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# Scale Inhibition Properties of Metallic Cations on CaCO<sub>3</sub> Formation using Fast Controlled Precipitation and a Scaling Quartz Microbalance

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## **Abstract**

Scaling process is the main problem encountered in industrial plants using water. Several factors, (pH, temperature, hydrodynamic conditions, metal surface, and especially, water composition), can affect the scaling kinetics of calcium carbonate ( $\text{CaCO}_3$ ), one of the main component of scaling. In addition, some foreign ions added can considerably modified the scaling rates. In this work, the inhibiting effects of  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  cations on  $\text{CaCO}_3$  precipitation were studied in a  $50^\circ\text{F}$  synthetic carbonic solution by using fast controlled precipitation (FCP) and scaling quartz crystal microbalance (SQCM) methods, for homogeneous and heterogeneous scaling deposition, respectively. Results showed that  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  ions are efficient, at high concentrations ( $\geq 1$  mg/L), to delay or even to prevent nucleation/growth of  $\text{CaCO}_3$ . FCP measurements showed a complete inhibition of the homogeneous  $\text{CaCO}_3$  precipitation after 120 min in synthetic solution containing 5 mg/L and 4 mg/L of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ , respectively. SQCM measurements showed that the surface coverage of the metallic substrate by a layer of  $\text{CaCO}_3$  is reduced when the amount of these cations increased.  $\text{Zn}^{2+}$  cations inhibited the heterogeneous  $\text{CaCO}_3$  precipitation more efficiently than  $\text{Cu}^{2+}$ . SEM and XRD results indicated that both cations affect calcium carbonate nucleation by changing the morphology of  $\text{CaCO}_3$  crystals.

**Keywords:** Scale inhibition, Zinc cation, Copper cation, Fast controlled precipitation, Scaling quartz crystal microbalance

**Abbreviations:** EQCM: electrochemical quartz crystal microbalance; FCP: fast controlled precipitation; SEM: scanning electron microscopy; SQCM: scaling quartz crystal microbalance; XRD: X-Ray diffraction

## 1. Introduction

Scaling phenomenon constitutes a major problem in industrial and domestic installations. Indeed, scaling is usually observed in heat exchangers [1], boilers, cooling towers [2], desalination and water softening systems [3-6]. The  $\text{CaCO}_3$  deposits may cause serious technical damages such as the obstruction of the drains, a loss of effectiveness of the heat exchangers, and a seizing of the stopping devices (taps, valves...). The influence of several ions on both growth kinetics and morphology of calcium carbonate has been often mentioned in literature. Studies have focused specially on the inhibition effect of  $\text{Fe}^{2+}$  [7-9],  $\text{Mg}^{2+}$  [10-12] and  $\text{Mn}^{2+}$  [13] as metallic cations and  $\text{SO}_4^{2-}$  anions [10, 14, 15]. Meyer [7] evaluated the effect of thirty-four different organic and inorganic additives on the calcite growth rate. The  $\text{Fe}^{2+}$  ion showed the greatest effectiveness for inhibiting the  $\text{CaCO}_3$  growth process. A concentration of  $1 \cdot 10^{-6}$  mg/L of  $\text{Fe}^{2+}$  ions was efficient to reduce the calcite growth rate by 80 %. For zinc ions, a concentration of  $3 \cdot 10^{-6}$  mg/L could reduce the growth rate of calcite crystals by 80%.

The scaling inhibiting properties of  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  in solution towards calcium carbonate scaling, at very low concentrations, were well established by several researchers [16-19]. These metallic cations cause a substantial increase of the induction time and lead to the formation of the aragonite polymorph rather than the calcite polymorph [16-19]. Lisitsin et al. [20] investigated the scaling inhibition using reverse osmosis (RO) membranes with  $\text{Zn}^{2+}$  ions. The characterization of the inhibition effectiveness of  $\text{Zn}^{2+}$  ions in full recycle experiments was carried out by measuring permeate flow rate, solution composition and solution turbidity versus time. Results suggested that  $\text{Zn}^{2+}$  at the concentration 2 mg/L was able to inhibit the precipitation of  $\text{CaCO}_3$  and protect membranes towards scaling in hard water (220 mg/L  $\text{Ca}^{2+}$ ).

Recently, Liu et al. [21], showed, by using FCP method, a complete inhibition of the scaling process, when 0.4 mg/L of  $\text{Zn}^{2+}$  and 0.9 mg/L of  $\text{Cu}^{2+}$  were injected in 31.6 °F carbonic solution. Other investigations [22], focused on the influence of trace amounts of  $\text{Cu}^{2+}$  ions on the

precipitation of calcite in an aqueous and supersaturated  $\text{CaCO}_3/\text{NaCl}$  system and in natural water of moderate hardness, showed a significant increase of  $\text{CaCO}_3$  nucleation induction period. In this case, a 90% inhibition efficiency was observed with  $\text{Cu}^{2+}$  concentration greater than 2 mg/L. Moreover, Pernot et al. [23] indicated that the number of  $\text{CaCO}_3$  crystals increased in solution containing 0.5 and 5 mg/L  $\text{Zn}^{2+}$ . They suggested that zinc ions might act as an accelerator of heterogeneous nucleation in the bulk solution, which is not the case on a surface. More recently, Semine Ras and Ghizellaoui [24] evaluated the scaling power of 59 °F drinking water in the presence of Cu and Zn metallic cations by applying FCP tests and scaling test on polyethylene surface. A total scaling inhibition was obtained with a maximum concentration of 1 mg/L  $\text{Zn}^{2+}$  and 0.8 mg/L  $\text{Cu}^{2+}$ , at 20°C.

