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Abstract

In this work, the scaling protection performance of Zn^{2+} and Cu^{2+}, added to a phosphosilicate hybrid sol-gel coating and applied on both carbon and stainless steel surface, was evaluated for the first time in a solution containing initially 200 $mg.L^{-1}$ of Ca^{2+} (corresponding to a water hardness of 50 °F) at 30 °C. Inhibition efficiency was estimated using chronoamperometry (CA) and quartz crystal microbalance (QCM). Results showed that these smart coatings were efficient to protect steel surface against scaling phenomenon. The coatings containing the Cu^{2+} inhibitor was the most effective of the systems tested. Moreover, CA and QCM measurements showed that the formation of calcium carbonate deposition on carbon steel decreased when the amount of zinc and copper ions added to the sol-gel film increased. Scanning electronic microscopy and X-ray diffraction results indicated that both cations included in the sol-gel film affected calcium carbonate nucleation by changing the morphology of $CaCO_3$ crystals.

Keywords: Scale inhibition, zinc (II) cation, copper (II) cation, sol-gel coating, quartz crystal microbalance

Abbreviations: EQCM: electrochemical quartz crystal microbalance; CA: chronoamperometry; QCM: quartz crystal microbalance; SEM: scanning electronic microscopy; XRD: X-Ray diffraction;

1. Introduction

The problems related to the scaling phenomena of industrial facilities in contact with waters become more massive and more insidious. These issues can, as already pointed in numerous scientific papers, lead to a decrease of the thermal efficiency of the circuit, an obstruction of pipes as well as the proliferation of living organisms [1-7]. Thus, the economic losses associated with $CaCO_3$ precipitation can be significant [8-10]. To fight this phenomenon, several protection methods have been applied to preserve installations against scaling. These methods can be divided into two types: physical and chemical methods. Among the physical methods, magnetic treatments are generally used [11]. Chemical methods are based on the use of organic molecules as anti-scalant in numerous situations to prevent scale precipitation [12, 13]. Some synthetic and natural water-soluble polymers used as scaling inhibitors have been investigated and reported in literature [12-16]. However, many inhibitors showed up has a secondary effect, causing damages on the environment. Indeed, poly-phosphonates are very efficient but they can cause eutrophication when they are rejected in natural waters [17, 18]. Thus, the scientific community began searching for environmentally friendly inhibitors (green inhibitors) derived from petrochemicals [14-22], plant extracts [23-33] and chemical modified natural products from industrial process [34-36]. Nevertheless, the compatibility with the water environment and the respect of the different safety rules are always questionable even if these products come from plants or similar. Alternate approach must be found in this context and smart films based on sol-gel technique can be examined [37]. Materials such as organic-inorganic hybrid compounds are one of the feasible solutions that enable protection from $CaCO_3$ precipitation reactions during application. They constitute a new generation of multifunctional materials with useful properties and diverse applications. In addition, polymeric materials are characterized by their low weight to volume ratio, their excellent resistance to chemical attack, their eco-friendly properties and their low cost [38]. Further modification of polymer matrix by doping with ions at low concentrations can proffer superior physical properties of such polymer.

