SORBONNE UNIVERSITÉ

Sorbonne Université/China Scholarship Council program 2021

Thesis proposal

Title of the research project: **SMART AND GREEN MATERIALS FOR ANTISCALANT/ANTICORROSION PROPERTIES IN NATURAL WATERS**

Keywords: **scaling effect, corrosion, electrochemistry, sol-gel material, quartz microbalance**

Joint supervision: yes (name/surname) ~~/no~~ **Dr Hélène CHARPENTIER-CHEAP at LISE, SU/EPF**

Joint PhD (cotutelle): ~~yes (name/surname)~~ /no

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Institution: **Sorbonne Université, Paris, France**

Doctoral school (N°+name): **ED 388, Chimie Physique et Chimie Analytique de Paris Centre**

Research laboratory: **Laboratory of Interfaces and Electrochemical Systems, "LISE UMR 8235"**

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Subject description (2 pages max):

1) Study context

Scaling phenomena, mainly related to the precipitation of mineral compounds such as calcium carbonate ($CaCO_3$) or calcium sulphate ($CaSO_4$), cause significant technical and economic problems, especially in industries using water. The reduction of mineral deposits is a major challenge in many industrial sectors. Environmental and health issues lead industry to seek environmentally friendly solutions to control scaling phenomena. One of the most effective ways of slowing down and/or inhibiting the formation of scale is the use of scale inhibiting chemicals. Another promising avenue is to apply "sol-gel" coatings with an antiscale purpose to a surface to prevent scale deposits. The advantage of using such films is that it does not change the composition of the water. Among the techniques used in the study of calcium carbonate precipitation, the quartz crystal microbalance (QCM) is a very sensitive technique that allows the measurement of small masses of $CaCO_3$ that can be deposited on an active surface as well as the determination of scaling rates for a given water quality [1].

A previous thesis (Ph.D. student: Manel Gritli) was first carried out in collaboration with Tunisia (El Manar University) and our laboratory (LISE, Sorbonne Université) [2]. The subject of the thesis was the protection of carbon steel electrode against scaling by a treatment based on a non-toxic polymer and an appropriate doping with copper and zinc cations. A first proof of this concept demonstrating the interest of the quartz crystal balance and the efficiency of the proposed films for this type of study was brought during this thesis. The objectives of the future thesis are to optimize the synthesis of the sol-gel film with green antiscaling molecules and to elaborate other intelligent materials that would have the capacity to release inhibitors over time. Then, the study of the antiscaling effect and the characterization of these coatings will be carried out using techniques such as QCM and electrochemical impedance spectroscopy.

2) Details of the proposal

The project has two main parts:

1/ Elaboration and characterization of antiscaling films for surface treatment in collaboration with Prof. Christel LABERTY (Laboratoire de Chimie de la Matière Condensée de Paris-LCMCP, Sorbonne Université),

2/ Study of the inhibition of calcium carbonate precipitation using sol-gel films by electrochemical quartz crystal microbalance (Hubert PERROT and Hélène CHEAP-CHARPENTIER).

Initially, the objective is to develop and design a smart material with an anti-scaling aim that could perform different functions. On the one hand, the "dense" sol-gel film of controlled thickness will act as a barrier, preventing the formation of scale on the surface of the metal. The protective capabilities of this film could be enhanced by trapping metal cations in or on the surface of the sol-gel film. On the other hand, a hybrid film, containing surfactants, where natural scale inhibitors would be trapped, will be designed. This film would "release" the inhibitors as needed over time via an external stimulus such as pH. The advantage of this gentle chemistry is that it does not dissolve toxic products in water. In addition, the compounds used will be non-toxic, in order to limit water pollution. The microstructure (porosity and thickness) of the films will be evaluated by SEM and ellipsometry, a technique mastered at the LCMCP laboratory [3,4]. This technique can also be studied to monitor the release of "antiscalants" by monitoring the optical index of the film.

Then, the antiscaling properties of the films will be characterized by the QCM and electrochemical techniques of the LISE laboratory. In the case of films diffusing natural scale inhibitors, the quantity of

species "released" as well as their speed will be studied by QCM. If the film is porous, electrochemical techniques (chronoamperometry, electrochemical impedance spectroscopy) will be considered. The results can be compared to those obtained by ellipsometry. The porosity rate as well as the pore size will be controlled by the concentration of surfactants and their nature. The thesis work will focus in part on the control of the release of the inhibitor: by external stimuli (pH, temperature) and non-stimulated (based on the interaction between the complexing agent and calcium ions for example). The concentration of the released species will also be controlled.

This project will be developed within the LISE in Paris, which is part of Sorbonne University. The laboratory is highly qualified in deposits and surface treatments (https://www.lise.upmc.fr/). This work will be carried out in collaboration with the EPF, an engineering school and with the Laboratoire Chimie de la Matière Condensée de Paris, Sorbonne University, which is specialized in the elaboration of thin films by sol-gel process of controlled porosity based on surfactant.

3) References

[1] H. Cheap-Charpentier, O. Horner, J. Lédion and H. Perrot, "Study of the influence of the supersaturation coefficient on scaling rate using the pre-calcified surface of a quartz crystal microbalance", Water Research 142 (2018) 347 – 353.

[2] M. Gritli, H. Cheap-Charpentier, O. Horner, H. Perrot, Y. Ben Amor, "Scale inhibition properties of metallic cations on $CaCO_3$ formation using fast controlled precipitation and a scaling quartz microbalance", Desalination and Water Treatment, 167(2019)113-121.

[4] G. Muller, R.N. Vannier, G. Baldinozzi, A. Ringuede, C. Laberty–Robert, C. Sanchez, Nanocrystalline, Mesoporous NiO/Ce0.9Gd0.1O2-delta Thin Films with tuned Microstructures and Electrical Properties: In situ Characterization of Electrical responses during the Reduction of NiO, J. Mater. Chem. A., 1 (36)(2013)10753-10761.

[5] S. Hilliard, G. Baldinozzi, H. Stux, S. Kresmann, V. Artero, C. Laberty-Robert, "Mesoporous Thin Film WO_3 Photoanode for Photoelectrochemical Water Splitting: A Sol-Gel Dip Coating Approach", Sustainable Energy and Fuels, 1(2017)145-153.

4) Profile of the Applicant (skills/diploma…)

The candidate must have a Master's Degree in:

- Materials science or physical chemistry obtained with excellent grades.
- Knowledge in electrochemistry and/or in water analysis is required.
- A good command of English (written and oral) is necessary.

Contacts:

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