In this work, we focused on the inhibiting properties of copper and zinc cations towards  $\text{CaCO}_3$  scaling at low concentration. The main objective of the present study was to assess the influence of  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  cations on the scaling rate on a pre-calcified surface by using an *in situ* gravimetric method. In this respect, a quartz crystal microbalance with a pre-calcified surface (SQCM) [25, 26] was used for the first time to determine the optimal metallic cations concentrations to inhibit scale formation on a surface. As a purpose of comparison, fast controlled precipitation (FCP) [27, 28] method was used to quantify the scaling propensity of water, which allowed to characterize the nucleation step as well as the homogeneous precipitation of calcium carbonate in solution, in the absence and presence of  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$ . In order to get more insight into the inhibition mechanisms, the morphology of the deposits formed by FCP method were studied by SEM observations and X-ray analysis.

## **2. Materials and methods**

### *2.1. Synthetic solution*

The blank solution is 200 mg/L  $\text{Ca}^{2+}$  synthetic carbonically pure water prepared by dissolving calcium carbonate ( $\text{CaCO}_3$ ) (VWR AnalaR NORMAPUR, 99.7% purity) in bi-distilled water. In

order to ensure the complete dissolution of calcium carbonate, carbon dioxide CO<sub>2</sub> gas was introduced in the solution for 24 h with moderate magnetic stirring (450 rpm). After the total dissolution of the solid, the pH of the solution was in the range of 5.5 – 5.7. The synthetic water was then filtered using a filter with a porosity of 0.45 µm to remove impurities. Suitable amounts of stock solutions of analytical grade ZnCl<sub>2</sub> (Merck, 98% purity) and CuCl<sub>2</sub> · 2H<sub>2</sub>O (Acros Organics, 99 % purity) were prepared for SQCM and FCP tests. For the inhibition tests, metallic ions concentrations ranged from 1 mg/L to 5 mg/L.

## 2.2. Fast controlled precipitation (FCP)

The fast controlled precipitation method (FCP) is an accelerated CaCO<sub>3</sub> precipitation technique, generally used to evaluate the effectiveness of scaling inhibitors [28, 29]. The kinetics of nucleation and massive precipitation are followed by measuring at the same time, under moderate stirring, the pH and conductivity values of the solution with time. This method is based on the moderate degassing of CO<sub>2</sub> gas dissolved in water, which generates an increase of pH according to the following reactions [10, 30]:



The reaction rate of solid calcium carbonate formation is enhanced by the formation of OH<sup>-</sup> ions according to Eqs. (4) and (5):



and



The inhibition efficiency ( $E_{\text{FCP}}$ ) for a given inhibitor was calculated from FCP measurements by using the values of the initial resistivity ( $\rho_0$ ), the resistivity of the untreated ( $\rho_{\text{NT}}$ ) and treated ( $\rho_{\text{T}}$ ) water, according to the following equation [28]:

$$E_{FCP} = \left( \frac{\int_0^t (\rho_{NT} - \rho_0) - \int_0^t (\rho_T - \rho_0)}{\int_0^t (\rho_{NT} - \rho_0)} \right) \times 100 \quad (6)$$

The FCP experimental setup is shown in Fig. 1a.

(Figure 1)

A volume of 400 ml of the studied synthetic water was transferred to a Teflon container placed in a thermostated bath at 30°C. CO<sub>2</sub> degassing was achieved by a magnetic stirring at 850 tr/min. The tested synthetic water was treated with Zn<sup>2+</sup> or Cu<sup>2+</sup> at various concentrations from stock solutions of chloride. A pH-meter (PHM250 Radiometer Analytical) and a conductivity-meter (CDM230 Radiometer Analytical) were used to measure the pH and the resistivity values simultaneously. To ensure repeatability, all experiments were performed in triplicate.

After each experiment, the calcium carbonate crystals formed during the FCP experiment were collected by filtration in order to analyze the morphology by scanning electronic microscopy (SEM) and X-ray powder diffraction (XRD) analysis.

### 2.3. SEM and XRD characterizations

The SEM pictures were obtained on a FEG-SEM Zeiss Ultra55 microscope model to characterize the different scaling products formed under different FCP experimental conditions. The XRD spectra were recorded with an angle 2θ in the range of 20-80° with a X-ray diffractometer type X-*Empyrean Panalytical* employing Cu-Kα radiation (λ = 1.54 Å). Intensities of the diffraction peaks at 104 (2θ = 29.5°), 221 (2θ = 46°) and 110 (2θ = 25°) were used to calculate the molar fraction of the calcite (X<sub>C</sub>), aragonite (X<sub>A</sub>) and vaterite (X<sub>V</sub>) varieties, respectively. The following equations were used [31]:

$$\frac{I_C^{104}}{I_A^{221}} = 3.157 \times \frac{X_C}{X_A} \quad (7)$$

$$\frac{I_C^{104}}{I_V^{110}} = 7.691 \times \frac{X_C}{X_V} \quad (8)$$

$$X_C + X_V + X_A = 1 \quad (9)$$

## 2.4. Scaling quartz crystal microbalance (SQCM)

### 2.4.1. Principle of the quartz crystal microbalance (QCM)

QCM is a high-precision instrument for measuring mass variation on the active surface of a quartz crystal. The piezoelectric properties of the quartz crystal correlate the frequency change and the mass deposited on the active surface of quartz crystal. The frequency change,  $\Delta f$ , is proportional to the mass deposited,  $\Delta m$ , on the electrode surface according to the Sauerbrey equation [25, 26]:

$$\Delta f = -2 \frac{f_0^2}{S\sqrt{d}v} \Delta m \quad (10)$$

where  $f_0$  is the quartz resonance frequency,  $d$ , the quartz density,  $v$ , the quartz shear modulus and  $S$ , the active surface of the quartz. In a typical QCM set-up, the working electrode is made of a 0.2 cm<sup>2</sup> gold disc deposited in a 9 MHz AT cut quartz crystal resonator.

