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Study of the inhibition effect of two polymers on calcium carbonate formation by fast controlled precipitation method and quartz crystal microbalance

Dimitri Peronno[a,b,c], Hélène Cheap-Charpentier[a,b,c], Olivier Horner[a,b,c], Hubert Perrot[b,c,*]

[a] *EPF Ecole d'Ingénieur, 3 bis rue Lakanal, 92330 Sceaux, France*
[b] *Sorbonne Universités, UPMC Université Paris VI, UMR 8235, Laboratoire Interfaces et Systèmes Electrochimiques (LISE), 4, place Jussieu, case courrier 133, F-75005 Paris, France*
[c] *CNRS, UMR 8235, LISE, F-75005 Paris, France*

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ABSTRACT

In this paper, the inhibition efficiency of two inhibitors, namely poly(acrylic acid-*co*-maleic acid) and polyaspartic acid, towards calcium carbonate scaling was evaluated using fast controlled precipitation (FCP) method and electrochemical quartz crystal microbalance (EQCM). FCP method gave some insight to the calcium carbonate precipitation in solution, whereas EQCM was used to study the calcium carbonate formation on a metallic substrate. It has been shown that these polymers were efficient to delay or to prevent nucleation/growth process, depending on their concentration. Moreover they significantly decreased the crystal growth rate. The FCP method showed that these inhibitors were very efficient at low concentrations ($4\,\mathrm{mg\,L^{-1}}$) when no precipitation occurred. In addition, EQCM showed that the surface coverage of deposits on a substrate was reduced by the presence of these inhibitors at very low concentration ($4\,\mathrm{mg\,L^{-1}}$). Scanning electronic microscopy and X-ray diffraction showed that the presence of these polymers modified the morphology of calcium carbonate crystal. In order to model nucleation/growth process of calcium carbonate on surface, mass–time transients were interpreted using a 3D model based on a nucleation following a Poisson law associated to vertical and lateral growth rates.

1. Introduction

Scale deposition (e.g., $CaCO_3$, $CaSO_4$, $BaSO_4$) is a difficulty encountered in industry and domestic equipment such as heat exchangers [1], in cooling systems [2] and desalination plants [3]. It can cause important technical and economic problems [4,5] in various industrial processes. Indeed, undesirable scale deposits may cause partial or total obstruction of pipes, limitation of heat exchange or a collapse of the structures. The non-productive expenses related to scaling were estimated at 1.5 milliards euros per year in France [6].

Calcium carbonate $CaCO_3$ is the most abundant component of scales deposited from natural water [7]. It exhibits three polymorphs: vaterite (hexagonal), aragonite (orthorhombic) and calcite (rhombohedric) listed in order of increasing stability [8]. Calcite is thermodynamically stable at atmospheric pressure within the 0–90 °C temperature range [9] whereas aragonite and vaterite form metastable phases. It has been shown that vaterite could convert into calcite or aragonite in a later stage of growth [10]. At ambient temperature, $CaCO_3$ precipitates under calcite form.

The precipitation of calcium carbonate occurs in two steps: heterogeneous nucleation step [11] followed by a crystal growth step [12]. It depends on several factors such as ionic activities, pH, temperature, presence of foreign ionic or molecular species [9,13,14], calcium carbonate concentration, water composition, water hardness, presence of additives [15,16] and saturation level of water [17,18].

During the three last decades, several non-electrochemical methods have been developed to study the scaling process in natural waters [19–21]. Fast controlled precipitation (FCP) method was

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Abbreviations: EQCM, electrochemical quartz crystal microbalance; FCP, fast controlled precipitation; PAMA, poly(acrylic acid-*co*-maleic acid); PASP, polyaspartic acid; SEM, scanning electronic microscopy; XRD, X-ray diffraction.

[*] Corresponding author at: CNRS, UMR 8235, LISE, F-75005 Paris, France. Tel.: +33 1 44 27 72 16.

E-mail address: hubert.perrot@upmc.fr (H. Perrot).

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used to assess the calcium carbonate precipitation in bulk solution. In this technique, precipitation of $CaCO_3$ is accelerated by removing dissolved CO_2 under moderate stirring [22,23]. It is slow enough to model natural processes. In another study, quartz microbalance allowed studying calcium carbonate deposited thermally [24].

Electrochemical methods (e.g., chronoamperometry [25], electrochemical impedance [26,27]) have been developed in order to estimate the scaling propensity of waters involving calcium carbonate precipitation. Electrochemical precipitation [28–30] was usually used as a method to predict scale deposition or to determine inhibitor efficiency. Quartz crystal microbalance coupled with chronoamperometry was used to study $CaCO_3$ deposition [31,32] and the adhesion mechanism of calcareous scaling on a surface [33].

One of the most effective ways to prevent scaling process is to add scale inhibitors in the solution. Indeed, many water soluble additives or polyelectrolytes may influence crystal growth mechanism, nucleation, shape and size of the crystals [34] and polymorph of calcium carbonate [35]. Additives commonly used for scale inhibition are polymers containing carboxylic acid groups such as polyacrylic acid [36–38], polymaleic acid [38] and polyaspartic acid (PASP) [15,39]. These polymers have important properties including low concentration effect or high temperature endurance. To our knowledge, the copolymer poly(acrylic acid-*co*-maleic acid) (PAMA) is not widely used as antiscalant [40,41] whereas polyaspartic acid (PASP) is a well-known green inhibitor, in terms of biodegradability, non-toxicity and non-bioaccumulation [42,43].