The use of eco-friendly sol-gel coatings to prevent scale inhibition can constitute an emerging area of applications such as it is the case in the corrosion domain [39-45]. In a similar manner, sol-gel hybrid coatings for metal protection against scaling phenomenon appears as an interesting field of research. Indeed, it is an attractive technique used to synthesize hybrid materials with various composition that allow to entrap molecules in an inorganic glassy matrix [41, 46]. The properties of these sol-gel coatings are strongly dependent on their processing conditions, pH, temperature and molar ratio of precursors [42, 47]. Silica hybrid sol-gel coatings are particularly studied and employed for corrosion protection due to their interesting properties, such as hydrophobicity and good adhesion to metallic substrates [48]. The use of precursors containing non–hydrolysable bonds allows the organic network to bind directly to the inorganic network in the structure. Thus, hybrid sol-gel coatings can have the combined properties of both organic and inorganic functions [43, 44]. The nature of the organic function (phenyl function, epoxy function, vinyl function and methacrylate function) influences the properties of the network [39, 49]. The integration of phosphate or phosphonate groups in the sol-gel network has been published in several works [50-52]. The outcomes proved a good adhesion to the metallic surface of the film containing phosphorus groups. Santana et al. [49] studied the effect of the pre-treatment of the carbon steel surface with a phosphoric acid solution before applying a hybrid sol-gel film. SEM images showed that the pre-treatment step produces a rougher surface than that of untreated steel. This roughness results in better adhesion of the sol-gel film to the treated steel substrate. The microstructure of the film obtained by the sol-gel process depends on the pH of the solution [43, 44]. Therefore, an acid catalysis leads to the formation of longitudinal fibers and an increase in the condensation generated while a basic catalysis leads to clusters formation characterized by a spherical shape [53]. Under acidic conditions, the cation H_3O^+ facilitates the substitution of the OR groups and therefore hydrolysis. With basic catalysts, the OH^- anion is attracted towards the electronegative metal (M) and favours the formation of M–O–M bond by condensation [54, 55]. According to Phan

et al. [56], adding phosphoric acid H_3PO_4 provides the most resistant hybrid coating. A denser network with a greater number of Si–O–P bonds promotes good adhesion to the metallic surface. The formation mechanism is given in [56] and these authors have used this coating to study the corrosion of a metallic surface.

As it is summarized above, many compounds were applied as scaling inhibitors. All of them were added to the studied water while the metallic surface treatments such as sol-gel coating process, were mainly applied to protect metal against corrosion. To our knowledge, no investigations on the scaling inhibition via sol-gel doped coatings on steel surface in pure carbonic solution have been performed to date. The present investigation shows the first attempt to synthesize a sol-gel film on a surface and doped with metallic ions to prevent scale formation. In this work, hybrid sol-gel coatings were deposed on both carbon steel and stainless steel from 3-[(methacryloyloxy)propyl] trimethoxysilane (MEMO) and bis-[2-(methacryloyloxy) ethyl] phosphate (BMEP) via sol-gel process (Fig. 1). The experimental procedure is similar to that adopted by Phan et al. [56]. To improve their anti-scaling properties, deposited coatings were doped by Cu^{2+} and Zn^{2+} cations. Chronoamperometry (CA) and quartz crystal microbalance (QCM) methods were performed to evaluate the scaling inhibition efficiency of these layers. To complete the information about the composition and the morphology of the doped sol-gel coatings, scanning electron microscopy (SEM) observations and X-ray diffraction (XRD) analysis were done to link the layer properties to the electrochemical and gravimetric characterizations.

2. Materials and methods

2.1. Scaling solution

The synthetic carbonically pure water, containing initially 200 mg. L^{-1} of Ca^{2+} (water hardness of 50 °F), was prepared by dissolving calcium carbonate ($CaCO_3$) powder (VWR AnalaR NORMAPUR, 99.7% purity) in bi-distilled water. To dissolve calcium carbonate, carbon dioxide CO_2 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.

2.2. Doping solution

Suitable amounts of solutions of analytical grade $ZnCl_2$ (Merck, 98 % purity) and $CuCl_2$-$2H_2O$ (Acros Organics, 99 % purity) were prepared for doping coatings tests. For the doping process, metallic cations molar quantities ranged from 10^{-5} to 10^{-3} mol.

2.3. Sol-gel coating solution

The sol-gel coating process was applied using 3-[(methacryloyloxy)propyl] trimethoxysilane (MEMO) and bis [2-(methacryloyloxy) ethyl] phosphate (BMEP) precursors from Sigma-Aldrich and ethanol provided by VWR. All compounds were used without any further purification and chemical formulas are given in Fig. 1.