### 2.4.2 Pre-calcification of the surface of a QCM electrode

The pre-calcification of the active surface of the working electrode was carried out by adapting the electrode to a submerged jet cell [25] and by applying a cathodic potential of -1.0 V<sub>SCE</sub>. The flow of water was provided by a peristaltic pump ensuring a regular and stable flow of 1200 tr/min. A saturated calomel electrode (SCE) was used as a reference electrode. The counter electrode was a large platinum grid. The monitoring of the variation of the mass of calcium carbonate deposited electrochemically on the surface of the working electrode was carried out by chrono-electrogravimetric measurements. The scale mass on the gold surface increased with time until stabilization. At this time, the polarization and circulation of the synthetic solution were stopped.

### 2.4.3. SQCM tests

A typical SQCM experimental setup is shown in Fig. 1b. The working electrode is made of a 0.2 cm<sup>2</sup> gold disc previously pre-calcified and the measurements were carried out at a temperature of 30 °C. The flow of water, in the QCM cell, was provided by a peristaltic pump ensuring a regular and stable flow of 1200 mL/min.

The saturation level ( $\delta=31.4$ ) of the studied solution was obtained by moderate CO<sub>2</sub> degassing. The CaCO<sub>3</sub> particles generated in the degassing operation were sent to the SQCM tool and could be adsorbed on the pre-calcified surface of the SQCM set-up. The related CaCO<sub>3</sub> mass changes were recorded over time. The scaling rate was determined from the slopes of the current–time and the mass–time curves [28]. The maximum of the curve obtained from the derivative of the mass–time transient as a function of time gave the maximal recovery rate ( $V_R^{max} = \left(\frac{dm}{dt}\right)_{max}$ ). The values of the maximal recovery rate with ( $v_{R0}^{max}$ ) and without ( $v_{Ri}^{max}$ ) metallic cations allowed to estimate the scaling inhibition efficiency ( $E_{SQCM}$ ) according to the following equation [28]:

$$E_{SQCM} = \frac{v_{R0}^{max} - v_{Ri}^{max}}{v_{R0}^{max}} \quad (11)$$

### 3. Results and discussion

#### 3.1. FCP measurement

FCP curves (pH-time and resistivity-time) obtained in the presence and the absence of zinc and copper cations are shown in Fig. 2.

(Figure 2)

The shapes observed in Fig. 2 are similar to those observed elsewhere [26, 28]. Without cations (blank solution curve), two steps could be observed. The first step corresponds to the nucleation step [28] where the pH increases until a maximal value (Figs. 2b and 2d). During this step, the resistivity remains substantially constant (Figs. 2a and 2c). The second step corresponds to the massive CaCO<sub>3</sub> precipitation where the pH decreases over time until reaching a constant value, and the resistivity increases drastically (Figs. 2a and 2c). Similar variations were also mentioned by Gauthier et al. [32] who demonstrated a good reproducibility of the FCP measurements. The time of CaCO<sub>3</sub> precipitation, noted  $t_p$  (Table 1), is defined by the maximum of the pH-time curve, but also by the break of the slope of the resistivity-time curve [18, 21, 29, 32].

(Table 1)

A careful comparison between doped and blank systems parameters showed that, for the same concentration, the inhibitory effect of  $Zn^{2+}$  is more pronounced than that of  $Cu^{2+}$  [24, 33-35]. Without cations,  $t_p$  is equal to 38 min (Table 1).  $t_p$  increases with cations concentrations, as noted by Benslimane et al. [35]. In all cases,  $Zn^{2+}$  ions are more effective than  $Cu^{2+}$  ions to inhibit calcium carbonate formation, in line with previous results [19, 34]. For example,  $t_p$  reached a value of 68 min for  $Cu^{2+}$  4 mg/L, while the same concentration of  $Zn^{2+}$  provokes a complete inhibition of calcium carbonate precipitation. A concentration of 5 mg/L of  $Cu^{2+}$  is required to achieve a total inhibition of calcium carbonate precipitation.

Other scaling parameters (Table 1), such as the limit saturation level ( $\delta_{limit}$ ), the pH of precipitation ( $pH_p$ ), the resistivity ( $\sigma_p$ ) at the precipitation point, the precipitation rate ( $V_p$ ) and the inhibition efficiency ( $E_{FCP}$ ) [26, 28], were obtained from these FCP measurements. The values of the limit saturation level  $\delta_{limit}$ , parameter characterizing the deviation of the system from its equilibrium state [36, 37], were depicted in Table 1. For the blank solution,  $\delta_{limit}$  is equal to 55.9. It increases with  $Cu^{2+}$  and  $Zn^{2+}$  concentrations [35]. For 4 mg/L  $Cu^{2+}$  and 3 mg/L  $Zn^{2+}$ ,  $\delta_{limit}$  reached 97.1 and 101.7, respectively. For a greater concentration, total inhibition was observed. Moreover, the  $pH_p$  value remains below 8.4.

