic strength[‡] to obtain a new equation for calculating the iron carbonate solubility product constant as a function of both temperature and ionic strength as follows:

$$\log K_{sp} = f(T_K) + f(I) = -59.3498 - 0.041377 \times T_K - \frac{2.1963}{T_K} + 24.5724 \times \log(T_K) + 2.518 \times I^{0.5} - 0.067 \times I \quad (1)$$

Where T_K is temperature in Kelvin and I is ionic strength in mol/L.

They claimed that the new proposed equation agreed well with experimental data. However, as will be shown in this article, Sun *et al.*'s equation is only valid for low ionic strengths and does not yield to correct predictions of K_{sp} in concentrated brines that are often encountered in the field. Therefore, it is necessary to calculate K_{sp} [§] accurately to be able to understand better CO_2 localized corrosion caused by partial dissolution of $FeCO_3$. Two approaches can be followed to obtain K_{sp} . The first approach is to use concentrations for calculating the saturation index (S_{FeCO_3} (Eq. (2)), assuming ideality of the aqueous solution. The second approach is to use activities (product of concentrations and activity coefficients) for S_{FeCO_3} calculations as shown by Eq. (3)**. Although the second approach will be more accurate, it requires the use of complicated water chemistry models such as those proposed by Pitzer *et al.*^{6,7}, and Li and Duan⁸ to calculate the concentrations and corresponding activity coefficients. However, if K_{sp} in Eq. (1) is defined accurately as a function of both temperature and ionic strength, then concentrations can be used to calculate S_{FeCO_3} which makes the whole calculation much easier.

$$S_{FeCO_3} = \frac{c_{Fe^{2+}}(T, P) \cdot c_{CO_3^{2-}}(T, P)}{K_{sp}(T, I)} \quad (2)$$

$$S_{FeCO_3} = \frac{a_{Fe^{2+}} \cdot a_{CO_3^{2-}}}{K_{sp}(T)} = \frac{(c_{Fe^{2+}}(T, P) \cdot \gamma_{Fe^{2+}}(T, P, I)) \cdot (c_{CO_3^{2-}}(T, P) \cdot \gamma_{CO_3^{2-}}(T, P, I))}{K_{sp}(T)} \quad (3)$$

When $S_{FeCO_3} > 1$, $FeCO_3$ forms and precipitates in solution. When $S_{FeCO_3} = 1$, the $FeCO_3$ precipitation rate is equal to the dissolution rate and the system is in equilibrium. Accordingly, the mass of a precipitated layer should not change over time at equilibrium and should begin to dissolve when $S_{FeCO_3} < 1$.

The purpose of this study is to obtain an accurate equation for K_{sp} as a function of both temperature and ionic strength for calculating S_{FeCO_3} in order to be able to analyze $FeCO_3$ precipitation. To reach this goal, the equilibrium constant equations for carbonic acid dissociation proposed by Oddo and Tomson⁹ will be revisited first to ensure a correct speciation calculation. After that, a very accurate technique, EQCM (Electrochemical Quartz Crystal Microbalance), will be employed to measure the $FeCO_3$ precipitation, so that the accuracy of the obtained K_{sp} equation can be validated.

[†] Valid from 25°C to 94°C.

[‡] Valid from 0.1 to 5.5 mol/L at 25°C

[§] The pressure dependency of K_{sp} is negligible and therefore it is not considered here.

** Activity of $FeCO_3$ is considered to be 1.

Reactions and Equilibrium Constant in H₂O-NaCl-CO₂ system

In the present study, the system of interest is an open system in which CO₂ gas, at a constant partial pressure, is in contact with an aqueous NaCl solution. It can be assumed that the solution is saturated with CO₂. When iron is exposed to this system and corrodes, ferrous ions will be introduced in the solution. Ferrous and carbonate ions can react to form FeCO₃ if $S_{FeCO_3} > 1$. For this, the equilibrium concentration of CO₃²⁻ is needed.

The occurring reactions in our system are listed in Table 1. This paper will take the first approach (Eq. (2)) to obtain K_{sp} since it is more convenient and could provide as good predictions when the equations are correct.