2.4. Metallic substrate and covered QCM resonators

Two different metallic substrates were used in this study. The first one is carbon steel with a chemical composition (in wt %) of 0.28 % C, 0.28 % Si, 1.25 % Mn, 0.03 % P, 0.16 % Cr, 0.15 % N, 0.07 % Ni, 0.009 % Mo and Fe balance. The carbon steel working electrode, 0.2 cm^2 of active area, was embedded in inert resin, polished with silicon carbide paper up to 1200 grade before each experiment. A rotating disk electrode (Tacussel model EDI 101) was used with a rotation speed (Ω) which was fixed at 500 rpm. The second substrate is based on stainless steel AISI 316L (Fe/Cr18/Ni10/MO3) sheet (Good fellow, reference FF210320). Thin stainless steel 316L films were prepared on quartz resonators surface using a commercial RF magnetron sputtering system (Pfeiffer PLS500) from 316L steel disc target of 50 mm diameter. More precisely, stainless steel was deposited on the gold electrode (0.2 cm^2) of the resonators (9 MHz, AWS Sensors, Spain) to perform QCM-based analysis.

2.5. Sol-gel coating

2.5.1. Pre-treatment of the surface

160 The pre-treatment of the electrode surface was carried out by crystalline phosphating process
161 with a commercial solution Decorrdal 47-15-1 (Klüthe). It is a mixture of ethanol (molar
162 fraction between 50 and 75%) and sodium 3-nitrobenzenesulphonate $C_6H_4NNaO_5S$ (molar
163 fraction between 50 and 75% and molecular weight 225.15 $g.mol^{-1}$). Crystalline phosphating
164 process, recommended by Klüthe, reduces the flaking surface by forming a phosphate-
165 converting layer that constitutes a base for bonding the coatings, making the surface rougher
166 and improving the adhesion of the coating on the metallic surface [56].
167 The surfaces of 316L steel and carbon steel were pre-treated with a Decorrdal 47-15-1
168 commercial solution for 5 min at a temperature of 40 °C. The increase in temperature is more
169 favourable to phosphating, which eliminates the presence of iron oxide on the steel surface.
170 *2.5.2. Sol-gel preparation*
171 The sol–gel process is based on the hydrolysis and condensation reactions of silicons alcoxydes
172 $Si(OR)_n$ in solution (sol) allowing to achieve an infinite viscosity network (gel), where *n* is the
173 oxidation state and OR is an alkoxy group with R an alkyl chain [37]. The most often used
174 precursors for this type of application are tetra–functional silicon alkoxides of formula $Si(OR)_4$
175 [57]. Herein, the sol–gel preparation was done in two stages: hydrolysis (the synthesis of "sol")
176 following by the condensation (the formation of "gel"). The mechanism was well detailed by
177 Phan et al. [56]. Hydrolysis of MEMO in aqueous medium took place via $Si\text{-}OCH_3$ methoxy-
178 silane groups according three successive reactions:

179 $$R\text{-}Si(OCH_3)_3 + H_2O \rightarrow R\text{-}Si(OCH_3)_2(OH) + CH_3OH \quad (1)$$

180 $$R(Si(OCH_3)_2(OH) + H_2O \rightarrow R\text{-}Si(OCH_3)(OH)_2 + CH_3OH \quad (2)$$

181 $$R(Si(OCH_3)(OH)_2 + H_2O \rightarrow R\text{-}Si(OH)_3 + CH_3OH \quad (3)$$

182 Then, condensation reactions occurred according the following reactions:

183 $$R\text{-}Si(OH)_3 + R\text{-}Si(OH)_3 \rightarrow R\text{-}(OH)_2Si - O - Si(OH)_2\text{-}R + H_2O \quad (4)$$

184 $$R\text{-}Si(OCH_3)_3 + R\text{-}Si(OH)_3 \rightarrow R\text{-}(OCH_3)_3Si - O - Si(OH)_2\text{-}R + CH_3OH \quad (5)$$

