



Study of the influence of the supersaturation coefficient on scaling rate using the pre-calcified surface of a quartz crystal microbalance

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ABSTRACT

Scale deposition is a common issue in industrial plants, which creates technical problems, *i.e.* reduction of heat transfer, decrease of flow rate due to an obstruction of pipes. Therefore, the development of some appropriate methods based on well suitable *in situ* sensors to evaluate and predict the scaling propensity of water is a major concern in current research. This would be a good strategy for the optimization of anti-scaling treatments.

In this study, scaling tests were carried out using a sensitive sensor, which has been developed using a quartz crystal microbalance with a pre-calcified electrode surface (SQCM). This technique allowed studying the influence of the supersaturation on the scaling rate. The set-up was tested with different water samples which were brought to a given supersaturation coefficient by degassing the dissolved CO₂. The prediction of the scaling propensity of water was then possible through the relationship between the scaling rate on a pre-calcified surface and the supersaturation coefficient. In addition, the kinetics of CaCO₃ deposit on the pre-calcified SQCM surface was found to be slower for natural water than for synthetic water (same calcium concentration). Furthermore, the activation energy for scale deposit, in synthetic water, was found to be 22 kJ.mol⁻¹, which may be related to the diffusion of ions and/or CaCO₃ nuclei in solution.

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1. Introduction

Scale deposit on solid surfaces causes serious problems in many industries using or processing water, *e.g.* in cooling systems (Abd-El-Khaled and Abd-El-Nabey, 2013) or in heat exchangers (Yang, 2002). Indeed, the thickness of the scale deposit may limit thermal exchanges or the water flow in pipes. The use of chemicals is a common approach to control scale deposit. However, those chemicals may have an important impact on environment, *i.e.* in the eutrophication process. On the one hand, scale deposit could occur when water becomes supersaturated, *i.e.* the product of ions activities, $[Ca^{2+}] \times [CO_3^{2-}]$, exceeds the solubility product K_{sp} of CaCO₃ (Xyla *et al.*, 1991). On the other hand, scale deposit may take

place due to an external cause, *i.e.* the introduction of a substrate or seed crystals (Donnet *et al.*, 2010). Thus, preventing scale formation has raised a great interest. It is relevant to develop some efficient methods based on *in situ* sensors to follow the scaling propensity of water in order to prevent scale deposit.

Some methods based on the determination of the scaling rates have been developed in order to estimate the scaling propensity of water (Hui and Lédion, 2002; Leroy *et al.*, 1993; Al Nasser and Al Salhi, 2013). For example, Hui *et al.* (2003) have studied the scaling rates using witness tubes with pre-calcified surface. Zhang *et al.* (2001) considered thermodynamic models in order to evaluate the tendency for scaling from solutions and kinetics models to predict the rate of scaling. The use of chronoamperometry at constant reduction potential was the more fruitful approach to investigate the scaling rate (Gabrielli *et al.*, 1996; Lédion *et al.*, 1985). However, correlation between supersaturation coefficient and scaling rate on a solid surface was not very well developed in literature. Some discrepancies were detected between real deposit on solid surfaces and scaling rates estimated from predictive models based on thermodynamic data where precipitation

Abbreviations: QCM, Quartz Crystal Microbalance with a regular bare electrode surface; SQCM, Quartz Crystal Microbalance with a pre-calcified electrode surface; TOC, Total Organic Carbon; XRD, X-Ray Diffraction.

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tendency were predicted (Hasson et al., 1996).

Recently, a quartz crystal microbalance with a pre-calcified sensitive surface (SQCM) has been developed (Chao et al., 2014a). The sensitive surface could be used as an adsorption layer for CaCO₃ nuclei present in water. It was installed in a cell simulating an industrial fluid stream with a laminar flow. A preliminary relationship was obtained between the instantaneous scaling rate and the supersaturation coefficient of synthetic water at different concentrations of Ca²⁺ ([Ca²⁺] in the range 60 mg.L⁻¹ - 200 mg.L⁻¹) and at a given temperature (T = 35 °C). This opens the possibility to quantify the scaling propensity of a tested water.

In this work, the pre-calcified QCM electrode was installed in a miniaturized lab-made cell. This original set-up was tested with synthetic water which was brought to a given supersaturation coefficient related to the precipitation of calcium carbonate by CO₂ degassing (Gauthier et al., 2012; Chao et al., 2014b). Indeed, only calcium carbonate (CaCO₃), one of the most abundant mineral scale compound (Keysar, 1994), will be considered in this study. This work is focused on calcium carbonate scaling, *i.e.* the deposit of calcium carbonate on a surface, and not with calcium carbonate precipitation in solution, *i.e.* the appearance of a Ca CO₃ solid phase within the bulk solution. The deposit kinetics of calcium carbonate nuclei on the active electrode of the SQCM was measured at different supersaturation coefficients for two temperatures (T = 30 °C and 40 °C), either for a synthetic or a natural water. Indeed, it was possible to compare, in a very sensitive way, the scaling propensity of a synthetic and a natural mineral water (same calcium concentration). Thus, this work investigates, thanks to the SQCM electrode, the effect of several parameters like supersaturation level, temperature and composition of water on scaling rate. For the first time, the activation energy of the scaling process on the pre-calcified surface, for synthetic water, was investigated.

