Investigation of FeCO₃ and FeS Precipitation Kinetics by EQCM

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ABSTRACT

Corrosion product layers play a key role in the corrosion processes by precipitating on the steel surface and can lead either to enhanced corrosion protection or, in some cases, to severe pitting, depending on the conditions. The kinetics of precipitation of corrosion product layers has a direct impact on the layers properties and their level of protectiveness. In the present study, the precipitation kinetics of iron carbonate (FeCO₃) and iron sulfide (FeS) were studied over a range of temperatures to gain a better understanding of their effect on corrosion resistance. An Electrochemical Quartz Crystal Microbalance (EQCM) was used to investigate the FeCO₃ precipitation kinetics in an aqueous CO₂ environment, as well as the FeS precipitation kinetics in an aqueous H₂S environment. In addition, different substrates were used to isolate specific aspects of the precipitation mechanisms: a cathodically polarized gold-coated quartz crystal, a cathodically polarized iron-coated quartz crystal, and a freely corroding iron-coated quartz crystal were used for FeCO₃ precipitation; the two latter ones were used for FeS precipitation. The measured precipitation rates in both environments were repeatable and consistent across different substrates and over the range of temperatures tested. The FeCO₃ precipitation rates exhibited a relatively strong dependency on system temperature and bulk saturation level of FeCO₃. However, FeS precipitation kinetics appeared only weakly sensitive to the change of temperature. In addition, it is also postulated that the FeS saturation level at the substrate surface (rather than in the bulk), should be taken into consideration when the bulk saturation level of FeS is relatively low. The theoretical kinetic constant and the activation energy for both FeCO₃ and FeS (based on bulk) were derived from the obtained EQCM results and compared with literature values.

Keywords: EQCM, iron carbonate, iron sulfide, precipitation kinetics

INTRODUCTION

Corrosion of carbon steel pipelines in oil and gas applications is often divided into two main categories: sweet corrosion that is mainly caused by aqueous carbon dioxide (CO₂), and sour corrosion which is due

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to aqueous hydrogen sulfide (H₂S). Iron carbonate (FeCO₃) is the most common corrosion product that can be observed in sweet corrosions. In sour conditions, different types of iron sulfides may form depending upon the system conditions. In both environments, the formation of corrosion product layers plays a key role in governing the corrosion processes by serving as diffusion barrier, and by blocking the underlying metal from dissolving (when the layer is well attached to the steel surface). However, these corrosion product layers are not always protective, especially when the metal underneath is suffering from rapid corrosion. It has been suggested that the protectiveness of a corrosion product layer is dependent on the competition between the precipitation rate and corrosion rate of the underlying substrate metal. Therefore, a better understanding of the factors governing the rate of corrosion product layer formation would help develop more efficient corrosion mitigation methods.

In an aqueous CO₂ environment, FeCO₃ precipitates from solution if the concentration product of [Fe²⁺] and [CO₃²⁻] exceeds the solubility product, $K_{sp,FeCO₃}$, which is a function of temperature and ionic strength as defined by Equation (1).

$$K_{sp,FeCO₃} = [Fe^{2+}]_{eq} [CO₃^{2-}]_{eq} \quad mol^2 \cdot L^{-2}$$

Sun and Nesic proposed a kinetic model (S&N Model, 2008) to calculate the FeCO₃ precipitation rate ($PR_{FeCO₃}$). $PR_{FeCO₃}$ is a function of the solubility limit, the saturation value of FeCO₃ ($S_{FeCO₃}$), and temperature, as shown by Equation (2):

$$PR_{FeCO₃} = k_{r,FeCO₃} e^{-\frac{\Delta G_{FeCO₃}}{RT}} K_{sp,FeCO₃} (S_{FeCO₃} - 1) \quad mol \cdot m^{-2} \cdot s^{-1}$$

where the kinetic constant $k_{r,FeCO₃}$ = $1.8 \times 10^6 \ m^4 \cdot mol^{-1} \cdot s^{-1}$, the activation energy of FeCO₃ precipitation $\Delta G_{FeCO₃}$ = 64,851.4 J/mol, and the saturation level of FeCO₃, $S_{FeCO₃}$, is defined by

$$S_{FeCO₃} = [Fe^{2+}] [CO₃^{2-}] / K_{sp,FeCO₃}$$

It has been argued that the S&N model gives more realistic predictions when compared with earlier models for FeCO₃ precipitation rate calculations. It is the only model that was based on the direct measurements of the precipitated FeCO₃ mass on steel surface, whereas the other models were relying on the indirect measurement of Fe²⁺ concentration change in the bulk solution. Furthermore, the expression for the precipitation driving force in this model is more theoretically sound: $(S_{FeCO₃} - 1)$ rather than the empirical expressions that have been used by the other main models: $(S_{FeCO₃}^{0.5} - 1)^2$ and $(S_{FeCO₃} - 1)(1 - S_{FeCO₃}^{-1})$.