185

186 The sol-gel procedures used in this work are schematised in Fig. 2. In a first step, MEMO is
187 hydrolysed in an ethanol/water mixture with MEMO/ethanol/water molar ratio of 1/2/3
188 (corresponding to the volumes 2.85/1.4/0.65 mL) and then, by stirring at room temperature
189 during 3h. This selected duration makes it possible to obtain a complete hydrolysis. Ca^{2+} and
190 Zn^{2+} cations were injected in the ethanol solution at the beginning with different molar amounts
191 ranged from 10^{-5} mol to 10^{-3} mol. Then, 0.3 mL of BMEP was added to the above solution in
192 order to obtain MEMO/BMEP molar ratio of 10/1 (10Si-1P). This mixture was stirred
193 vigorously at 65 °C for 1 hour, diluted with 1.61 mL of ethanol to obtain a mass concentration
194 of 80% of sol–gel in ethanol. Afterwards, the mixture was stirred for at least 15 min until
195 complete dissolution. The methoxy-silane groups of MEMO precursor are capable to form an
196 inorganic network Si–O–Si through sol-gel reactions and a polymerizable methacrylate group
197 capable of producing an organic network. The BMEP precursor containing the functional P–
198 OH group allows the coating to have good adhesion and a better-condensed inorganic network
199 by forming strong Fe–O–P bonds with metallic substrates and Si–O–P bonds with a silica
200 network [56, 58]. The obtained sol-gel films were deposited on polished carbon steel and
201 stainless steel substrates deposited on the gold electrode of a quartz resonator using a
202 micropipette (2 µL). The film is maintained at room temperature for 5 min, then, dried at 80 °C
203 for 20 h, and finally at 120 °C for 2 h in an oven.

204 *2.6. Scaling study techniques*

205 *2.6.1. Quartz crystal microbalance (QCM)*

206 The piezoelectric properties of the quartz crystal correlate the frequency change and the mass
207 change deposited on the active surface of quartz crystal according to the Sauerbrey equation [1,
208 59]:

209 $$\Delta f = -2 \frac{f_0^2}{S\sqrt{\rho\,\mu}} \Delta m \quad (6)$$

where Δf and Δm are the frequency change and the mass change deposited on the electrode surface, respectively, f_0 is the quartz resonance frequency, ρ, the quartz density, μ, the quartz shear modulus and S, the active surface of the quartz given by the shape of one of the gold electrodes. In a typical QCM set-up, the working electrode is made of a 0.2 cm^2 gold disc deposited in a 9 MHz AT cut quartz crystal resonator. Typically, the theoretical sensitivity using Eq. 6 is around 1 ng/Hz. The gold surface of the quartz was previously covered with a layer of stainless steel 316L covered by a sol-gel film as described in the previous paragraph.

During the QCM test, a volume of 400 ml of the studied synthetic water (carbonically pure solutions containing 200 $mg.L^{-1}$ of Ca^{2+}, corresponding to 50 °F) was transferred to a Teflon container placed in a thermostated bath at 30 °C. CO_2 degassing was achieved by magnetic stirring at 850 rpm. The degassing of the solution was blocked by stopping the stirring and closing the opening of the beaker lid in order to block its level of supersaturation corresponding to a pH of 7.9. Then, a peristaltic pump was used to transfer the solution in the QCM cell. The QCM setup was monitored by a lab-made software, allowing the recording of the frequency changes as a function of time. At the end, mass variations over time can be estimated using Eq. 6. Details of this methodology were already given in other works [1, 6].

2.6.2. Chronoamperometry (CA)

CA was used to investigate the scaling process under different conditions [5, 60]. During measurement, the current was recorded as a function of time at a fixed scaling optimal potential of -1 V/SCE [60]. Experiments were carried out in a classical three electrodes cell. A saturated calomel electrode (SCE) was used as a reference electrode. The carbon steel with and without sol-gel coating acted as a working electrode. The counter electrode was a large platinum grid.

2.7. Surface characterizations

2.7.1. SEM observations

After each experiment, the morphology of calcium carbonate crystals deposited on both carbon steel and stainless steel with and without sol-gel coating during the QCM and CA experiments

was analysed using scanning electronic microscopy (SEM). The SEM pictures were obtained on a SEM-FEG Zeiss Ultra55 microscope model. SEM-EDS spectra were recorded using a Quanta 250 FEG (Field Emission Gun) model accompanied by an EDS detector for elemental composition measurement, at an accelerating voltage of 10 kV, keeping the magnifications up to 1,000.000 and 1 nm resolution.

