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Direct detection of calcium carbonate scaling via a pre-calcified sensitive area of a quartz crystal microbalance

Yanjia Chao [a,b,c], Olivier Horner [a], Franck Hui [b,c], Jean Lédion [d], Hubert Perrot [b,c,*]

[a] EDF Research and Development, Laboratoire National d'Hydraulique et Environnement, 6 Quai Watier, 78401 Chatou Cedex, France
[b] CNRS, Laboratoire Interfaces et Systèmes Electrochimiques (LISE), Case 133, 4, place Jussieu, 75252 Paris Cedex 05, France
[c] Université P. et M. Curie, LISE, 4, Place Jussieu, 75252 Paris Cedex 05, France
[d] ARTS, 151 boulevard de l'Hôpital, 75013 Paris, France

HIGHLIGHTS

- A microbalance with a pre-calcified sensitive electrode was developed.
- This gravimetric sensor can be used as an adsorption layer for carbonate nuclei.
- It was successfully applied to evaluate the scaling propensity of waters.
- This sensor can be used to assess the efficiency of humic substances towards scaling.

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ABSTRACT

In an industrial cooling circuit supplied with raw river water, the scaling phenomenon can reduce cooling efficiency and even lead to the shutdown of the power plant. During the last twenty years, various methods have been developed in order to estimate the scaling propensity of natural waters, which involve the precipitation of calcium carbonate ($CaCO_3$), the main component of scale. FCP (Fast Controlled Precipitation) is a non-electrochemical method which consists in CO_2 degassing from water by moderate stirring. FCP allows quantifying the scaling propensity of natural water. However, FCP is not well adapted in the case of waters with low scaling propensities, or for in situ measurements.

In this study, a quartz crystal microbalance with a pre-calcified sensitive electrode surface or SQCM (Scaling Quartz Crystal Microbalance) was developed. The sensitive surface of this gravimetric sensor could be used as an adsorption layer for calcium carbonate nuclei present in water. Thus, the SQCM method is able to detect the phenomenon of scaling, even if the water does not precipitate, due to its high gravimetric sensitivity. This method is described in details in this paper, and was successfully applied to evaluate the scaling propensity of synthetic waters. The SQCM could be used in situ to assess the efficiency of humic substances in synthetic water towards scaling.

1. Introduction

Scaling is a major concern in different industrial processes and domestic installations [1,2]. Undesirable scale deposits often cause numerous technical problems, such as total or partial obstruction of pipes, leading to a decrease in flow rate, reduced heat transfer, seizure of valves and clogging of filters. The non-productive expenses related to scaling were estimated to beat 1.5 billion euros per year in France [3]. In nuclear power plants, the scaling phenomena can reduce efficiency and limit the power production. Therefore, there is a need to develop some appropriate methods to follow this phenomenon in order to better prevent it.

During the last twenty years, various methods have been developed in order to estimate the scaling propensity of natural waters [4]. These methods involve the precipitation of calcium carbonate ($CaCO_3$), the main component of scale. These methods can be roughly divided into two categories: electrochemical methods and non-electrochemical

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Abbreviations: δ, saturation level; δ_{limit}, limiting saturation level; EQCM, electrochemical quartz crystal microbalance; GTT, Gravimetric Test on Tubes; QCM, quartz crystal microbalance; SCE, saturated calomel electrode; SQCM, quartz crystal microbalance with pre-calcified surface of the electrode; TOC, Total Organic Carbon; TSS, Total Suspended Solid.

[*] Corresponding author at: CNRS, Laboratoire Interfaces et Systèmes Electrochimiques (LISE), Case 133, 4, Place Jussieu, 75252 Paris Cedex 05, France. Tel.: +33 1 44 27 72 16; fax: +33 1 44 27 40 74.
E-mail address: hubert.perrot@upmc.fr (H. Perrot).

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methods. Among the first ones, the electrochemical quartz crystal microbalance or EQCM has been used for twenty years to promote accelerated scaling by imposing an electrochemical potential on its surface [5]. This technique allows in situ, fast (about an hour) and sensitive (nanograms of generated calcium carbonate) measurements of the scaling phenomenon. A decisive improvement was made by perfectly controlling the hydrodynamics with a submerged jet device incorporating a quartz crystal microbalance [6]. However, in the EQCM method, the scaling phenomenon is greatly accelerated by an electrochemical reaction on the electrode surface. Thus, the resulting scaling is not really representative of the natural phenomenon in an industrial circuit. It has been shown that, in the electrochemical method, the water samples reach very high saturation levels in the vicinity of the electrode [7]. In this case, the water is highly instable and is characterized by the spontaneous precipitation of $CaCO_3$. The thermodynamic conditions are no longer the same as in a real scaling phenomenon.

Among the non-electrochemical methods, the Fast Controlled Precipitation (FCP) method was developed by taking into consideration its representativeness relative to a real scaling phenomenon. It consists in degassing of CO_2 from the test water by moderated agitation leading to slight supersaturation of $CaCO_3$, in order to evaluate the scaling potential of waters. Still FCP is a laboratory method which cannot be easily applied in the industrial field. Thus, the Gravimetric Test on Tubes (GTT) has been developed [8]. In this method, tubes of various types were previously encrusted by a pre-scaling step so that the influence of tube nature towards scaling could be eliminated. Moreover, the newly formed surface of $CaCO_3$ is active for the adsorption of $CaCO_3$ formed at a later stage. GTT has been applied for evaluating the scaling potential of the water in a cooling circuit of a power plant. The results showed that, even with a double treatment by H_2SO_4 and by a scale inhibitor, water in a cooling circuit still kept a scaling potential of 0.3 g/m^2/day. However, GTT suffers from slow measurement due to the “out-situ” weighing by a classic balance.