In addition, the inhibition efficiency ( $E_{FCP}$ ) increases with the amount of the added cations (Table 1).  $E_{FCP}$  increases from 18.4 % to 78.8 % when the  $Cu^{2+}$  concentration rises from 1 to 4 mg/L. The inhibition efficiency reaches a percentage of 88.2% and 99 % for 2 mg/L and 3 mg/L  $Zn^{2+}$ , respectively. Numerous references indicated that soluble copper ( $CuOH^+$ ,  $Cu(OH)_2^0$ ,  $CuCO_3^0$  and  $Cu(CO_3)_2^{2-}$ ) and zinc complex ( $ZnOH^+$ ,  $Zn(OH)_2^0$ ,  $ZnCO_3^0$ ,  $Zn(CO_3)_2^{2-}$ ) are adsorbed on the  $CaCO_3$  nuclear crystals [17] blocking the growth sites, delaying the nucleation step and inhibiting crystal growth [28, 38]. The precipitation rate ( $V_p$ ) was determined from the slopes of the mass–time curves. The obtained values were almost constant, even in presence Cu and Zn cations (Table 1). This suggest that these cations act preferentially on the nucleation stage [16].

### 3.2. SEM micrographs and XRD analysis

The inhibitive action of zinc and copper cations on the scaling process and on the  $\text{CaCO}_3$  crystal morphology was examined by Scanning Electronic Microscopy (SEM) and X-ray diffraction (XRD). SEM micrographs (Fig. 3) were obtained after each FCP experiment.

(Figure 3)

Figure 3 showed that the presence of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions modified the morphology of the  $\text{CaCO}_3$  crystal. Without cations (Fig. 3a), the scale is formed by cauliflower-shaped crystals characteristic of vaterite [14, 15]. Under similar conditions, calcium carbonate precipitates as vaterite, which can turn into a more stable phase (aragonite or calcite) over time [9]. According to Peronno et al. [28], FCP method provokes a fast  $\text{CaCO}_3$  precipitation leading to vaterite formation. This observation was confirmed by the spectrum obtained by X-ray diffraction (XRD), which revealed mainly characteristic peaks of vaterite (Fig. 3d). Significant differences in the crystal form and size between the precipitate of the blank solution (Fig. 3a) and the precipitate in the presence of 2 mg/L cations (Figs. 3b and 3c) were observed. In the presence of 2 mg/L  $\text{Cu}^{2+}$  (Fig. 3b), an important difference was observed on the shape of crystals compared to those formed without copper ions. Indeed, the scale was formed, as confirmed by X-ray diffraction (Fig. 3e), by a mixture of vaterite and aragonite. Notable structural changes are also observed in the presence of 2 mg/L  $\text{Zn}^{2+}$  (Fig. 3c). The corresponding deposit is mostly formed by calcite. However, the X-ray peak analysis revealed the presence of aragonite (Fig. 3f). The molar fractions of observed crystalline varieties were estimated from Eqs. (7), (8) and (9) (*see section 2.3*) when 2 mg/L of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  were added to the blank solution. The values of these fractions, shown in Table 2, are dependent on the nature of the metallic ion at a given concentration, indicating that the nucleation process is dependent on the nature of the used salt.

(Table 2)

The CaCO<sub>3</sub> structure modifications observed in the presence of Cu and Zn cations were attributed to the adsorption of the complex formed between Zn<sup>2+</sup> or Cu<sup>2+</sup> and OH<sup>-</sup>, CO<sub>3</sub><sup>2-</sup> ions on the CaCO<sub>3</sub> nuclear crystals [36]. According to Coetzee et al. [34], the presence of zinc ions induced the formation of calcium carbonate preferentially in the aragonite form. When the Zn<sup>2+</sup>/Ca<sup>2+</sup> ratio was greater than 5.10<sup>-4</sup>, only aragonite was produced. From a ratio of 6.10<sup>-5</sup>, increasing amounts of calcite precipitated with aragonite. Below a ratio of 6.10<sup>-5</sup>, calcite was preferentially formed. At these ratios, even trace amounts of Zn<sup>2+</sup> could slow down the nucleation rate of CaCO<sub>3</sub> and promoted aragonite rather than calcite [36].

### 3.3. SQCM investigations

To the best of our knowledge, no evaluation of the scaling inhibition effect of copper and zinc cations using quartz crystal microbalance with a scaling electrode surface (SQCM) have been performed so far. The following investigation constitutes a first attempt to characterize the inhibiting effect of copper and zinc cations towards scaling in hard water. All SQCM tests were carried out at a supersaturation coefficient value of  $\delta = 31.4$  (fixed value lower than  $\delta_{\text{limit}}$ ) with a pH of 7.9.

First of all, the behaviors of a QCM (bare gold surface electrode) and a SQCM (pre-calcified surface electrode) towards scaling in hard water were compared. Fig. 4 shows a comparison between the two experiments.

(Figure 4)

For the bare gold electrode (QCM experiment), a limited mass change was observed, even after two hours of measurement, and no CaCO<sub>3</sub> crystals were deposited on the electrode surface during 80 minutes. By contrast, the mass of calcium carbonate crystals deposited on the pre-calcified surface increased progressively and continuously. This strongly suggests that the first adsorbed germs from the pre-calcification step constitute preferential sites of CaCO<sub>3</sub> crystalline growth [39-41]. In conclusion, the pre-calcified surface of the quartz is, in hard water solution, very sensitive

towards  $\text{CaCO}_3$  particles adsorption in comparison with the bare gold electrode. This is in agreement with previous investigations in waters with lower hardness [42, 43].

Fig. 5 shows the SQCM data obtained with different copper and zinc concentrations, in order to evaluate the scaling inhibiting effectiveness of these cations.

