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1	Scaling inhibition by sol-gel phosphosilicate hybrid films: Influence of
2	doping Cu ²⁺ and Zn ²⁺ cations
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30 Abstract

In this work, the scaling protection performance of Zn²⁺ and Cu²⁺, added to a phosphosilicate 31 hybrid sol-gel coating and applied on both carbon and stainless steel surface, was evaluated for 32 the first time in a solution containing initially 200 mg. L^{-1} of Ca²⁺ (corresponding to a water 33 hardness of 50 °F) at 30 °C. Inhibition efficiency was estimated using chronoamperometry (CA) 34 and quartz crystal microbalance (QCM). Results showed that these smart coatings were 35 efficient to protect steel surface against scaling phenomenon. The coatings containing the Cu²⁺ 36 inhibitor was the most effective of the systems tested. Moreover, CA and QCM measurements 37 showed that the formation of calcium carbonate deposition on carbon steel decreased when the 38 39 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 40 affected calcium carbonate nucleation by changing the morphology of CaCO₃ crystals. 41 42 43 44 45 46 47 48 Keywords: Scale inhibition, zinc (II) cation, copper (II) cation, sol-gel coating, quartz crystal 49 50 microbalance 51 **Abbreviations:** electrochemical 52 EQCM: quartz crystal microbalance; CA:

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

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2

56 **1. Introduction**

The problems related to the scaling phenomena of industrial facilities in contact with waters 57 become more massive and more insidious. These issues can, as already pointed in numerous 58 scientific papers, lead to a decrease of the thermal efficiency of the circuit, an obstruction of 59 pipes as well as the proliferation of living organisms [1-7]. Thus, the economic losses associated 60 with CaCO₃ precipitation can be significant [8-10]. To fight this phenomenon, several 61 protection methods have been applied to preserve installations against scaling. These methods 62 can be divided into two types: physical and chemical methods. Among the physical methods, 63 magnetic treatments are generally used [11]. Chemical methods are based on the use of organic 64 molecules as anti-scalant in numerous situations to prevent scale precipitation [12, 13]. Some 65 synthetic and natural water-soluble polymers used as scaling inhibitors have been investigated 66 and reported in literature [12-16]. However, many inhibitors showed up has a secondary effect, 67 causing damages on the environment. Indeed, poly-phosphonates are very efficient but they can 68 cause eutrophication when they are rejected in natural waters [17, 18]. Thus, the scientific 69 community began searching for environmentally friendly inhibitors (green inhibitors) derived 70 from petrochemicals [14-22], plant extracts [23-33] and chemical modified natural products 71 from industrial process [34-36]. Nevertheless, the compatibility with the water environment 72 73 and the respect of the different safety rules are always questionable even if these products come 74 from plants or similar. Alternate approach must be found in this context and smart films based 75 on sol-gel technique can be examined [37]. Materials such as organic-inorganic hybrid 76 compounds are one of the feasible solutions that enable protection from CaCO₃ precipitation reactions during application. They constitute a new generation of multifunctional materials with 77 useful properties and diverse applications. In addition, polymeric materials are characterized by 78 79 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 80 at low concentrations can proffer superior physical properties of such polymer. 81