Table 1 Main chemical reactions occurring in an aqueous CO₂ solution and corresponding equilibrium constants expression

Reactions	Equilibrium constant	Reaction #
CO ₂ Dissolution	$CO_{2(g)} \xrightleftharpoons{K_{sol}} CO_{2(aq)}$	$K_{sol} = c_{CO_{2(aq)}}/P_{CO_2}$ (4)
CO ₂ hydration	$CO_{2(aq)} + H_2O \xrightleftharpoons{K_{hyd}} H_2CO_{3(aq)}$	$K_{hyd} = c_{H_2CO_3}/c_{CO_{2(aq)}}$ (5)
Carbonic acid dissociation	$H_2CO_{3(aq)} \xrightleftharpoons{K_{ca}} H^+_{(aq)} + HCO^-_{3(aq)}$	$K_{ca} = c_{H^+}c_{HCO^-_3}/c_{H_2CO_3}$ (6)
Bicarbonate ion dissociation	$HCO^-_{3(aq)} \xrightleftharpoons{K_{bi}} H^+_{(aq)} + CO^{2-}_{3(aq)}$	$K_{bi} = c_{H^+}c_{CO^{2-}_3}/c_{HCO^-_3}$ (7)
Water dissociation	$H_2O_{(l)} \xrightleftharpoons{K_{wa}} H^+_{(aq)} + OH^-_{(aq)}$	$K_{wa} = c_{H^+}c_{OH^-}$ (8)
Iron carbonate precipitation	$Fe^{2+}_{(aq)} + CO^{2-}_{3(aq)} \xrightleftharpoons{1/K_{sp}} FeCO_{3(s)}$	$K_{sp} = c_{Fe^{2+}}c_{CO^{2-}_3}$ (9)

c_i is the concentration of i .

It is important to mention that, for Eq. (9), $C_{Fe^{2+}}$ is not the total bulk $C_{Fe^{2+}}$ (measured by the spectrophotometer) in the solution because when NaCl is present in the system, the formation of ferrous chloride complexes should be considered ¹⁰,



The formation of FeCl⁺ decreased the available $C_{Fe^{2+}}$ for FeCO₃ precipitation. $C_{Fe^{2+}}$ can be calculated as follows:

$$C_{Fe^{2+}} = C_{Fe^{2+}, \text{ measured}} - C_{FeCl^+} \quad (11)$$

To find out the equilibrium concentrations of CO₃²⁻, the equilibrium constants for the reactions listed in Table 1 are needed. These equations, mentioned earlier in the introduction, are taken from Oddo and Tomson ⁹ and Kharaka ¹¹ publications. Table 2 lists these equations.

Table 2 The empirical equations for the equilibrium constants

Equilibrium constant	Unit	Equation #	Ref
$K_{sol} = 14.46 \times 10^{-(2.27+5.65 \times 10^{-3}T_f-8.06 \times 10^{-6}T_f^2+0.075 \times I)}$	molar/bar	(12)	9
$K_{hyd} = 2.58 \times 10^{-3}$	-	(13)	12
$K_{ca} = 387.6 \times 10^{-(6.41-1.594 \times 10^{-3}T_f+8.52 \times 10^{-6}T_f^2-3.07 \times 10^{-5}P-0.4772I^{0.5}+0.118I)}$	molar	(14)	9
$K_{bi} = 10^{-(10.61-4.97 \times 10^{-3}T_f+1.33 \times 10^{-5}T_f^2-2.624 \times 10^{-5}P-1.166I^{0.5}+0.3466I)}$	molar	(15)	9
$K_{wa} = 10^{-(29.3868-0.0737549T_k+7.47881 \times 10^{-5}T_k^2)}$	molar ²	(16)	11
$K_{sp} = 10^{-59.3498-0.041377 \times T_K - \frac{2.1963}{T_K} + 24.5724 \times \log(T_K) + 2.518 \times I^{0.5} - 0.067 \times I}$	molar ²	(17)	5
$K_1 = 10^{-(7.1783 + \frac{911.13}{T_k} + 0.013407T_k)}$	1/molar	(18)	10

T_f is temperature in Fahrenheit, T_k is absolute temperature in Kelvin, $I = \frac{1}{2} \sum c_i z_i^2$ is ionic strength in molar, and P is total pressure in psi.

In the current system, a known concentration of Fe^{2+} was injected to adjust the S_{FeCO_3} . Four equations are needed to solve for the four unknown concentrations (H^+ , OH^- , HCO_3^- , CO_3^{2-}). Besides the three equations listed in in Eqs. (14), (15) and (16), the solution was always electroneutral, which leads to the fourth equation:

$$C_{H^+} + 2C_{Fe^{2+}} + C_{Na^+} = C_{HCO_3^-} + 2C_{CO_3^{2-}} + C_{Cl^-} + C_{OH^-} \quad (19)$$

The bulk solution pH and concentrations of all the aqueous species can be calculated from the above equations. And the bulk solution pH can also be measured by a pH meter.

