Thermodynamic study of Zn^{2+} inhibition properties and mechanism on calcium carbonate precipitation by chemical and electrochemical methods

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HIGHLIGHTS

- The Zn^{2+} inhibition mechanisms on $CaCO_3$ precipitation was investigated in this work.
- The Zn^{2+} efficiency at very low concentration is a well established experimental fact.
- Novel mechanism: Zn^{2+} - OH^- reactivity in the 7–9 pH range inhibits $CaCO_3\downarrow$.
- Highlight of the Zn2+ synergetic double inhibiting effect in pre and post-precipitation
- Confirmation by the comparison of chemical-electrochemical experimental methods

ARTICLE INFO

ABSTRACT

In this paper, The Zn^{2+} inhibition mechanism on $CaCO_3$ precipitation was investigated. It is well established that Zn^{2+} delays the precipitation, even at very low concentrations; however, the related mechanism remains not well understood. This paper proposes a novel thermodynamic mechanism to explain the key inhibiting pre-precipitation step of Zn^{2+} on $CaCO_3$ precipitation. It is based on the hypothesis of the Zn^{2+}/OH^- spontaneous complexation reaction to form $ZnOH^+$. This OH^- removal by Zn^{2+}, an established Lewis acid, prevents the HCO_3^-/OH^- reaction. These predictions were verified thermodynamically. It confirms the spontaneous formation and predominance of $ZnOH^+$ complex in the 7.0–9.0 pH range. This Zn^{2+} inhibiting property is strengthened by other complex formation ($ZnCO_{3(aq)}$, $Zn(CO_3)_2^{2-}$, $Zn(OH)_{2(aq)}^\circ$) and by the absence of any Zn precipitate at low Zn^{2+} concentrations. Furthermore, the comparison of chemical-electrochemical experimental methods clarified their differences and evidenced more the thermodynamic and stoichiometric inhibition mechanisms.

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1. Introduction

The research on the $CaCO_3$ scaling inhibition was driven by industrial problems, energy efficiency and commercial motivations. In fact, the $CaCO_3$ inhibition in heat exchangers [1,2], boilers, cooling towers [3,4], desalination and water softening processes [5–8], marine cathodic protection [9], oilfield water injection [10] constituted an enormous market as well as a powerful research driving force.

The high efficiency of Zn^{2+}, at very low concentrations, is well established with a large agreement [11–18].

The Zn^{2+} practical advantages were showed with reverse osmosis [19], and Zn^{2+} electrolytic generation [20]. Even the magnetic inhibiting effect was explained by a corrosion induced phenomenon [21] which generated Zn^{2+} ions. This remarkable inhibition property combined with the low toxicity of Zn^{2+}, opened promising perspectives, especially in this "green inhibitors" area. Its main property is its ability to prevent scale formation.

This Zn^{2+} inhibition effect was quantified by an important increase of the induction time: it was twice compared with the Cu^{2+} treatment and many more than Mg^{2+} [13].

It is well established that Zn^{2+} delays the precipitation induction time and pH: Zn^{2+} prevents the scale formation and acts in homogeneous phase before any $CaCO_3$ precipitation; many references [13,14, 18,21] have confirmed that the Zn^{2+} pre-precipitation effect that was measured by the induction time. This is the key inhibition step which occurs before any neither ulterior crystal growth nor crystal habit inhibiting steps. However, the Zn^{2+} prevention mechanism remained not well understood [15].

A recent study [18] confirms the pre-precipitation effect. Furthermore, it evidenced the absence of any $CaCO_3$ precipitation and a very

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long induction time (70 min) and excellent efficiency (100%). However the related mechanism is not well understood.

There is also a large agreement on the Zn^{2+} inhibiting effect by crystal growth kinetic and crystal habit modification mechanisms. Zn^{2+} promotes the aragonite crystal formation [12,13,15]. However, this mechanism does not explain the pre-precipitation step, before the crystal formation.

The Zn^{2+} pre-precipitation effect, before any $CaCO_3$ precipitate or crystal formation, is an evident experimental reality which cannot be explained by crystal growth kinetic nor crystal habit modification. These last mechanisms become coherent after the precipitation step and the crystal formation. It is then clear that the first and most important inhibiting step, illustrated by the long induction time, remains without explanation and needs an alternative mechanism.

This research work proposes a thermodynamic mechanism based on the Zn^{2+} reactivity with its neighboring environment, just before the $CaCO_3$ precipitation.

It investigates specifically the (Zn^{2+}/OH^-) and (Zn^{2+}/CO_3^{2-}) interactions and their influence on the $CaCO_3$ precipitation delay. It is based on following hypothesis: Zn^{2+} and HCO_3^- compete to react with OH^- to form $ZnOH^+$ and CO_3^{2-} respectively. Here, the key questions are the following: does this OH^- react firstly with Zn^{2+}, to form the hydro-complex $ZnOH^+$ and delay the calcium carbonate precipitation or with HCO_3^- to form CO_3^{2-} and promotes the $CaCO_3$ precipitation? This hypothesis were verified and confirmed using thermodynamic associated with numerical calculations and with electrochemical method.

2. Theory

This section aims to enlighten the exceptional thermodynamic roles of micro quantities of Zn^{2+} to explain the inhibition mechanisms of calcium carbonate precipitation. This approach is focused on the interactions of OH^- and CO_3^{2-} with Zn^{2+}.