82 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, 83 sol-gel hybrid coatings for metal protection against scaling phenomenon appears as an 84 interesting field of research. Indeed, it is an attractive technique used to synthesize hybrid 85 materials with various composition that allow to entrap molecules in an inorganic glassy matrix 86 [41, 46]. The properties of these sol-gel coatings are strongly dependent on their processing 87 88 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 89 properties, such as hydrophobicity and good adhesion to metallic substrates [48]. The use of 90 precursors containing non-hydrolysable bonds allows the organic network to bind directly to 91 the inorganic network in the structure. Thus, hybrid sol-gel coatings can have the combined 92 properties of both organic and inorganic functions [43, 44]. The nature of the organic function 93 (phenyl function, epoxy function, vinyl function and methacrylate function) influences the 94 properties of the network [39, 49]. The integration of phosphate or phosphonate groups in the 95 sol-gel network has been published in several works [50-52]. The outcomes proved a good 96 adhesion to the metallic surface of the film containing phosphorus groups. Santana et al. [49] 97 studied the effect of the pre-treatment of the carbon steel surface with a phosphoric acid solution 98 99 before applying a hybrid sol-gel film. SEM images showed that the pre-treatment step produces 100 a rougher surface than that of untreated steel. This roughness results in better adhesion of the 101 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 102 103 formation of longitudinal fibers and an increase in the condensation generated while a basic 104 catalysis leads to clusters formation characterized by a spherical shape [53]. Under acidic 105 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 106 (M) and favours the formation of M–O–M bond by condensation [54, 55]. According to Phan 107

et al. [56], adding phosphoric acid H₃PO₄ 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 112 were added to the studied water while the metallic surface treatments such as sol-gel coating 113 process, were mainly applied to protect metal against corrosion. To our knowledge, no 114 investigations on the scaling inhibition via sol-gel doped coatings on steel surface in pure 115 carbonic solution have been performed to date. The present investigation shows the first attempt 116 to synthesize a sol-gel film on a surface and doped with metallic ions to prevent scale formation. 117 In this work, hybrid sol-gel coatings were deposed on both carbon steel and stainless steel from 118 3-[(methacryloyloxy)propyl] trimethoxysilane (MEMO) and bis-[2-(methacryloyloxy) ethyl] 119 120 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 121 doped by Cu²⁺ and Zn²⁺ cations. Chronoamperometry (CA) and quartz crystal microbalance 122 (QCM) methods were performed to evaluate the scaling inhibition efficiency of these layers. 123 To complete the information about the composition and the morphology of the doped sol-gel 124 125 coatings, scanning electron microscopy (SEM) observations and X-ray diffraction (XRD) analysis were done to link the layer properties to the electrochemical and gravimetric 126 127 characterizations.

- 128 **2. Materials and methods**
- 129 2.1. Scaling solution

The synthetic carbonically pure water, containing initially 200 mg. L⁻¹ of Ca²⁺ (water hardness
of 50 °F), was prepared by dissolving calcium carbonate (CaCO₃) powder (VWR AnalaR
NORMAPUR, 99.7% purity) in bi-distilled water. To dissolve calcium carbonate, carbon
dioxide CO₂ 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.

137 2.2. Doping solution

- 138 Suitable amounts of solutions of analytical grade ZnCl₂ (Merck, 98 % purity) and CuCl₂-2H₂O
- 139 (Acros Organics, 99 % purity) were prepared for doping coatings tests. For the doping process,

140 metallic cations molar quantities ranged from 10^{-5} to 10^{-3} mol.

- 141 2.3. Sol-gel coating solution
- 142 The sol-gel coating process was applied using 3-[(methacryloyloxy)propyl] trimethoxysilane
- 143 (MEMO) and bis [2-(methacryloyloxy) ethyl] phosphate (BMEP) precursors from Sigma-

Aldrich and ethanol provided by VWR. All compounds were used without any furtherpurification and chemical formulas are given in Fig. 1.

- 146 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 147 chemical composition (in wt %) of 0.28 % C, 0.28 % Si, 1.25 % Mn, 0.03 % P, 0.16 % Cr, 0.15 148 % N, 0.07 % Ni, 0.009 % Mo and Fe balance. The carbon steel working electrode, 0.2 cm² of 149 active area, was embedded in inert resin, polished with silicon carbide paper up to 1200 grade 150 151 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 152 AISI 316L (Fe/Cr18/Ni10/MO3) sheet (Good fellow, reference FF210320). Thin stainless steel 153 316L films were prepared on quartz resonators surface using a commercial RF magnetron 154 sputtering system (Pfeiffer PLS500) from 316L steel disc target of 50 mm diameter. More 155 precisely, stainless steel was deposited on the gold electrode (0.2 cm^2) of the resonators (9 MHz, 156 AWS Sensors, Spain) to perform QCM-based analysis. 157