EXPERIMENTAL PROCEDURE

Experimental Setup

In order to study the effect of salt concentration on $FeCO_3$ layer precipitation, an EQCM, designed and manufactured by Stanford Research Systems^{††}, was used to monitor the *in-situ* mass change caused by $FeCO_3$ precipitation/dissolution on the specimen surface. A gold coated EQCM crystal was used in the experiments because Au is inert under the experimental conditions, and so any mass change captured by the EQCM was only caused by $FeCO_3$ precipitation/dissolution. Experiments were carried out in a 2-liter glass cell with three electrodes as shown in Figure 1a. In order to exclude a possible oxygen effect on corrosion, the solution was sparged with CO_2 at least two hours before the experiment and the sparging remained for the entire experiment duration. A special container (Figure 1b) was implemented to remove O_2 from the dry NaCl crystals when adding the extra NaCl during the experiment. The gold coated quartz crystal was polarized cathodically to -700 mV vs. Ag/AgCl to simulate the corrosion potential of mild steel in CO_2 environments.

†† Trade Name

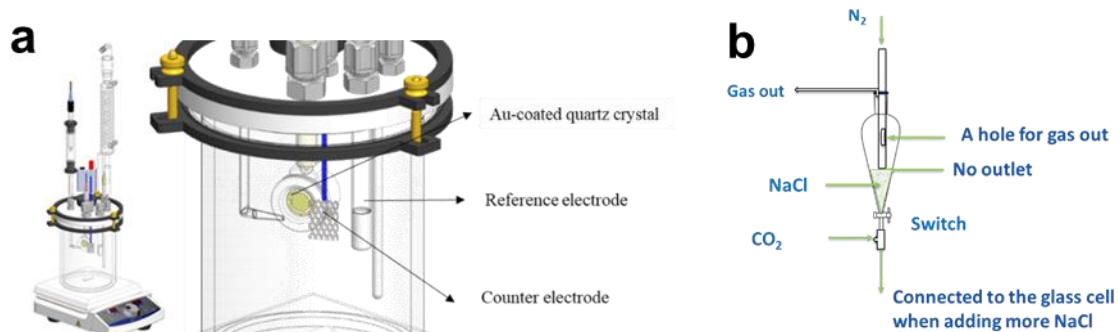


Figure 1. (a) Experimental setup with EQCM (Image courtesy of Cody Shafer, ICMT) [17] (b) Specially designed container for adding NaCl into the glass cell

Experimental Procedure

Each experiment had three stages: (1) FeCO_3 layer formation, (2) set $S_{\text{FeCO}_3} = 1$, and (3) addition of NaCl to the solution. At stage one, 20.2 g NaCl and 2 L DI water were added into the glass cell to make 1 wt.% NaCl solution, and 2.62 g NaHCO_3 to adjust pH value to 6.6. The solution was sparged with CO_2 for at least 2 h to remove oxygen and saturate the solution with CO_2 . Then, 100 ppm total Fe^{2+} was injected into the glass cell to produce a super saturation condition with respect to FeCO_3 ($S_{\text{FeCO}_3} \gg 1$). For stage two, the bulk pH was adjusted at 5.0 by adding 1N HCl to the system to make the S_{FeCO_3} stable at 1. In the stage three, NaCl was added to the solution to study the effect of NaCl concentration on solubility of FeCO_3 layer. Six final NaCl concentrations of 3, 5, 10, 15, 20, and 25 wt.% were tested. $C_{\text{Fe}^{2+}}$ was measured periodically during each experiment by an HACH^{††} DR 3000 spectrophotometer.

For all three stages, to calculate S_{FeCO_3} , the total bulk $C_{\text{Fe}^{2+}}$ was measured, and available $C_{\text{Fe}^{2+}}$ was calculated by Eqs. (11) and (18), $C_{\text{CO}_3^{2-}}$ was calculated from Eqs. (12)-(16), and K_{sp} was calculated using Eq. (17). Finally, Eq. (2) was employed to compute S_{FeCO_3} .

Experimental Conditions

The test conditions for the experiments at stage 1 associated with aqueous equilibrium of FeCO_3 on Au-coated crystals is shown in Table 3.

Table 3 Experimental conditions for the first stage of the experiment

Total pressure/bar	1
Sparge gas	CO_2
Temperature/ $^{\circ}\text{C}$	80
Initial solution pH	6.6
EQCM crystal	Etched Au-coated quartz crystal
Initial total $[\text{Fe}^{2+}]$ /ppm	~100
Initial solution	1 wt.% NaCl
Polarization /mV vs. Ag/AgCl	-700

RESULTS AND DISCUSSION

Stage one: Iron Carbonate Layer Formation

The mass change monitored by EQCM is shown in Figure 2. In the first two hours, the mass increased quickly from 0 to around $450 \mu\text{g}/\text{cm}^2$ due to the precipitation of FeCO_3 on the quartz crystal. A liquid

^{††} Trade Name