2.7.2. X-ray diffraction analysis

The XRD spectra were recorded with 2θ angle in the range of 20-80° with an X-ray diffractometer type X-*Empyrean Panalytical* employing Cu-K_α 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 quantify the calcite, aragonite and vaterite crystallographic forms, respectively. The calculation of the molar fraction of each variety was reported elsewhere [59].

3. Results and discussion

3.1. Scaling inhibition on sol–gel coating carbon steel electrode

3.1.1. Comparison between a bare electrode and a sol-gel coating electrode

Firstly, experiments were carried out by chronoamperometry in order to verify if the sol-gel film could prevent the formation of $CaCO_3$ on the electrode. The scaling inhibition of the sol-gel film was studied on a carbon steel electrode using chronoamperometry and compared to a bare electrode. Measurements were carried out using a classical rotating disk electrode in a solution containing initially Ca^{2+} ions at a concentration of 200 $mg.L^{-1}$ (50 °F). A cathodic potential of -1 V/SCE was applied during the accelerated scaling test to induce the $CaCO_3$ electrochemical precipitation [1-3, 6]. The current was normalized by I_0, which is the current value at the maximum of the curve. This current-time coordinate system was adopted by Barchiche et al. [61] to facilitate the comparison between results. The chronoamperometric curves performed with a bare carbon steel electrode and a carbon steel electrode covered by a sol-gel film are presented in Fig. 3. The two-recorded curves of Fig. 3 show a similar evolution. Firstly, an increase of the normalized current is related to the reduction of atmospheric oxides

formed on the active area of the working electrode before immersion [5]. Then, a rapid decrease of I/I_0 was observed and attributed to a fast kinetics of $CaCO_3$ deposition on the electrode [3]. The scaling time parameter (t_s) can be obtained from chronoamperometric curve (Table 1). As indicated in Fig. 3, this parameter represents the time needed to lower the current to a stable value corresponding to the plateau current [62]. For the bare electrode, the t_s value is 38 min and the I/I_0 value of the plateau is around 0.19 meaning that the electrode surface was totally covered by an isolating layer of $CaCO_3$. When the carbon steel electrode was coated by a sol-gel film, the I/I_0 value of the plateau is obtained more quickly and is higher (0.41) than for a bare carbon steel electrode. This first result shows that the sol-gel film is porous as the O_2 can be reduced on the electrode and acts as a barrier against the formation of $CaCO_3$ on the electrode.

3.1.2. Scaling on doped sol–gel film coating carbon steel electrode

Fig. 4 regroups the chronoamperometric curves recorded during scaling tests on the doped coating carbon steel electrode polarised at -1 V/SCE for the two doping cations (Cu^{2+} and Zn^{2+}). For the coating doped with 10^{-5} mol of Cu^{2+} (blue curve in Fig. 4(a)), the first increase of the normalized current was not really observed compared to the undoped coating. Then, I/I_0 rapidly decreased to reach a nearly constant value indicating that the formation of $CaCO_3$ on the surface of the coating was stopped after about 40 min of immersion that correspond to the scaling time. However, the plateau current was higher than that of undoped coating, which means that Cu^{2+} ions prevented slightly the $CaCO_3$ formation. For the coating doped with 10^{-4} mol of Cu^{2+} (green curve in Fig. 4(a)), the current did not decrease over time so the scaling process was inhibited during the whole experiment. The scaling time (t_s) was undefined. Indeed, practically no variation of the I/I_0 value was observed during 120 min of experiment which shows that the kinetics of $CaCO_3$ precipitation was extremely slow. For a sol-gel film containing 10^{-4} mol of Cu^{2+}, the formation of $CaCO_3$ is considered as completely inhibited.