- 158 2.5. Sol-gel coating
- 159 2.5.1. Pre-treatment of the surface

The pre-treatment of the electrode surface was carried out by crystalline phosphating process with a commercial solution Decorrdal 47-15-1 (Klüthe). It is a mixture of ethanol (molar fraction between 50 and 75%) and sodium 3-nitrobenzenesulphonate C₆H₄NNaO₅S (molar fraction between 50 and 75% and molecular weight 225.15 g.mol⁻¹). Crystalline phosphating process, recommended by Klüthe, reduces the flaking surface by forming a phosphateconverting layer that constitutes a base for bonding the coatings, making the surface rougher 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

The sol–gel process is based on the hydrolysis and condensation reactions of silicons alcoxydes Si(OR)^{*n*} in solution (sol) allowing to achieve an infinite viscosity network (gel), where *n* is the oxidation state and OR is an alkoxy group with R an alkyl chain [37]. The most often used precursors for this type of application are tetra–functional silicon alkoxides of formula Si(OR)⁴ [57]. Herein, the sol–gel preparation was done in two stages: hydrolysis (the synthesis of "sol") 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-OCH₃ methoxy-
- 178 silane groups according three successive reactions:

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

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

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

182 Then, condensation reactions occurred according the following reactions:

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

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

185

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

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

$$\Delta f = -2 \, \frac{f_0^2}{s_{\sqrt{\rho \, \mu}}} \Delta m \tag{6}$$

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 cm² 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 217 solutions containing 200 mg.L⁻¹ of Ca²⁺, corresponding to 50 °F) was transferred to a Teflon 218 container placed in a thermostated bath at 30 °C. CO₂ degassing was achieved by magnetic 219 stirring at 850 rpm. The degassing of the solution was blocked by stopping the stirring and 220 221 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 222 223 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. 224

6. Details of this methodology were already given in other works [1, 6].

226 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.

232 2.7. Surface characterizations

233 2.7.1. SEM observations

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

236 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

238 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.
- 241 2.7.2. X-ray diffraction analysis

The XRD spectra were recorded with 2 θ angle in the range of 20-80° with an X-ray diffractometer type X-*Empyrean Panalytical* employing Cu-K_a radiation (λ =1.54 Å). Intensities of the diffraction peaks at 104 (2 θ = 29.5°), 221 (2 θ = 46°) and 110 (2 θ = 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].

247 **3. Results and discussion**

248 3.1. Scaling inhibition on sol–gel coating carbon steel electrode

249 *3.1.1. Comparison between a bare electrode and a sol-gel coating electrode*

250 Firstly, experiments were carried out by chronoamperometry in order to verify if the sol-gel film could prevent the formation of CaCO₃ on the electrode. The scaling inhibition of the sol-251 252 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 253 solution containing initially Ca²⁺ ions at a concentration of 200 mg.L⁻¹ (50 °F). A cathodic 254 255 potential of -1 V/SCE was applied during the accelerated scaling test to induce the CaCO₃ electrochemical precipitation [1-3, 6]. The current was normalized by I₀, which is the current 256 value at the maximum of the curve. This current-time coordinate system was adopted by 257 258 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 259 260 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 261

formed on the active area of the working electrode before immersion [5]. Then, a rapid decrease 262 of *I/I*⁰ was observed and attributed to a fast kinetics of CaCO₃ deposition on the electrode [3]. 263 The scaling time parameter (t_s) can be obtained from chronoamperometric curve (Table 1). As 264 indicated in Fig. 3, this parameter represents the time needed to lower the current to a stable 265 266 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 267 covered by an isolating layer of CaCO₃. When the carbon steel electrode was coated by a sol-268 gel film, the I/I_0 value of the plateau is obtained more quickly and is higher (0.41) than for a 269 bare carbon steel electrode. This first result shows that the sol-gel film is porous as the O₂ can 270 271 be reduced on the electrode and acts as a barrier against the formation of CaCO₃ on the electrode. 272