However, the S&N model was based on a crude time-averaged mass change of precipitated FeCO₃ which was taken before and after each exposure. To improve the accuracy of the S&N model, a more accurate technique is clearly needed, one that can monitor the in-situ mass change throughout the experiment duration. Besides, the S&N model was only validated at 80°C. This model needs to be validated at different temperatures to extend its validity.
Little research on FeS formation kinetics has been reported. According to Rickard, the kinetics of the formation reaction for mackinawite, one type of polymorphous of FeS that usually forms first, is of the order of milliseconds. At 25°C, Harmandas et al. measured the order of precipitation rate dependence on the saturation value of FeS at 25°C and 80°C. An estimated activation energy of 40 kJ was suggested. Based on the observation from Harmandas et al., Lee proposed an expression for mackinawite precipitation rates (PR\textsubscript{FeS}, in the unit of \textit{mol m}^{-2} \textit{s}^{-1}) calculation that includes both the effect from temperature and solution saturation of mackinawite (S\textsubscript{FeS}):

$$ PR_{FeS} = 11.5 \times e^{9520.648 \over T} (S^{0.5}_{FeS} - 1)^2 $$

where the supersaturation for mackinawite can be calculated by:

$$ S_{FeS} = \frac{[Fe^{2+}][S^{2-}]}{K_{sp,FeS(S^{2-})}} $$

with the $K_{sp,FeS(S^{2-})}$ being the solubility of mackinawite:

$$ K_{sp,FeS(S^{2-})} = [Fe^{2+}]_{eq} [S^{2-}]_{eq} $$

However, Harmandas et al. collected the data from a homogeneous precipitation process, i.e. bulk precipitation. The kinetics of bulk precipitation is very different from the kinetics of a heterogeneous precipitation process on a surface, a process that occurs much more readily than homogeneous precipitation. Later on, Zheng proposed an new expression based on an analogy with the S&N FeCO\textsubscript{3} model to calculate the mackinawite layer precipitation rate:

$$ PR_{FeS} = 7.02 \times 10^{14} \times e^{-40000 \over RT} K_{sp,S^{2-}}(S_{FeS} - 1) $$

In this expression, the solubility limit of mackinawite, $K_{sp,S^{2-}}$, is determined from the literature, and the kinetic constant $k_{r,FeS}$ was used by Zheng’s corrosion model to perform optimally. He did not do any precipitation experimentation, and no other experimental precipitation data has been offered to support this expression, which makes its accuracy questionable without comprehensive validation. Therefore, a comprehensive understanding of the FeS layer precipitation kinetics is necessary. As a starting point, the type of FeS considered in this study is limited to mackinawite.

In the current work, a very accurate device, Electrochemical Quartz Crystal Microbalance (EQCM), was used to monitor the \textit{in-situ} mass change. Theoretically, a nano-scale mass change on the quartz crystal surface leads to a detectable change in its oscillation frequency. According to Sauerbrey’s equation, there is a linear relationship between the mass change on the quartz crystal surface and its oscillation frequency change:

$$ \Delta f = -C_f \cdot \Delta m $$

(2) Private communication
where the $\Delta f$ is frequency change (Hz), $C_f$ is the sensitivity factor for the quartz crystal (Hz $\mu g^{-1} \cdot cm^2$), and $\Delta m$ is the change in mass per unit area ($\mu g \cdot cm^{-2}$).

Besides the ability of monitoring the in-situ mass change in high resolution, the EQCM also allows simultaneous electrochemical measurements. This makes the EQCM a good tool for the current work.

**EXPERIMENTAL**

**Methodology**

The methodology developed for using the EQCM to study the precipitation kinetics of both FeCO$_3$ and FeS is presented in this section. In order to differentiate the various effects on corrosion precipitation as detected by the EQCM mass change, different substrates were used: polarized Au-coated quartz crystal, cathodically protected Fe-coated quartz crystal, and actively corroding Fe-coated quartz crystal. These substrates all had advantages and disadvantages that are discussed below.