This prompted us to develop a quartz crystal microbalance with a pre-calcified sensitive surface, or SQCM. The choice of quartz crystal microbalance was fully justified. Indeed, it enables to continuously follow extremely tiny $CaCO_3$ mass changes. The electrochemical pre-calcification step of the electrode surface is well controlled. It can also eliminate the influence of support material nature towards scaling [8].

In this paper, the SQCM method is described in details and is applied to evaluate the scaling propensity of synthetic waters. Additionally, SQCM tests were carried out in the presence of humic substances, which are often found in natural river waters. These tests were performed in order to get some insight into the influence of humic substances on water scaling propensity.

2. Experimental

2.1. Studied waters

The synthetic waters (60, 100, 150 or 200 mg L^{-1} in calcium) 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 $M\Omega \cdot cm$ resistivity and TOC < 5 mg L^{-1}) by bubbling CO_2 gas. After the solid dissolution, the pH of the solution was about 5.2–5.5. Under those experimental conditions, no spontaneous precipitation of $CaCO_3$ occurred. The solution was then filtered with a Millipore filter (514-8073 Whatman, 0.45 μm porosity) to remove any impurities.

A stock solution containing humic substances (5 mg L^{-1}) was obtained by dissolving humic acid as sodium salt (technical grade, Aldrich) in 2 L of synthetic water ($[Ca^{2+}] = 100$ mg L^{-1}). This stock solution was diluted to obtain solutions with lower concentrations of humic substances (0.2, 0.5, 1.0, 2.0 and 5.0 mg L^{-1}). In natural water, the concentration of humic substances is only part of the TOC value. Those values vary widely, depending on the source and the seasons. According to Klimenko et al., TOC values between 0.7 and 17 mg L^{-1} were obtained for water from various natural environments around the world [9]. This range of humic acid concentration was retained in this work.

Turbidity was measured using a TURB 430IR turbid meter. The turbidity value was evaluated from the average of five consecutive measurements.

To determine the TSS (Total Suspended Solid) concentration, 250 mL of solution was filtered through a glass fiber filter (0.7 μm porosity). The filter was dried in an oven at 105 °C for 1 h and then weighted with a precision balance. The TSS concentration was calculated by dividing the mass obtained by the initial volume of the sample (250 mL).The values of TSS and turbidity are reported in Table S1 (Supplementary data).

2.2. XRD characterization

XRD measurements were performed on a Panalytical (Empyrean Diffractometer Panalytical) device equipped with a Pixcel 1D detector and a copper anode as the source of radiation (1.54 Å/Kα), with a power of 45 kV and under an operating temperature of 20 °C. For samples in the form of powders, the total acquisition time per sample was 31 min and the diffraction angle 2θ was in the range 15°–90°, with a resolution of 0.0131°. The measurement parameters were the same for samples of calcium carbonate deposited on the QCM electrode. However, a longer acquisition time (19 h, 30 min) was necessary because the amount of material available on the QCM electrode surface was very small (around a few μg).

The different crystalline forms of calcium carbonate were quantified by XRD measurements, as described in Supplementary data.

2.3. Pre-calcification of the surface of the electrode in the SQCM

The gold electrode (gold deposited on the quartz resonator) involved in the SQCM was pre-calcified by using an electrochemical procedure described elsewhere [6]. The deposition conditions in a synthetic water solution ($[Ca^{2+}] = 100$ mg L^{-1}) were as follows: a temperature of 35 °C, a flow rate of 300 mL min^{-1} and an applied potential of −1.0 V/SCE. When the electrode surface was totally covered by calcium carbonate (stabilization of the chronoeletrogravimetric curve), the polarization and the solution flow were stopped.

2.4. SQCM setup

The pre-calcified electrode (see above) was installed in a cell that is representative of an industrial fluid stream (studied water) with a laminar flow, as shown in Fig. 1.

This set-up simulates pipes for a cooling circuit. The fluid flows parallel to the surface of the walls under a laminar regime (flow rate = 300 mL min^{-1}). In a typical SQCM experiment, the flow of water is provided by a gear pump which is rotated by an electric motor (GEC Alsthom TBN103) slaved to a stabilized power supply. The pumping and the connecting systems ensured a particularly regular and stable flow. In order to perform gravimetric measurements via the SQCM, the following devices were used to measure and record the signals describing the microbalance frequency changes, in order to estimate the mass changes: a frequency meter (Fluke universal counter PM6685) and a computer equipped with a lab-made software (FRQM software). This allowed controlling the different devices and recording numerically the experimental curves.

One liter of pre-heated water was introduced in a Teflon beaker. Two different ways of operating were used in this study. On the one hand, the water with an initial pH value around 6.0 was continuously stirred for CO_2 degassing. In this configuration, pH and microbalance frequency changes were recorded over time (configuration I). On the other hand, the water with an initial pH value in the range 6.8–7.8 obtained by CO_2 pre-degassing was used in the SQCM system. In this case, CO_2 degassing of the solution was blocked by both closing carefully the openings in the beaker lid and stopping the solution stirring. The