273 *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 274 coating carbon steel electrode polarised at -1 V/SCE for the two doping cations (Cu^{2+} and Zn^{2+}). 275 For the coating doped with 10^{-5} mol of Cu²⁺ (blue curve in Fig. 4(a)), the first increase of the 276 normalized current was not really observed compared to the undoped coating. Then, I/Io rapidly 277 decreased to reach a nearly constant value indicating that the formation of CaCO₃ on the surface 278 of the coating was stopped after about 40 min of immersion that correspond to the scaling time. 279 However, the plateau current was higher than that of undoped coating, which means that Cu²⁺ 280 ions prevented slightly the CaCO₃ formation. For the coating doped with 10⁻⁴ mol of Cu²⁺ 281 (green curve in Fig. 4(a)), the current did not decrease over time so the scaling process was 282 283 inhibited during the whole experiment. The scaling time (t_s) was undefined. Indeed, practically no variation of the *I/Io* value was observed during 120 min of experiment which shows that the 284 kinetics of CaCO₃ precipitation was extremely slow. For a sol-gel film containing 10⁻⁴ mol of 285 Cu^{2+} , the formation of CaCO₃ is considered as completely inhibited. 286

Fig. 4(b) shows the chronoamperometric curves for scaling tests on coating doped with Zn²⁺ 287 cations. Their shapes were similar to that observed for the coating doped with 10⁻⁵ mol of Cu²⁺ 288 (blue curve in Fig. 4(a)). The initial decrease of the normalized current was followed by a 289 plateau of different I/I_0 values depending on the Zn^{2+} doping cation amount. The scaling time 290 291 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 292 doped with copper ions is more pronounced than that doped with zinc ions. Indeed, the values 293 of scaling time mentioned in Table 1 show that t_s is undefined for 10^{-4} mol of Cu while it is 294 equal to 51 min for the same amount of Zn^{2+} . 295

These results obtained by chronoamperometry showed that doping the sol-gel-film with metallic ions prevented the formation of CaCO₃ on the metallic surface of the electrode. The sol-gel film with Cu^{2+} shows a greater inhibition effect than that with Zn^{2+} .

299 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 CaCO₃ nuclei deposited

302 when the electrode was covered by this coating.

303 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 calciumcarbonate nuclei before precipitation in solution.

306 *3.2.1. Undoped sol-gel film*

307 The mass variations of the CaCO₃ nuclei deposited on stainless steel sol-gel coating electrode

308 (without and with doping cations) were recorded vs. immersion time in synthetic pure carbonic

solution containing initially 200 mg.L⁻¹ of Ca²⁺ (water hardness of 50 °F) at a sursaturation

310 coefficient of 32.

Firstly, a comparison of the CaCO₃ 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

313 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 CaCO₃ increases progressively with 314 the immersion time without reaching a constant value, even after 120 min of immersion (black 315 curve in Fig. 5). However, the mass variation (Δm) of CaCO₃ deposited on sol-gel coating 316 stainless steel electrode is different. As it can be observed from the red curve in Fig. 5, an initial 317 increase of the Δm was clearly recorded for 50 min of immersion. Afterwards, Δm reached a 318 steady state value about 42 µg.cm⁻². This mass variation means that the active metallic surface 319 was reduced and the progression of scaling process was stopped. In addition, no loss of mass 320 has been observed for the sol-gel coating electrode which means that the film is adherent on the 321 322 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 323 a discontinuity in the propagation of the ultrasonic wave that can be detected immediately 324 thanks to the very high sensitivity of the QCM. Covering stainless steel working electrode with 325 a phosphosilicate hybrid coating promotes an important reduction of the mass of CaCO₃ 326 deposit, proving that the sol-gel coating prevents the formation of calcium carbonate on the 327 metallic surface, even without doping cations. 328