- The polarized Au-coated quartz crystal was used so that the precipitation was the only process that affected the EQCM measurements since Au is inert in these test conditions. To simulate the corrosion potential and surface water chemistry seen with carbon steel corroding under similar conditions, a cathodic polarization was applied on the crystal.
- The Fe-coated quartz crystal is closer in nature to the carbon steel surface, and the cathodic polarization was used to minimize the effect of substrate corrosion and to ensure the precipitation was the dominant process during the measurement.
- The precipitation kinetics of corrosion product on an actively corroding Fe-coated quartz crystal was also measured to simulate the most realistic situation as both of the precipitation and spontaneous iron corrosion were occurring on the substrate surface simultaneously. However, this made distinguishing mass loss by corrosion from mass gain by precipitation harder.

Furthermore, the experiments were performed at different temperatures so that the effects on the precipitation kinetics of FeCO$_3$ and FeS could be defined over a wider range of conditions.

In the case of FeCO$_3$ precipitation, three sets of experiments were conducted on polarized Au-coated quartz crystal surface, cathodically protected Fe-coated quartz crystal surface, and actively corroding Fe-coated quartz crystal surface. The results were compared with S&N model's predictions. High initial saturation of FeCO$_3$ was used in the related experiments to speed up this relatively slow process.

For the FeS precipitation, both cathodically protected Fe-coated quartz crystal surface and actively corroding Fe-coated quartz crystal surface were used. The Au-coated quartz crystal was not used as it could not provide repeatable results. High initial saturation of FeS was not required as the FeS precipitation kinetics is much faster than that of FeCO$_3$.

**Apparatus**

The EQCM device by Stanford Research System (QCM200) was used. The Au-coated and Fe-coated quartz crystals with a 1.37 $cm^2$ effective area are shown in Figure 1. Before the experiment, the quartz crystal was installed into the crystal holder and immersed into a 2-liter glass cell (shown in Figure 2) to serve as the working electrode. A saturated Ag/AgCl electrode was used as the reference electrode and the counter electrode was a platinum wire mesh as shown in the figure. The solution pH was monitored through a pH probe immersed in the electrolyte. A desired CO$_2$ or H$_2$S concentration was maintained by
a sparge tube through the entire duration of the experiment. A thermocouple was also immersed in solution and connected to a heating plate to control the temperature of the electrolyte.

Figure 1: Gold-coated (left) and iron-coated (right) quartz crystal

Figure 2: Experimental set-up with EQCM (Image courtesy of Cody Shafer, ICMT).

Procedure

The experimental matrix for the three sets of FeCO₃ precipitation experiments is shown in Table 1. All the experiments were conducted in a 2-liter glass cell filled with 1wt.% NaCl solution. CO₂ gas was sparged before and during the test to remove oxygen and maintain a saturated CO₂ environment. After the solution temperature was set to the desired value, the solution pH was adjusted to 6.6 by adding a deoxygenated NaHCO₃ solution. The quartz crystal was cleaned with a N₂ gas stream before each test to remove any dust from the surface. The working electrode potential was adjusted using a potentiostat (Gamry Reference 600™). A deaerated ferrous chloride (FeCl₂·4H₂O) solution was added to adjust the Fe²⁺ concentration i.e. the level of FeCO₃ or FeS supersaturation. Solution samples were drawn periodically from the glass cell to record the change in the bulk pH and Fe²⁺ concentration. When using the actively corroding iron coated quartz crystal, linear polarization resistance (LPR) was employed to measure the corrosion rate using a B value of 26 mV. The surface of the quartz crystal specimen was taken out for analysis by scanning electron microscope (SEM) after the experiment.

The experimental matrix covering the two sets of FeS precipitation experiments is shown in Table 2. The experimental procedure of FeS precipitation was very similar to that of FeCO₃ precipitation with three differences: instead of using CO₂, the solution was de-aerated by sparging with N₂ for at least two hours,

† Trade Name
followed by sparging with a mixture of H$_2$S/N$_2$ to saturate the bulk solution at a desired H$_2$S partial pressure; to adjusted the solution pH, a deoxygenated NaOH solution was added instead of a NaHCO$_3$ solution; higher stirring speed was employed during FeS precipitation to improve the mixing in the electrolyte and prevent buildup of unreasonably high local $S_{\text{FeS}}$ at the steel surface and uncontrollable precipitation rates.