(Figure 5)

As shown in Fig. 5, the mass variation of the scale deposited on the pre-calcified surface depends clearly on the value of the cation concentration. The higher the cations concentration was, the slower the scaling rate was, which induced a decrease of the amount of  $\text{CaCO}_3$  deposit. The presence of  $\text{Cu}^{2+}$  (Fig. 5a) and  $\text{Zn}^{2+}$  (Fig. 5b) in synthetic water reduced the deposition of  $\text{CaCO}_3$  germs on the pre-calcified surface. With 5 mg/L of  $\text{Cu}^{2+}$  (Fig. 5a) and 4 mg/L of  $\text{Zn}^{2+}$  (Fig. 5b) an almost complete inhibition can be reached. These metallic cations can prevent the  $\text{CaCO}_3$  precipitation by delaying the nucleation process, thus blocking the growth sites, reducing the scaling rate and modifying the surface of calcium carbonate crystals [28, 34, 36].

The  $E_{\text{SQCM}}$  values, calculated from Eq. (11), are indicated in Table 3.

(Table 3)

The inhibition efficiency increased with  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  concentrations. Again, the zinc ions were more efficient than the copper ions to inhibit calcium carbonate on the active surface of the quartz crystal. For example, when the concentration of copper ions increased from 1 mg/L to 5 mg/L, the inhibition efficiency ( $E_{\text{SQCM}}$ ) increased from 6.8 % to 93.2 % whereas it is about 92% with 4 mg/L of  $\text{Zn}^{2+}$ . This is in line with the FCP analysis (*see section 3.1*).

## 4. Conclusion

The investigations presented in this paper allow us to draw the following conclusions:

1- The pre-calcified quartz crystal microbalance (SQCM) shows a higher sensitivity than the classical electrochemical QCM method for 50°F synthetic water containing Cu and Zn cations. It has been successfully applied to study the scale inhibition efficiency of Cu and Zn cations. Maximum inhibition efficiency were reached with 5 mg/L  $\text{Cu}^{2+}$  and 4 mg/L  $\text{Zn}^{2+}$ .

2- In addition, the FCP method showed that these inhibitors are very efficient at concentrations greater than 1 mg/L. The optimal concentration of  $\text{Zn}^{2+}$  ion was 4 mg/L and that of the  $\text{Cu}^{2+}$  ion was 5 mg/L, for which no calcium carbonate precipitation occurred. Trace amounts of inhibitor can substantially block the  $\text{CaCO}_3$  nucleation process.

3- FCP and SQCM results are in good agreement. They are very sensitive to detect the presence of inhibiting substances in water at very low concentrations. Indeed, similar concentrations used with SQCM tests showed that the surface coverage of deposits on a pre-calcified surface was reduced by the presence of these inhibitors.

4- The deposits formed by FCP method essentially consist of vaterite in the absence of inhibitor, aragonite in the presence of copper ion and calcite with addition of zinc ion.

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## Highlights

- A pre-calcified sensitive surface was used for the detection of the scaling process in the presence of copper and zinc ions.
- Scaling quartz crystal microbalance measured the inhibiting effect of copper and zinc ions.
- The kinetics of  $\text{CaCO}_3$  deposit is slower in the presence of copper and zinc ions in hard synthetic water.

## Figure captions

Figure 1: (a) FCP and (b) QCM experimental setup.

Figure 2: FCP curves for (a and b)  $\text{Cu}^{2+}$  and (c and d)  $\text{Zn}^{2+}$  ions. Synthetic water containing initially 200 mg/L  $\text{Ca}^{2+}$ , 30°C and 850 rpm.

Figure 3: SEM images and X-ray diffraction spectra of the  $\text{CaCO}_3$  scale formed by FCP method: (a and d) without cations (b and e) with 2 mg/L of  $\text{Cu}^{2+}$  and (c and f) with 2 mg/L of  $\text{Zn}^{2+}$ , respectively. V, C, A and R designed vaterite, calcite, aragonite and the reference, respectively.

Figure 4: Comparison of QCM and SQCM methods. 50°F synthetic water, 30°C and 850 rpm.

Figure 5: Evolutions of the mass change during  $\text{CaCO}_3$  deposition through SQCM measurements at 30 °C in 50°F synthetic water (initially containing 200 mg/L  $\text{Ca}^{2+}$ ) (a) with copper and (b) with zinc ions at various concentrations.