329 *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 330 coating stainless steel electrode without and with doping Cu^{2+} cations. The obtained curves 331 show an important decrease of the deposit of CaCO₃ on the doped sol-gel coating with the 332 333 increase of cations quantities. Comparing to the undoped system, the steady state was reached faster leading to a decrease of CaCO₃ deposit mass. For instance, when the sol-gel film was 334 doped with 10^{-5} mol of Cu²⁺ (red curve in Fig. 6(a)), the mass change reached a steady value 335 of 13.8 μ g.cm⁻². Doping progressively the film with Cu²⁺ ions (from 10⁻⁵ mol and 10⁻⁴ mol of 336 Cu²⁺ added during the preparation of the film) reduces the amount of CaCO₃ deposited to 13.8 337 μ g.cm⁻² and 4.5 μ g.cm⁻², respectively. The mass change decrease is very important compared 338

to the quantity of CaCO₃ deposited on the undoped coating (42 μ g.cm⁻²) which reflects the 339 340 particularly pronounced effect of copper ions on the improvement of the anti-scale effectiveness of sol-gel films. Scaling parameters, such as nucleation time (T_N) , scaling gravimetric time (T_S) 341 and scaling rate (Vs) were extrapolated from the gravimetric curves as defined by Tlili et al. 342 [63]. The corresponding values are given in Table 2. The increase of Cu^{2+} doping cation amount 343 influences mainly the scaling rate (Vs) that was reduced from 2.21 μ g cm⁻² min⁻¹ (undoped film) 344 to 0.15 μ g cm⁻² min⁻¹ for the film doped with 10⁻⁴ mol of Cu²⁺. The values of T_N and T_S for 345 doped system are higher than that of the undoped system. 346

The effect of Zn^{2+} doping cations on the anti-scaling properties of the sol-gel phosphosilicate 347 hybrid coating was also studied by QCM. Four amounts of Zn^{2+} cations ranged from 10^{-5} mol 348 to 10^{-2} mol were also examined. The extrapolated scaling parameters are also added to the Table 349 2 and the corresponding recorded gravimetric curves are shown in Fig. 6(b). The increasing 350 amounts of Zn^{2+} cations in the sol-gel film progressively inhibit the formation of scale on the 351 surface of the sol-gel phospohosilicate hybrid coating. The mass of calcium carbonate decreases 352 from 42 μ g.cm⁻² to 7 μ g.cm⁻². The Vs value (Table 2) decreases from 1.46 μ g⁻¹ cm⁻² min⁻¹ to 353 0.39 μ g.cm⁻².min⁻¹ when Zn²⁺ molar quantity increases from 10⁻⁵ mol to 10⁻³ mol. The value 354 of T_N seems to be independent of the doping process while the values of T_S for doped system 355 356 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 CaCO₃ 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.

368 *3.2.3. SEM micrographs and XRD analysis on 316L stainless steel*

SEM images of the sol-gel film and CaCO₃ formed on the surface of 316L stainless steel, under different experimental conditions (undoped and doped with ions), are shown in Fig. 7 and Fig. 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 CaCO₃ crystals formed on the sol-gel coating without 373 doping cations covering the surface of the stainless steel 316L electrode. The shapes of the 374 crystals are difficult to identify. However, the presence of calcite has been confirmed by XRD 375 analysis as shown in Fig. 7(d), which revealed characteristic peaks of this crystalline variety. 376 When the sol-gel coating was doped with 10^{-5} and 10^{-4} mol of Cu²⁺ (Figs. 7(b) and (c) 377 respectively), SEM images show that the deposit was mainly formed by circular crystal typical 378 of vaterite [5, 6], which is confirmed by XRD analysis (Fig. 7(e) and (f)). In addition, the 379 presence of Cu²⁺ ions decreased the number of CaCO₃ crystals deposited on the doped sol-gel 380 film. On the film doped with Cu^{2+} , XRD analysis (Fig. 7(e)) confirmed the presence of both 381 382 calcite and vaterite as observed in the SEM images of Fig. 7(b).