### Table 1
Experimental Matrix for FeCO$_3$ Precipitation on Different Substrates.

<table>
<thead>
<tr>
<th>Description</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution</td>
<td>1wt.% NaCl</td>
</tr>
<tr>
<td>Total pressure/bar</td>
<td>1</td>
</tr>
<tr>
<td>Purging gas</td>
<td>CO$_2$</td>
</tr>
<tr>
<td>Initial solution pH</td>
<td>6.6±0.05</td>
</tr>
<tr>
<td>Stir bar stirring speed/rpm</td>
<td>50</td>
</tr>
<tr>
<td>Materials</td>
<td>Etched Au-coated quartz crystal</td>
</tr>
<tr>
<td>Polarization</td>
<td>-0.68 V vs. Sat. Ag/AgCl</td>
</tr>
<tr>
<td>Temperature/°C</td>
<td>60, 70, 80</td>
</tr>
<tr>
<td>Initial $S_{\text{FeCO}_3}$</td>
<td>~600</td>
</tr>
</tbody>
</table>

### Table 2
Experimental Matrix for FeS Formation on Different Substrates.

<table>
<thead>
<tr>
<th>Description</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution</td>
<td>1wt.% NaCl</td>
</tr>
<tr>
<td>Total pressure/bar</td>
<td>1</td>
</tr>
<tr>
<td>H$_2$S partial pressure/ppm</td>
<td>100</td>
</tr>
<tr>
<td>Initial solution pH</td>
<td>6.6±0.05</td>
</tr>
<tr>
<td>Stir bar stirring speed/rpm</td>
<td>250</td>
</tr>
<tr>
<td>Materials</td>
<td>Polished Fe-coated quartz crystal</td>
</tr>
<tr>
<td>Temperature/°C</td>
<td>30, 40, 50</td>
</tr>
<tr>
<td>Initial $[\text{Fe}^{2+}]$/ppm</td>
<td>15~30</td>
</tr>
<tr>
<td>Polarization/V</td>
<td>-0.05~0.1 V vs. OCP</td>
</tr>
</tbody>
</table>
**Procedure for FeCO₃ and FeS Precipitation Rate Calculation**

The precipitation rates of FeCO₃ and FeS from EQCM measurement were calculated by using the same methodology, illustrated in Figure 3 by using an example of FeCO₃ precipitating on a polarized Au-coated quartz crystal. During the experiment, the pH value and Fe²⁺ concentration in the bulk solution were measured multiple times to get the bulk saturation values of FeCO₃ according to Equation (3) or the bulk saturation value of FeS according to Equation (5). Given that the accuracy of measuring the Fe²⁺ concentration was up to 1% of the measurement range, and the accuracy of the pH measurement was approximately 0.1 pH unit, 12% error bars were added to all the graphs below to represent an estimated error in determining the saturation value. The error in measuring the mass change using the EQCM was not accounted for as the error was too small to be adequately shown on the plots.

As shown in Figure 3, the mass change monitored by EQCM increased due to the FeCO₃ precipitated on the surface of the quartz crystal. Each time when the saturation of FeCO₃ was measured, the instantaneous slope (mass changes per unit area vs. time) at those specific times was calculated and used to determine the precipitation rate and the corresponding saturation value. The measured precipitation rates having the unit of \( \mu g \cdot cm^{-2} \cdot s^{-1} \) were converted to \( mol \cdot m^{-2} \cdot s^{-1} \) for easier comparison with literature data⁶, ¹³. Even though the precipitation is a two-step process that includes both crystal nucleation and crystal growth¹⁶, the current work aims at finding the precipitation rate during crystal growth period only, as the nucleation step is usually short and surface preparation dependent¹⁷. In addition, the crystal growth step is a process that is more relevant to the understanding of the corrosion product layers formation¹⁸.

When using an actively corroding Fe-coated quartz crystal, the calculated precipitation rate would appear to be lower than its true value if the EQCM captured mass gain were to be used directly without compensation for mass loss due to corrosion. The total mass change captured by the EQCM is equal to the precipitation mass gain minus the corrosion mass loss. A mass compensation protocol was put in place to address this issue whenever an actively corroding Fe-coated quartz crystal was used (except the results obtained at 80°C for which corrosion rates were not measured): the mass loss was calculated from the LPR measured corrosion rate data and then added to the mass gain recorded by EQCM. The obtained new value was used for precipitation rate calculation.

![Figure 3: Illustration of FeCO₃ precipitation rate calculation methodology using EQCM on a polarized Au-coated quartz crystal, pH 6.6, initial \( S_{FeCO₃} = 600 \), 80°C.](image)
Validation of the Precipitation Rate Measurement Methodology