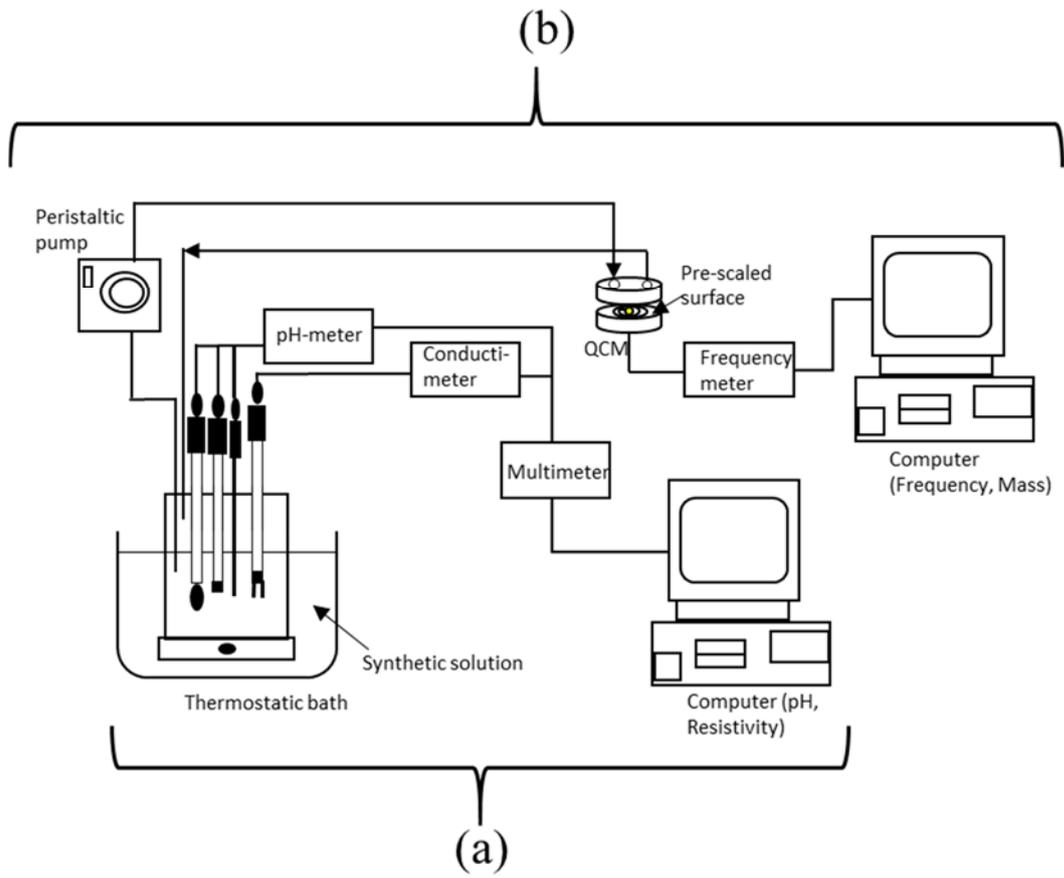


Figure 1

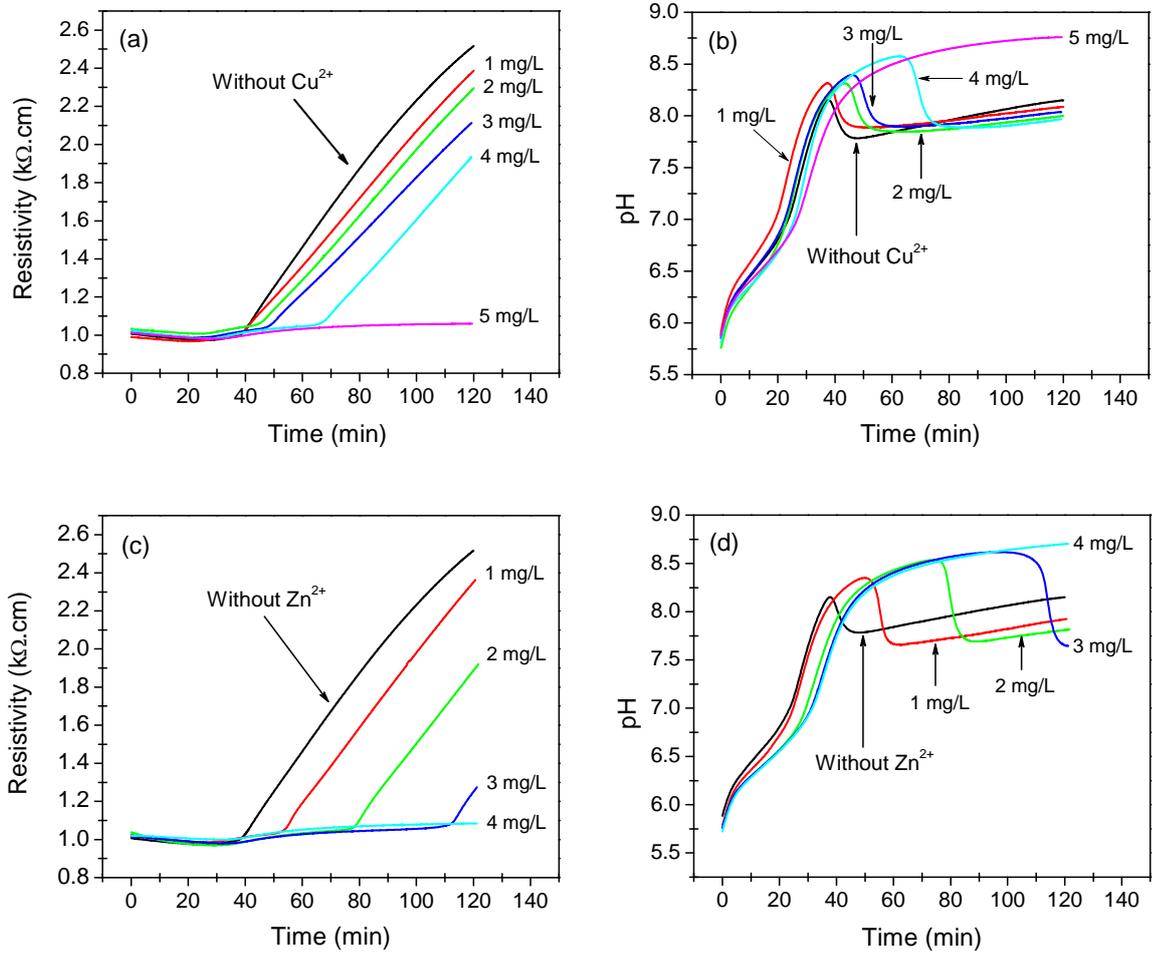


Figure 2

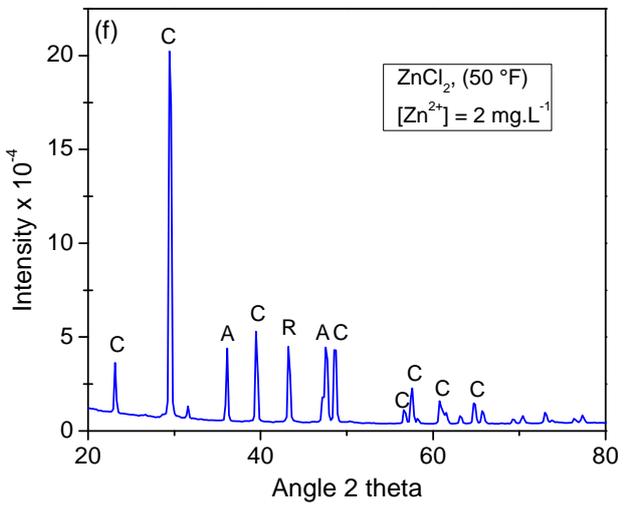
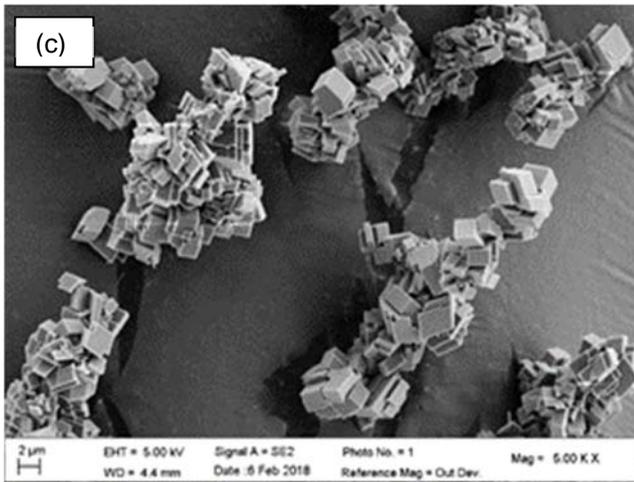