The morphology of CaCO₃ scale formed on the surface of the hybrid coating doped with Zn²⁺ 383 are shown in Fig. 8. When the sol-gel film is doped with 10^{-5} mol of Zn^{2+} , vaterite form is 384 observed (Fig. 8(a)) which is confirmed by the XRD spectrum in Fig. 8(e). Calcite appear when 385 the doping cations rises to 10^{-4} to 10^{-3} mol, as it can be observed in the Fig. 8(b) and (c) and 386 Table 3. Doping the sol-gel coating with 10^{-2} mol of Zn^{2+} lead to the aragonite formation (Fig. 387 388 8(d) and Table 3). The presence of these CaCO₃ crystallographic forms was also confirmed by X-ray diffraction analysis (Fig. 8 (e) to (h)). XRD spectra were also recorded on coating doped 389 with different amounts of Zn^{2+} cation. Results are in agreement with SEM observations (Fig. 390

8(a) to (d)). For 10^{-5} mol to 10^{-3} mol of doping Zn^{2+} cation, vaterite and calcite were the constituents of the CaCO₃ deposit (Fig. 8(e) to (g) and Table 3). With 10^{-2} mol of doping Zn^{2+} , X-ray analysis (Fig. 8(h) and Table 3) showed the presence of aragonite.

The molar fractions of observed crystalline varieties formed on sol gel coating stainless steel 394 395 electrode (Table 3) were estimated using the calculation method described in a previous paper [59]. The calculated values shown in Table 3 are dependent on the doping cations amount 396 indicating the inhibiting role of this added ions on the scaling process and the CaCO₃ structure. 397 The molar fractions of vaterite and calcite decreased when the molar quantities of ions 398 increased. It can be noted the appearance of aragonite for a sol-gel film doped with 10^{-2} mol of 399 Zn^{2+} at a molar fraction of 24% (Table 3). The inhibition effect of Cu²⁺ and Zn²⁺ cations added 400 to the coating hybrid structure was demonstrated as it was the case when they were injected in 401 solution as soluble scaling inhibitor [59, 64-66]. Gritli et al. [59] have demonstrated by FCP a 402 total efficiency of Cu^{2+} and Zn^{2+} in solution for a concentration of 5 and 4 mg.L⁻¹ respectively. 403 Other authors [65] have determined with the same technique lower concentrations for the 404 inhibition of CaCO₃ formation (0.5 mg.L⁻¹ of Cu²⁺ and 0.15 mg.L⁻¹ of Zn²⁺). Zeppenfeld [66] 405 have showed an inhibition efficiency at about 90% for a concentration superior at 2 mg. L^{-1} of 406 Cu^{2+} . To conclude this part, the doped sol-gel film acts as an antiscaling barrier. 407

408 4. Conclusion

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

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

416	2.	The different techniques of investigations (QCM and CA) confirmed that doping the	
417		hybrid coating with Cu^{2+} and Zn^{2+} cations delayed the scaling process proving the	
418		scaling inhibiting performance of this doped film in synthetic water containing initially	
419		200 mg. L^{-1} of Ca ²⁺ (water hardness of 50 °F).	
420	3.	Crystalline form of CaCO ₃ appeared at the studied interface. They were mainly	
421		influenced by the amount of Zn^{2+} and Cu^{2+} doping cations that are included in the	
422		different films.	
423	4.	Surface analysis techniques (SEM and X-ray diffraction) supported investigations and	
424		confirmed the anti-scaling properties of the doped coatings.	
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