The precipitation rate measurement methodology using EQCM described above was validated by comparing with the S&N model’s calculation at 80°C as shown in Figure 4. This specific temperature was chosen as it was the only temperature that S&N used to validate the model with their experimental measured precipitation rates. In the current study, an initial $S_{FeCO_3}$ around 600 was used for both polarized Au-coated quartz crystal and polarized Fe-coated quartz crystal. When using the actively corroding Fe-coated quartz crystal, the precipitation tests were repeated starting with four different initial $S_{FeCO_3}$ as noted in Table 1. In general, a reasonable agreement was reached between the EQCM measured precipitation rate and S&N model’s calculation, given that the difference between the model prediction and measurements was of the same order of magnitude as the variation within the different measurements. Additionally, the EQCM experimental results showed reasonable consistency, i.e., they were similar in magnitude, even though different substrates were used. Furthermore, a similar exponent with respect to $S_{FeCO_3}$ of approximately 1 was obtained on all substrates. This supports the linear relationship between the FeCO$_3$ precipitation rate and $S_{FeCO_3}$ as described in the S&N model. Overall, it can be concluded that the EQCM technique was validated for the precipitation rate measurements.

![Figure 4: Comparison between S&N model calculation and EQCM experimental results on different substrates at 80°C, pH 6.6.](image)

**EXPERIMENTAL RESULTS AND DISCUSSION**

**Precipitation Rate of FeCO$_3$**

The experimental results related to FeCO$_3$ precipitation kinetics measured by EQCM over a broad range of temperatures (50 – 80°C) are pending publication elsewhere. However, the main results are briefly reviewed in this section to facilitate comparison with the precipitation kinetics of FeS.

When precipitating on a polarized Au-coated quartz crystal, the difference between the EQCM results and model’s predictions was more significant at lower temperature: the best average agreement with the model was found at 80°C as shown in Figure 4. The model’s calculation was about 60% higher than the EQCM results when the temperature decreased to 70°C. At 60°C, the EQCM measured precipitation rate
was about an order of magnitude lower than model's calculation, and about 2-3 times lower than the results obtained from the other two substrates. It was postulated that the Au-coated quartz crystal substrate artificially affected the nucleation process; this became more prominent and retarded the kinetics of the entire precipitation process at a lower temperatures. The precipitation kinetics was affected less by the relatively slow nucleation process at higher temperature, since the overall precipitation kinetics was faster. At 50°C, it was impossible to conduct a repeatable precipitation experiment on Au-coated quartz crystal.

The precipitation rates measured on actively corroding Fe-coated quartz crystal appeared to be in much better agreement with the S&N model's calculation when compared with what was found on polarized Au-coated quartz crystal. However, most of the measured precipitation rates on this type of substrate were considerably lower than the ones obtained on polarized Fe-coated quartz crystal up to a factor of two, at all the tested temperatures. This is because the results were altered by two competing processes that occur on the actively corroding substrate surface during the measurement: extra Fe²⁺ is generated at the substrate surface due to the corrosion process, increasing the surface FeCO₃ saturation level and making the precipitation rate faster; concurrently, a corroding Fe surface continuously undermined the substrate surface and made it harder for FeCO₃ to nucleate. These difficulties rendered the actively corroding Fe-coated quartz crystal a less than ideal substrate for measuring the FeCO₃ precipitation kinetics as it was difficult to resolve which of these effects dominated the precipitation process.

The cathodic polarization that was applied to the Fe-coated crystal made the polarized Fe the most suitable surface to measure the precipitation kinetics since the effect of Fe dissolution was greatly reduced. Theoretically, the surface pH close to the substrate surface was also increased by applying the cathodic polarization and this increased the surface \(S_{\text{FeCO}_3}\). However, the precipitation rate measured on this substrate surface presented the best agreement between the EQCM results and S&N model for all the tested temperature. This suggests that the variations at substrate surface had a minor effect on the FeCO₃ precipitation kinetics under the high bulk \(S_{\text{FeCO}_3}\) conditions tested.

When the temperature was decreased to 40°C, the repeatability of the experiments was rather poor even using the polarized Fe-coated crystal. The overall precipitation process became slow, erratic and irreproducible due to the low temperature.

**Precipitation Rate of FeS**

FeS was precipitated on both cathodically polarized Fe-coated crystal and actively corroding Fe-coated crystal at different temperatures as shown in Table 2. The bulk Fe²⁺ concentration was stable during the entire duration of the FeS precipitation measurements but the pH decreased significantly (anywhere between 0.5 to 2 pH unit). This caused a fast decrease of \(S_{\text{FeS}}\) as the \([\text{S}^{2-}\]\ in Equation (5) decreases with a lower solution pH. This was different from what had been seen in the FeCO₃ precipitation experiments where the solution pH change was minor (within 0.2 pH unit) because of the stronger buffering effect from H₂CO₃, and where the \(S_{\text{FeCO}_3}\) decreased mainly due to the decrease of Fe²⁺ concentration in the bulk solution.