Fig. 4(b) shows the chronoamperometric curves for scaling tests on coating doped with Zn^{2+} cations. Their shapes were similar to that observed for the coating doped with 10^{-5} mol of Cu^{2+} (blue curve in Fig. 4(a)). The initial decrease of the normalized current was followed by a plateau of different I/I_0 values depending on the Zn^{2+} doping cation amount. The scaling time values were mentioned in Table 1. Higher is the amount of the doping Zn^{2+}, higher is the scaling time. Comparing the effect of doping cations, it seems that the inhibitory effect of the film doped with copper ions is more pronounced than that doped with zinc ions. Indeed, the values of scaling time mentioned in Table 1 show that t_s is undefined for 10^{-4} mol of Cu while it is equal to 51 min for the same amount of Zn^{2+}.

These results obtained by chronoamperometry showed that doping the sol-gel-film with metallic ions prevented the formation of $CaCO_3$ on the metallic surface of the electrode. The sol-gel film with Cu^{2+} shows a greater inhibition effect than that with Zn^{2+}.

3.2. Sol–gel coating on stainless steel 316L through QCM tool

In order to assess the inhibiting effect of the metallic cations included in the sol-gel film, the quartz crystal microbalance (QCM) was used to quantify the mass of $CaCO_3$ nuclei deposited when the electrode was covered by this coating.

The studied solution was prepared by fast controlled precipitation (FCP) in order to bring the solution to a given sursaturation coefficient [6]. This method allowed forming calcium carbonate nuclei before precipitation in solution.

3.2.1. Undoped sol-gel film

The mass variations of the $CaCO_3$ nuclei deposited on stainless steel sol-gel coating electrode (without and with doping cations) were recorded vs. immersion time in synthetic pure carbonic solution containing initially 200 $mg.L^{-1}$ of Ca^{2+} (water hardness of 50 °F) at a sursaturation coefficient of 32.

Firstly, a comparison of the $CaCO_3$ mass variation deposited was carried out by QCM when the electrode was covered or not covered by a sol-gel film. The gravimetric curves for a bare

stainless steel electrode and for the undoped coating electrode obtained by QCM are presented in Fig. 5. For the bare stainless steel electrode, the mass of $CaCO_3$ increases progressively with the immersion time without reaching a constant value, even after 120 min of immersion (black curve in Fig. 5). However, the mass variation (Δm) of $CaCO_3$ deposited on sol-gel coating stainless steel electrode is different. As it can be observed from the red curve in Fig. 5, an initial increase of the Δm was clearly recorded for 50 min of immersion. Afterwards, Δm reached a steady state value about 42 $\mu g.cm^{-2}$. This mass variation means that the active metallic surface was reduced and the progression of scaling process was stopped. In addition, no loss of mass has been observed for the sol-gel coating electrode which means that the film is adherent on the electrode surface. QCM is a suitable technic to control the film adhesion on the electrode surface. Indeed, if the coating leaves the surface of the QCM or is no longer in contact, there is a discontinuity in the propagation of the ultrasonic wave that can be detected immediately thanks to the very high sensitivity of the QCM. Covering stainless steel working electrode with a phosphosilicate hybrid coating promotes an important reduction of the mass of $CaCO_3$ deposit, proving that the sol-gel coating prevents the formation of calcium carbonate on the metallic surface, even without doping cations.

3.2.2. Sol–gel film doped with metallic ions

Fig. 6(a) presents the variation of the mass change of calcium carbonate deposited on sol-gel coating stainless steel electrode without and with doping Cu^{2+} cations. The obtained curves show an important decrease of the deposit of $CaCO_3$ on the doped sol-gel coating with the increase of cations quantities. Comparing to the undoped system, the steady state was reached faster leading to a decrease of $CaCO_3$ deposit mass. For instance, when the sol-gel film was doped with 10^{-5} mol of Cu^{2+} (red curve in Fig. 6(a)), the mass change reached a steady value of 13.8 $\mu g.cm^{-2}$. Doping progressively the film with Cu^{2+} ions (from 10^{-5} mol and 10^{-4} mol of Cu^{2+} added during the preparation of the film) reduces the amount of $CaCO_3$ deposited to 13.8 $\mu g.cm^{-2}$ and 4.5 $\mu g.cm^{-2}$, respectively. The mass change decrease is very important compared