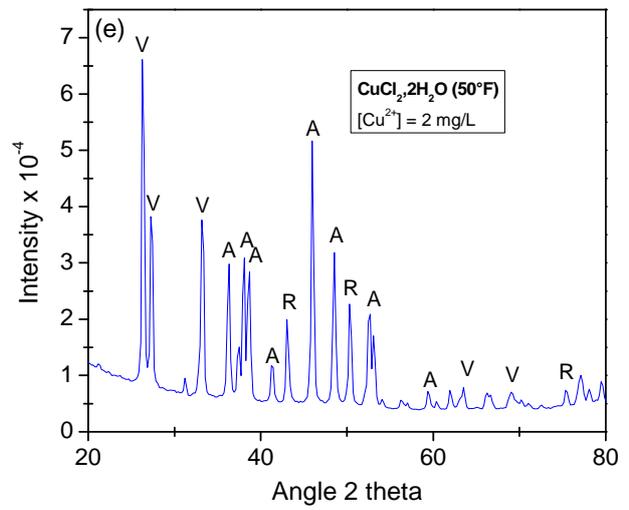
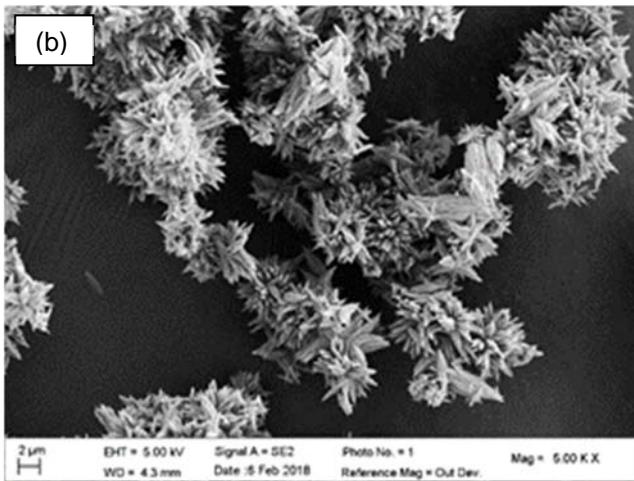
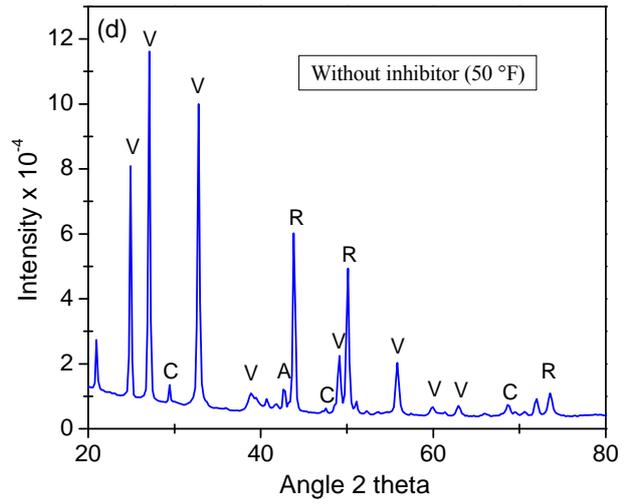
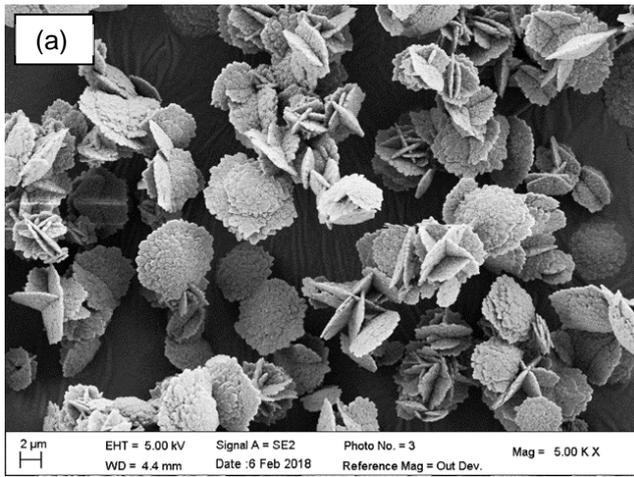