Figure 5 shows the change of EQCM measured mass and \(S_{\text{FeS}}\) in the bulk solution vs. the time on a polarized Fe-coated crystal at 30°C. As can be seen from the figure, the \(S_{\text{FeS}}\) in the bulk solution, \(S_{\text{FeS, bulk}}\), appeared to drop below 1 after 10 hours and became lower than 0.01 after 30 hours. During the entire experimental window, the EQCM mass gain was increasing even when the \(S_{\text{FeS, bulk}}\) was much lower than 1. The same phenomenon was observed at all the tested temperatures. This seems physically impossible as the precipitation could not have continued when the \(S_{\text{FeS}}\) reached 1 (saturation). By the same token,
the precipitation of FeS could not have led to a decrease of \( S_{\text{FeS}} \) below 1. However, with the increased pH at the substrate surface caused by the cathodic polarization, it is likely that the \( S_{\text{FeS}} \) at the substrate surface, \( S_{\text{FeS,surface}} \), was much higher than 1 and thus promoted the FeS precipitation while at the same time \( S_{\text{FeS,bulk}} \) was smaller than 1.

Based on this observation, it can be concluded that, in order to study the precipitation kinetics of FeS, the \( S_{\text{FeS}} \) on the substrate surface (\( S_{\text{FeS,surface}} \)) should be taken into consideration, especially when the precipitation takes place in a solution with a relative low \( S_{\text{FeS,bulk}} \). This is different from the FeCO\(_3\) precipitation where bulk conditions, rather than those at the substrate surface, qualify the process better. This is due to the fact that the FeCO\(_3\) precipitation kinetics is fairly slow as it has a relatively high activation energy\(^6\). A high \( S_{\text{FeCO3}} \) in the bulk solution is necessary to trigger the process and since the \( S_{\text{FeCO3}} \) in the bulk solution was really high, the bulk solution chemistry was not all that different from the solution chemistry at the substrate surface, both being highly supersaturated. In contrast, the FeS precipitation kinetics is much faster and a much lower \( S_{\text{FeS,bulk}} \) was used in H\(_2\)S experiments, when compared to the \( S_{\text{FeCO3,bulk}} \) used for FeCO\(_3\) precipitation kinetics study. Under such conditions, \( S_{\text{FeS,bulk}} \) was very different from the \( S_{\text{FeS,surface}} \) at the surface which was much higher. This meant that the surface \( S_{\text{FeS,surface}} \) needed to be considered in the FeS precipitation kinetics study, which was not readily measurable.

![Figure 5: Mass change and \( S_{\text{FeS}} \) change vs. time on polarized Fe-coated crystal, 30°C.](image)

The calculated precipitation kinetics of FeS on a polarized Fe-coated crystal are shown in Figure 6 for 30°C. Generally, \( PR_{\text{FeS}} \) decreased with the decrease of the \( S_{\text{FeS,bulk}} \). However, as has been discussed above, further study of the effect of surface process on the \( PR_{\text{FeS}} \) is required to reach a better understanding on the relationship between \( S_{\text{FeS}} \) and \( PR_{\text{FeS}} \).

Figure 7 presents the calculated \( PR_{\text{FeS}} \) vs. \( S_{\text{FeS,bulk}} \) on an actively corroding Fe-coated crystal at 30°C. Both \( PR_{\text{FeS}} \) before and after the mass compensation are included. It can be seen that the \( PR_{\text{FeS}} \) was up to 10 times larger after applying compensation for the total mass change and was affected more by the compensation at lower \( S_{\text{FeS,bulk}} \). This suggests that the mass loss due to corrosion was much higher than the EQCM measured mass gain, especially at lower \( S_{\text{FeS,bulk}} \). The best fit line is included in the figure for the compensated result to show the relationship between the \( PR_{\text{FeS}} \) and \( S_{\text{FeS,bulk}} \). The exponent value with respect to \( S_{\text{FeS,bulk}} \) of 0.19 is obtained, indicating a very weak dependency between \( PR_{\text{FeS}} \) and \( S_{\text{FeS,bulk}} \).
$S_{\text{FeS,bulk}}$. However, one needs to keep in mind that the $S_{\text{FeS,bulk}}$ in the bulk was very different from the $S_{\text{FeS,surface}}$ at the substrate surface. The $PR_{\text{FeS}}$ needs to be correlated with $S_{\text{FeS,surface}}$ rather than the $S_{\text{FeS,bulk}}$, however the former is not readily measurable.

Figure 6: Precipitation kinetics of FeS on polarized Fe-coated crystal, 30°C.