339 to the quantity of $CaCO_3$ deposited on the undoped coating (42 µg.cm^{-2}) which reflects the
340 particularly pronounced effect of copper ions on the improvement of the anti-scale effectiveness
341 of sol-gel films. Scaling parameters, such as nucleation time (T_N), scaling gravimetric time (T_S)
342 and scaling rate (Vs) were extrapolated from the gravimetric curves as defined by Tlili et al.
343 [63]. The corresponding values are given in Table 2. The increase of Cu^{2+} doping cation amount
344 influences mainly the scaling rate (Vs) that was reduced from 2.21 µg cm^{-2} min^{-1} (undoped film)
345 to 0.15 µg cm^{-2} min^{-1} for the film doped with 10^{-4} mol of Cu^{2+}. The values of T_N and T_S for
346 doped system are higher than that of the undoped system.
347 The effect of Zn^{2+} doping cations on the anti-scaling properties of the sol-gel phosphosilicate
348 hybrid coating was also studied by QCM. Four amounts of Zn^{2+} cations ranged from 10^{-5} mol
349 to 10^{-2} mol were also examined. The extrapolated scaling parameters are also added to the Table
350 2 and the corresponding recorded gravimetric curves are shown in Fig. 6(b). The increasing
351 amounts of Zn^{2+} cations in the sol-gel film progressively inhibit the formation of scale on the
352 surface of the sol-gel phospohosilicate hybrid coating. The mass of calcium carbonate decreases
353 from 42 µg.cm^{-2} to 7 µg.cm^{-2}. The Vs value (Table 2) decreases from 1.46 µg^{-1} cm^{-2} min^{-1} to
354 0.39 µg.cm^{-2}.min^{-1} when Zn^{2+} molar quantity increases from 10^{-5} mol to 10^{-3} mol. The value
355 of T_N seems to be independent of the doping process while the values of T_S for doped system
356 are higher than those characteristic of scaling on undoped coating (Table 2).
357 Zn^{2+} doping cations, as well as Cu^{2+}, improved the anti-scaling effect of the studied sol-gel film.
358 However, these results confirmed that Cu^{2+} ions are more efficient than Zn^{2+} ions towards scale
359 deposition. Indeed, for a sol-gel film doped with Cu^{2+} and Zn^{2+} at 10^{-4} mol, the amount of
360 $CaCO_3$ deposits was 4.5 µg.cm^{-2} and 13 µg.cm^{-2} respectively (Fig. 6). This difference
361 corroborates the result obtained by chronoamperometry for carbon steel, confirming the anti-
362 scaling properties of the studied sol-gel coating.
363 The inhibition effect of cations was assumed to be due to the weak release of the ions in the
364 solution. Indeed, some experiments were carried out by spectrophotometry UV-Vis (data not

shown here) in order to detect the presence of cations in the solution. The results showed that a very small quantity of cations was released from the sol-gel film towards the solution. As a consequence, the scaling inhibition is mainly related to an interfacial effect.

3.2.3. SEM micrographs and XRD analysis on 316L stainless steel

SEM images of the sol-gel film and $CaCO_3$ formed on the surface of 316L stainless steel, under different experimental conditions (undoped and doped with ions), are shown in Fig. 7 and Fig. 8 for Cu^{2+} and Zn^{2+} respectively. The molar fractions of vaterite, aragonite and calcite calculated from XRD spectra are presented in Table 3.

Fig. 7a shows the presence of small $CaCO_3$ crystals formed on the sol–gel coating without doping cations covering the surface of the stainless steel 316L electrode. The shapes of the crystals are difficult to identify. However, the presence of calcite has been confirmed by XRD analysis as shown in Fig. 7(d), which revealed characteristic peaks of this crystalline variety. When the sol-gel coating was doped with 10^{-5} and 10^{-4} mol of Cu^{2+} (Figs. 7(b) and (c) respectively), SEM images show that the deposit was mainly formed by circular crystal typical of vaterite [5, 6], which is confirmed by XRD analysis (Fig. 7(e) and (f)). In addition, the presence of Cu^{2+} ions decreased the number of $CaCO_3$ crystals deposited on the doped sol-gel film. On the film doped with Cu^{2+}, XRD analysis (Fig. 7(e)) confirmed the presence of both calcite and vaterite as observed in the SEM images of Fig. 7(b).