2. Materials and methods

2.1. Reactants

Synthetic waters were pure solutions, which only contained Ca²⁺ and CO₃²⁻ ions. The synthetic waters (100 or 200 mg/L in Ca²⁺, depending on the experiment) used in this work were prepared by dissolving solid calcium carbonate (AnalaR NORMAPUR VWR, 99.7% purity) in pure water (Milli.Q water, 18.2 MΩ cm resistivity and TOC <5 mg L⁻¹) by bubbling CO₂ gas. After the solid dissolution, the pH of the solution was about 5.2–5.5. Under those experimental conditions, no spontaneous precipitation of CaCO₃ occurred. The solution was then filtered with a Millipore filter (514-8073 Whatman, 0.45 μm porosity) to remove any impurities. Salvetat[®] water is a commercial natural water, which contains the following elements (Table 1). The ions and TOC concentrations in Salvetat water have been determined according to IANESCO laboratory (Poitiers, France) titration report.

2.2. QCM set-up

A quartz crystal microbalance with a pre-calcified electrode surface (SQCM) was used to measure the mass of calcium carbonate deposited on the pre-calcified surface (Fig. 1).

Table 1
Concentration of ions in Salvetat[®] water.

Ions	Ca ²⁺	Mg ²⁺	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	Na ⁺	K ⁺	TOC
Concentration (mg.L ⁻¹)	180	8.7	634	4.6	31	5.7	1.7	0.4

Table 2

Summary of data obtained from fitted curves (see text for signification of the parameters).

T (°C)	k/SI	n	R ^{2*}
30	0.19	1.3	0.95
40	0.36	1	0.98

*Goodness-of-fit measure for the linear regression model.

The volume of the SQCM cell was 500 μL. The flow rate was set to 2 mL.min⁻¹ using a peristaltic pump. The water jet arrived at 45° on the flat surface of the modified electrode. The bare surface of the electrode consisted in a 5 mm diameter gold disc covering a 9 MHz AT cut quartz crystal resonator (AWS, Spain).

The pre-calcifying process was performed in a classical “three-electrode” set-up with the bare gold electrode acting as a working electrode. All the electrodes were inserted in a submerged impinging jet cell (flow rate of 300 mL.min⁻¹), with a synthetic water (200 mg.L⁻¹ Ca²⁺) at 30 °C.

The frequency of the microbalance device was measured by a frequency-counter (Fluke PM6685). The mass deposited onto the bare or the pre-calcified surface of the sensor was measured over time from the microbalance frequency change (Bizet et al., 2000; Chao et al., 2014a). 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 (Sauerbrey, 1959):

$$\Delta f = -K_s \Delta m \quad (1)$$

where K_s is the sensitivity factor (K_s)⁻¹ = 1.09 ng per Hz for an electrode area of 0.2 cm².

2.3. Preparation of water with a given supersaturation coefficient δ

Stable solutions of calcium carbonate were brought to a given supersaturation coefficient δ (δ = 4; 5; 11; 25; 32) by CO₂ degassing (Gauthier et al., 2012; Chao et al., 2014b). Indeed, the degassing of dissolved CO₂ is accelerated by stirring the water sample. As the dissolved CO₂ was removed from the solution, the concentration of [H⁺] decreases, so the concentration of [OH⁻] or the pH increases according to the following equations:



As a consequence, the saturation level of the solution increases with stirring. Supersaturation coefficient δ, the extent of deviation of the solution from the equilibrium condition, is the driving force for the formation of a CaCO₃ crystalline phase in aqueous solutions. δ is defined according to the following equation (5): (Legrand et al., 1981)

$$\delta = [\text{Ca}^{2+}] \times [\text{CO}_3^{2-}] / K'_{\text{sp}} \quad (5)$$

where [Ca²⁺] and [CO₃²⁻] are the concentrations of calcium ions and carbonate ions respectively, and K'_{sp} is the apparent solubility product of calcium carbonate. As stated above, the supersaturation level δ of the studied water was increased by using a moderate stirring (400 rpm) of the solution. The pH of the solution was measured as a function of time using a pH-meter (Radiometer pHM220). The pH electrode was purchased from Radiometer

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