The fundamental theory of calcium carbonate precipitation remains based on thermodynamic considerations, whatever the crystal polymorphism is. The verification of the solubility product K_S (1) condition is a necessary step before any $CaCO_3$ precipitation:

$$Ca^{2+} + CO_3^{2-} \Leftrightarrow CaCO_3 \qquad Ks = \left(Ca^{2+}\right)\left(CO_3^{2-}\right) \qquad (1)$$
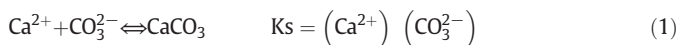
This $CaCO_3$ precipitation generally occurs in the pH range of 7.0 to 9.0. In this interval, the Ca^{2+} and CO_3^{2-} concentrations plays a key role in the scaling reaction and in this pH region the OH^- and CO_3^{2-} concentrations are in the ppm range. In spite of these very low concentrations they had a predominant influence on the precipitation process.

The masking of OH^- and CO_3^{2-} by the presence of Zn^{2+} constituted the main hypothesis of this research work to delay the precipitation.

Many references [22], thermodynamic equilibrium data [23–25] (Table 1), species distribution diagrams confirms the formation of $ZnOH^+$, $ZnCO_{3(aq)}^\circ$, $Zn(OH)_{2(aq)}^\circ$ and $Zn(CO_3)_2^{2-}$ complexes in the studied pH range.

Table 1
stability formation constants of Zn^{2+} complexes in H_2O and in carbonate systems.

Reaction	Log(K)	
$Zn^{2+} + H_2O \Leftrightarrow ZnOH^+ + H^+$	−8.96 [23]	−7.5 [24,25]
$Zn^{2+} + 2H_2O \Leftrightarrow Zn(OH)_{2(aq)}^\circ + 2H^+$	−16.9 [23]	−16.4 [24,25]
$ZnCO_{3(aq)}^\circ \Leftrightarrow Zn^{2+} + CO_3^-$	−3.9 [26]	−5.3 [25,27]
$Zn(CO_3)_2^{2-} \Leftrightarrow Zn^{2+} + 2CO_3^-$		−9.63 [25]
$ZnHCO_3^+ \Leftrightarrow Zn^{2+} + HCO_3^-$	−2.1 [25,27]	

More precisely, using the Hydra–Medusa program [25], the obtained speciation diagrams (Fig. 1) confirms the important proportions of these Zn^{2+} complex species.

3. Materials and methods

3.1. Solution preparation

The inhibiting effect of Zn^{2+} was investigated with a synthetic CalcoCarbonically pure (CCP) solution. It was prepared from bi-distilled water and a pure solid calcium carbonate (Fluka/Purity ≥ 99%). For a complete solubilisation of $CaCO_3$, the CCP was maintained under a CO_2 bubbling for 20 hours. The final solution is a very aggressive medium with an acidic pH of 5.60 and a calcium hardness of 30 °F or 40 °F (1 ° F = 10 mg/l $CaCO_3$) according to the studied experiments.

The solubilisation reaction was:

$$CaCO_{3(s)} + H_2O + CO_2 \Leftrightarrow Ca^{2+} + 2\ HCO_3^- \qquad (2)$$

3.2. Principle and set-up of the artificial chemical scaling (LCGE controlled degassing method)

This method was named as the **LCGE** laboratory was the first to develop the method and the set up [28]. Based on a progressive CO_2 evolution, this method tended to simulate the natural scaling process in real aquatic media.

The experimental cell, presented in Fig. 2, contains 500 ml of the CCP solution, and is immersed in a 30 °C thermo-stated bath. A controlled air flow bubbling system (atmospheric air) was placed at the cell bottom to degas progressively and uniformly the CO_2 saturated CCP solution.

At the same time, calcium concentration (conventional Ca^{2+} titration by EDTA) and pH measurements (Radiometer pHM240 pH meter) were performed. The maximum pH value of the pH-time plots (pH_p) corresponds to the beginning of the calcium carbonate precipitation is associated to the induction time (t_p), which characterize the inhibition efficiency.

In addition, the supersaturating β-time curves are also plotted. This curve presents a maximum noted $β_p$. This last measures and confirms the induction time t_p. It is calculated as follows:

$$\beta = \frac{\left(Ca^{2+}\right)\left(CO_3^{2-}\right)}{Ks} = \frac{10^{pH-pK_2}\left[Ca^{2+}\right]\left[HCO_3^-\right]\gamma_{Ca^{2+}}\gamma_{HCO_3^-}}{Ks} \qquad (3)$$

where $(Ca^{2+}) = [Ca^{2+}]\gamma_{Ca^{2+}}\gamma_{Ca^{2+}}$ and $\gamma_{HCO_3^-}$ are respectively the ionic activity coefficients of Ca^{2+} and HCO_3^-. K_s is the $CaCO_3$ solubility product. K_2 is the dissociation constant of the acid-base couple HCO_3-CO_3^{2-}.

3.3. Artificial electrochemical scaling method

The electrochemical scaling experiments were carried out with the system shown in Fig. 3. A potentiostat/Galvanostat (Autolab PGSTAT30 Metrohm), controlled by the GPES 4.9 software, was connected to a 100 ml electrochemical cell (Metrohm). A lab made silver-disc working electrode (keeping a large potential range for our academic experiments), a SCE (Saturated Calomel Electrode) reference electrode and a platinum auxiliary electrode constitutes the three classical electrodes used here. The studied solution was stirred with a magnetic stirrer at 700 r/min.

This electrochemical method was largely used by [29]. It is based on the forced precipitation of $CaCO_3$ on the working electrode surface where the applied reduction potential (−980 mV vs SCE) promotes the O_2 reduction and increases the local interfacial pH according to Reactions (4) et (5) [29–33].

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad (4)$$