The morphology of $CaCO_3$ scale formed on the surface of the hybrid coating doped with Zn^{2+} are shown in Fig. 8. When the sol-gel film is doped with 10^{-5} mol of Zn^{2+}, vaterite form is observed (Fig. 8(a)) which is confirmed by the XRD spectrum in Fig. 8(e). Calcite appear when the doping cations rises to 10^{-4} to 10^{-3} mol, as it can be observed in the Fig. 8(b) and (c) and Table 3. Doping the sol-gel coating with 10^{-2} mol of Zn^{2+} lead to the aragonite formation (Fig. 8(d) and Table 3). The presence of these $CaCO_3$ crystallographic forms was also confirmed by X-ray diffraction analysis (Fig. 8 (e) to (h)). XRD spectra were also recorded on coating doped with different amounts of Zn^{2+} cation. Results are in agreement with SEM observations (Fig.

391 8(a) to (d)). For 10^{-5} mol to 10^{-3} mol of doping Zn^{2+} cation, vaterite and calcite were the
392 constituents of the $CaCO_3$ deposit (Fig. 8(e) to (g) and Table 3). With 10^{-2} mol of doping Zn^{2+},
393 X-ray analysis (Fig. 8(h) and Table 3) showed the presence of aragonite.
394 The molar fractions of observed crystalline varieties formed on sol gel coating stainless steel
395 electrode (Table 3) were estimated using the calculation method described in a previous paper
396 [59]. The calculated values shown in Table 3 are dependent on the doping cations amount
397 indicating the inhibiting role of this added ions on the scaling process and the $CaCO_3$ structure.
398 The molar fractions of vaterite and calcite decreased when the molar quantities of ions
399 increased. It can be noted the appearance of aragonite for a sol-gel film doped with 10^{-2} mol of
400 Zn^{2+} at a molar fraction of 24% (Table 3). The inhibition effect of Cu^{2+} and Zn^{2+} cations added
401 to the coating hybrid structure was demonstrated as it was the case when they were injected in
402 solution as soluble scaling inhibitor [59, 64-66]. Gritli et al. [59] have demonstrated by FCP a
403 total efficiency of Cu^{2+} and Zn^{2+} in solution for a concentration of 5 and 4 $mg.L^{-1}$ respectively.
404 Other authors [65] have determined with the same technique lower concentrations for the
405 inhibition of $CaCO_3$ formation (0.5 $mg.L^{-1}$ of Cu^{2+} and 0.15 $mg.L^{-1}$ of Zn^{2+}). Zeppenfeld [66]
406 have showed an inhibition efficiency at about 90% for a concentration superior at 2 $mg.L^{-1}$ of
407 Cu^{2+}. To conclude this part, the doped sol-gel film acts as an antiscaling barrier.

408 **4. Conclusion**

409 The present study was devoted to investigate the anti-scaling performance of a sol-gel
410 phosphosilicate hybrid coating doped with copper or zinc cations deposited onto two different
411 metals, largely used in the water domain, stainless 316L steel and carbon steel. The outcomes
412 allow the following conclusions to be drawn:

413 1. An hybrid doped sol-gel phosphosilicate coating was successfully applied onto stainless
414 and carbon steel surfaces. The anti-scaling proprieties of this film was demonstrated
415 under different experimental conditions.

2. The different techniques of investigations (QCM and CA) confirmed that doping the hybrid coating with Cu^{2+} and Zn^{2+} cations delayed the scaling process proving the scaling inhibiting performance of this doped film in synthetic water containing initially 200 mg.L^{-1} of Ca^{2+} (water hardness of 50 °F).
3. Crystalline form of $CaCO_3$ appeared at the studied interface. They were mainly influenced by the amount of Zn^{2+} and Cu^{2+} doping cations that are included in the different films.
4. Surface analysis techniques (SEM and X-ray diffraction) supported investigations and confirmed the anti-scaling properties of the doped coatings.

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