![Figure 6](image)

Figure 7: Precipitation kinetics of FeS on actively corroding Fe-coated crystal, before and after mass compensation, 30°C.

![Figure 7](image)

The $PR_{\text{FeS}}$ obtained from the polarized Fe-coated crystal (Figure 6) and the compensated actively corroding Fe-coated crystal (Figure 7) at 30°C and for $S_{\text{FeS,bulk}}>10$ are compared in Figure 8. The $PR_{\text{FeS}}$ on the polarized Fe-coated crystal is generally higher than those obtained from compensated actively corroding Fe-coated crystal and this difference gets larger at lower $S_{\text{FeS,bulk}}$. This phenomenon agrees with what have been observed during the precipitation of FeCO$_3$ as explained in the previous section. Given the fact that the heterogeneous precipitation is notoriously difficult to reproduce, a 60% average difference in precipitation rates measured on the two substrate surfaces is acceptable.
Figure 8: Precipitation kinetics comparison of FeS on both substrates, 30°C.

Figure 9: Precipitation kinetics comparison of FeS on both substrates, 40°C.

The PR_{FeS} obtained for both the compensated actively corroding Fe-coated crystal and the polarized Fe-coated crystal at 40°C and for S_{FeS,bulk} > 10 are shown in Figure 9. Similar to the results at 30°C, the PR_{FeS} on different substrates agree better with each other at higher S_{FeS,bulk} and the discrepancy between the two different substrate surfaces becomes larger with the decrease of the S_{FeS,bulk}. The best fit line and equation are included based on the results obtained from compensated actively corroding Fe-coated crystal and the exponent value with respect to bulk S_{FeS} of approximately 1 was obtained. This indicates almost a linear relationship between PR_{FeS} and S_{FeS,bulk} under this condition. The raw data for the actively corroding Fe-coated crystal without compensation was not included in the figure as it did not provide useful information. However, it is noted that the PR_{FeS} was up to 5 times larger after applying compensation for the total mass change.
A similar comparison of \( \text{PR}_{\text{FeS}} \) vs. \( S_{\text{FeS,bulk}} \) for the polarized Fe-coated crystal and for the compensated actively corroding Fe-coated crystal at 50°C and \( S_{\text{FeS,bulk}} > 10 \) is presented in Figure 10. The experiment was repeated three times on the polarized Fe-coated crystal using the same environmental conditions. The results exhibit reasonable consistency, with most of the results being within a factor of 4 of each other. When using the actively corroding Fe-coated crystal, the compensated \( \text{PR}_{\text{FeS}} \) was up to 4 times larger than the one without using mass compensation (not shown in the figure). The exponent value with respect to \( S_{\text{FeS,bulk}} \) of approximately 1.31 was obtained based on the results from the compensated actively corroding Fe-coated crystal. In addition, the \( \text{PR}_{\text{FeS}} \) on the compensated actively corroding Fe-coated crystal are within the margin of error of the results obtained on the polarized Fe-coated crystal and they have the same order of magnitude.
Comparison of the compensated $\text{PR}_{\text{FeS}}$ vs. $S_{\text{FeS,bulk}}$ at different temperatures from 30°C to 50°C is shown in Figure 11. When comparing at similar $S_{\text{FeS,bulk}}$ values, the $\text{PR}_{\text{FeS}}$ at 50°C was barely two times higher than that at 30°C. This suggests a weak temperature dependency of FeS precipitation kinetics.

ACTIVATION ENERGY AND KINETIC CONSTANT IN THE PRECIPITATION RATE EQUATIONS

Precipitation Rate Equation of FeCO$_3$

The activation energy and kinetic constant for FeCO$_3$ can be extracted from the previously presented EQCM results by taking a natural logarithm of both side of Equation (2):

$$\ln \left( \frac{PR_{\text{FeCO}_3}}{K_{sp,\text{FeCO}_3} \cdot (S_{\text{FeCO}_3}-1)} \right) = -\frac{\Delta G_{\text{FeCO}_3}}{RT} + \ln k_{r,\text{FeCO}_3}$$

(9)