The aim of our study was to investigate the inhibition effect of poly(acrylic acid-*co*-maleic acid) (PAMA) and polyaspartic acid (PASP) (Fig. 1) on the nucleation/growth process of $CaCO_3$ in a bulk and on a metallic surface. The antiscaling performance of PAMA and PASP was studied using FCP and EQCM methods. The kinetics of electrochemical scaling was probed through the measurement and analysis of the mass and current changes with time. Crystal morphology was determined by scanning electronic microscopy (SEM) and X-ray diffraction (XRD). Moreover, in the present article, nucleation and growth rates were deduced on the basis of an original model discussed in some previous papers [28,44].

2. Materials and methods

2.1. Reactants

All the experiments were performed in carbonically pure waters, which only contained Ca^{2+} and $CO_3{}^{2-}$ ions. The concentration of Ca^{2+} ions in all test solutions was initially 200 mg L^{-1}. Preparation of test solutions of calcium carbonate has been previously described [45]. Poly(acrylic acid-*co*-maleic acid) solution and poly-(α,β)-D,L aspartic acid sodium salt powder were purchased from Sigma–Aldrich. The chemical structures of these polymers are shown in Fig. 1. Stock solutions of poly(acrylic acid-*co*-maleic acid) and poly-aspartic acid were prepared in pure water at a concentration of 1 g L^{-1}.

2.2. Fast controlled precipitation (FCP) method

FCP is a technique which allowed the nucleation step and the homogenous precipitation of calcium carbonate in solution in the absence and in the presence of inhibitor to be characterized. The principle of this technique was already detailed elsewhere [45]. All experiments were carried out at 30 °C and the temperature was controlled by a temperature probe. pH and resistivity were measured simultaneously using a pH-meter (Radiometer pHM220) and a conductivity-meter (Radiometer CDM230). pH and conductivity electrodes were purchased from Radiometer Analytical. Saturated calomel electrode (SCE, Radiometer Analytical) was used as reference electrode. The full set up was monitored by a PC computer allowing the simultaneous recording of pH and resistivity as a function of time. The time related to the maximum pH is characteristic of the time precipitation, t_p. For a given concentration, the scale inhibition efficiency E_{FCP} of each inhibitor was calculated as following (Eq. (1)):

$$E_{FCP} = \frac{\int \rho_0.\mathrm{dt} - \int \rho_i.\mathrm{dt}}{\int \rho_0.\mathrm{dt}} \times 100 \qquad (1)$$

where ρ_0 and ρ_i are the resistivities of the synthetic water in the absence and in the presence of inhibitor, respectively. The resistivity is more adapted to estimate the inhibitor efficiency as this parameter is a mirror of the evolution of the calcium carbonate concentration.

2.3. Electrochemical quartz crystal microbalance (EQCM)

EQCM was performed to measure the mass of calcium carbonate deposited on an active surface and to assess the scaling rate in the absence and in the presence of inhibitor. This technique has been previously described elsewhere [31]. The working electrode was a 5 mm diameter gold disc deposited in a 9 MHz AT cut quartz crystal resonator (Temex); it was adapted in a submerged impinging jet cell. The counter electrode was a large platinum grid. The electrochemical potential applied at the working electrode was maintained at −1 V/SCE, which led to the reduction of the dissolved dioxygen according to the electrochemical reaction (Eq. (2)):

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

The formed hydroxyl ions increased the local pH near the electrode surface up to 11.2 if no chemical reaction contributed to the consumption of OH^- ions [14,46]. It leads to $CaCO_3$ precipitation according to Eq. (3):

$$4Ca^{2+} + 4HCO_3{}^- + O_2 + 4e^- \rightarrow 4CaCO_3(s) + 2H_2O \qquad (3)$$

The full set up was monitored by a PC computer allowing the simultaneous recording of the current and the frequency change Δf as a function of time. The frequency change Δf of the quartz resonator due to the deposition of the scale on the working electrode was proportional to the mass change Δm according to Sauerbrey equation (Eq. (4)) [47]:

$$\Delta f = -K_s \cdot \Delta m \qquad (4)$$

where K_s is the sensitivity factor $(K_s)^{-1}$ = 1.09 ng per Hz for an electrode area of 0.2 cm^2. The frequency of the oscillator was measured by a frequency-counter (Fluke PM6685).

The current, recorded during calcium carbonate deposition, decreased over time to a residual value. The scaling time needed to reach this residual value was used to compare the effects of different kinds of inhibitors [28]. The scaling rate was determined by the slopes of the current–time and the mass–time curves. The maximum of the curve obtained from the derivative of the mass–time transient as a function of time gave the maximal recovery rate ($\nu_R^{max} = \left(\frac{dm}{dt}\right)_{max}$). The scaling inhibition efficiency E_{EQCM} was calculated as following (Eq. (5)):

$$E_{EQCM} = \frac{\nu_{R_0}^{max} - \nu_{R_i}^{max}}{\nu_{R_0}^{max}} \qquad (5)$$

where $\nu_{R_0}^{max}$ and $\nu_{R_i}^{max}$ are the maximum of the curve $dm/dt = f(t)$. For a given solution, this curve is obtained from the integration of the mass–time curve as a function of time in the absence and in the presence of inhibitor, respectively.