Figure 3

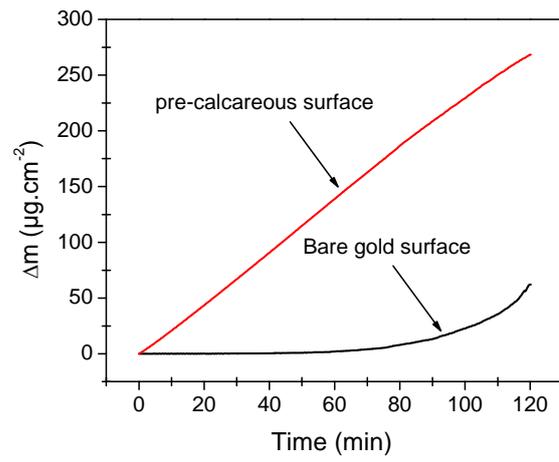


Figure 4

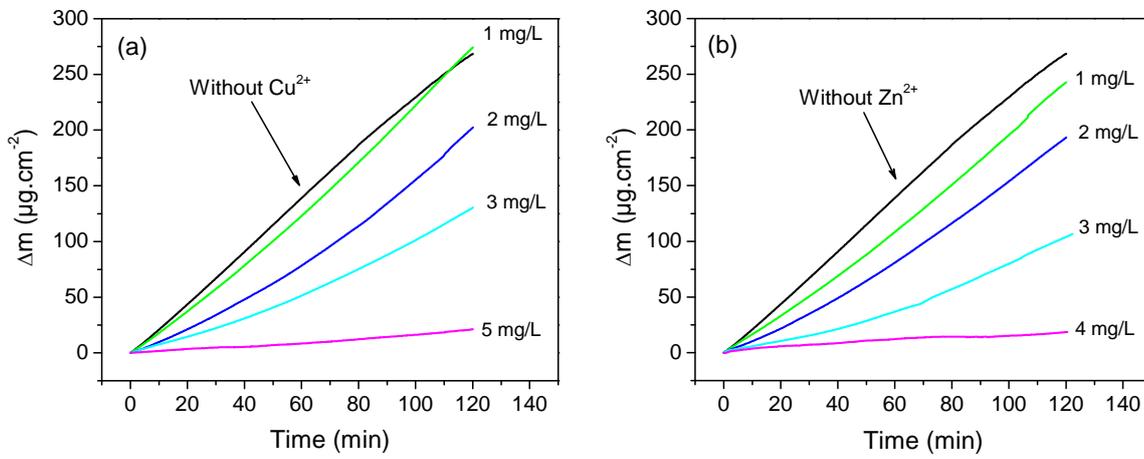


Figure 5

## **Table captions**

Table 1: FCP results for  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  cations.

Table 2: Percentage of different crystalline forms present in solution.

Table 3: Inhibition efficiency for copper and zinc ions determined by SQCM.

Table 1

FCP scaling parameters	pH <sub>i</sub>	t <sub>p</sub>	pH <sub>p</sub>	δ <sub>lim</sub>	V <sub>p</sub> (Ω cm min <sup>-1</sup> )	E <sub>FCP</sub> (%)
Blank solution (BS)	5.8	38	8.1	55.9	18.4	-
(BS)+1 mg/L Cu <sup>2+</sup>	5.9	38	8.3	80.8	17.3	18.4
(BS)+2 mg/L Cu <sup>2+</sup>	5.8	45	8.3	75.4	16.9	38.5
(BS)+3 mg/L Cu <sup>2+</sup>	5.8	49	8.3	78.9	15.3	50.7
(BS)+4 mg/L Cu <sup>2+</sup>	5.8	68	8.4	97.1	16.7	78.8
(BS)+5 mg/L Cu <sup>2+</sup>	5.8			Total inhibition		
(BS)+1 mg/L Zn <sup>2+</sup>	5.8	54	8.2	62.5	19.5	45.1
(BS)+2 mg/L Zn <sup>2+</sup>	5.8	79	8.3	80.4	19.2	88.2
(BS)+3 mg/L Zn <sup>2+</sup>	5.8	112	8.4	101.7	22.2	99.0
(BS)+4 mg/L Zn <sup>2+</sup>	5.7			Total inhibition		

C: concentration; pH<sub>i</sub>: initial pH; t<sub>p</sub>: precipitation time; pH<sub>p</sub>: precipitation pH; V<sub>p</sub>: precipitation rate; E<sub>FCP</sub>: inhibition efficiency calculated from FCP method.

Table 2

CaCO <sub>3</sub> variety	Vaterite (%)	Aragonite (%)	Calcite (%)
Blank solution (BS)	97.9	2.1	-
(BS)+2 mg/L Cu <sup>2+</sup>	75.7	24.3	-
(BS)+2 mg/L Zn <sup>2+</sup>	-	40.7	59.3

Table 3

Concentration mg/L	Efficiency for Cu <sup>2+</sup>	Efficiency for Zn <sup>2+</sup>
1	2.8	17.7
2	37.4	37.2
3	59.0	67.4
4	-	92.0
5	93.2	-