When plotting $\ln \left( \frac{PR_{\text{FeCO}_3}}{K_{sp,\text{FeCO}_3} (S_{\text{FeCO}_3}-1)} \right)$ vs. $(-\frac{1}{RT})$, the activation energy $\Delta G_{\text{FeCO}_3}$ can be obtained from the slope of the straight line and the $\ln k_{r,\text{FeCO}_3}$ can be determined from the y intercept as shown in Figure 12. By using the average experimental value at each temperature, the best fit line yielded $\Delta G_{\text{FeCO}_3}=73739 \text{ J/mol}$ and $k_{r,\text{FeCO}_3}=3.32 \times 10^7 \text{ m}^4 \text{ mol}^{-1} \text{ s}^{-1}$. When comparing with the constants that have been reported in S&N’s FeCO$_3$ model ($64,851.4 \text{ J/mol}$ and $1.8 \times 10^6 \text{ m}^4 \text{ mol}^{-1} \text{ s}^{-1}$), a higher activation energy and a higher kinetic constant were obtained here based on the EQCM results. When comparing the experimental FeCO$_3$ precipitation rate results with the calculated FeCO$_3$ precipitation rate results from the current model with the new constants and S&N model, an improvement was achieved particularly at the lower saturation levels$^{19}$.

Figure 12: The best fit line for activation energy and kinetic constant in the FeCO$_3$ precipitation rate equation. Adapted from Ma et al.$^{19}$.

Precipitation Rate Equation of FeS

The precipitation kinetics measured on different substrates generally agreed with each other over the range of temperatures used, when the $S_{\text{FeS,bulk}}$ was higher than 10. This is because the complications
due to surface effects on PR$_{FeS}$ were not as dominant at higher $S_{FeS,bulk}$. By analogy to the work done on FeCO$_3$ precipitation, an FeS precipitation rate model is proposed based on the compensated results from 30°C to 50°C. The theoretically correct exponent value with respect to $S_{FeS,bulk}$ of 1 is used to represent the linear relationship between PR$_{FeS}$ and $S_{FeS,bulk}$:

$$PR_{FeS} \left( \frac{mol}{m^2 \cdot s} \right) = k_{r,FeS} e^{\frac{-\Delta G_{FeS}}{RT}} K_{sp,FeS} (S_{FeS,bulk} - 1)$$ (10)

where $k_{r,FeS}$ is kinetic constant ($m^4 \cdot mol^{-1} \cdot s^{-1}$), and $\Delta G_{FeS}$ is the activation energy of FeS precipitation ($J \cdot mol^{-1}$).

By adopting a similar procedure as shown in the previous section, the best fit line yielded $\Delta G_{FeS} = 35,284 J \cdot mol^{-1}$ and $k_{r,FeS} = 5.88 \times 10^{13} m^4 \cdot mol^{-1} \cdot s^{-1}$ by using the average experimental value at each temperature (Figure 13). The activation energy is slightly lower than that of Harmandas et al.'s (40,000 $J \cdot mol^{-1}$)$^{11}$. However, one needs to keep in mind that the current research refers to the heterogeneous precipitation on a substrate while the literature data are from a homogeneous precipitation process and that precipitation rate of FeS was measured indirectly.

![Figure 13: The best fit line for activation energy and kinetic constant in the FeS precipitation rate equation.](image)

It can be seen that the required activation energy for FeS precipitation is about 50% of that for FeCO$_3$ precipitation (35,284 $J \cdot mol^{-1}$ vs. 73,739 $J \cdot mol^{-1}$). This suggests that the sensitivity of FeCO$_3$ precipitation to temperature is higher than that of FeS. Comparison of kinetic constants ($k_{r,FeS} = 5.88 \times 10^{13} m^4 \cdot mol^{-1} \cdot s^{-1}$ vs. $k_{r,FeCO_3} = 3.32 \times 10^{7} m^4 \cdot mol^{-1} \cdot s^{-1}$) shows that FeS precipitation is much faster. The precipitation kinetics of FeS and FeCO$_3$ at the same temperature are compared in Figure 14. At the same bulk saturation value as FeCO$_3$, the precipitation rate of FeS is close to two orders of magnitude higher than that of FeCO$_3$. 

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CONCLUSIONS

- By using EQCM, repeatable and consistent FeCO₃ precipitation rates were obtained using different substrates, across a temperature range of 50 – 80°C. Experiments conducted on a cathodically polarized iron-coated crystal tend to minimize the influence of surface dissolution.
- FeS precipitation rate on both cathodically polarized Fe-coated quartz crystal and compensated actively corroding Fe-coated quartz crystal were in good agreement, but suffered from lack of knowledge of surface FeS saturation S_FeS.
- When the S_FeS in the bulk solution was relatively high (i.e., S_FeS,bulk > 10), the precipitation rate PR_FeS could be directly calculated by using S_FeS,bulk; at lower values, the substrate surface condition needs to be considered.
- The PR_FeS was found to have a weak temperature dependence as the required activation energy was 50% lower than the same for FeCO₃ precipitation.
- The precipitation kinetics of FeS is almost two orders of magnitude faster than that of FeCO₃ at the same conditions.

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