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## **Fouling of reverse osmosis membranes by hydrocarbonated and fluorinated surfactants contained in firefighting water**

Clement Baudequin, Estelle Couallier, Zhaohuan Mai, Mohammed Rakib, Isabelle Deguerry, Romain Severac, Martial Pabon

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**Title:****Fouling of reverse osmosis membranes by hydrocarbonated and fluorinated surfactants contained in firefighting water****Authors & affiliations:**

Clement Baudequin (1), Estelle Couallier (1)\*, Zhaohuan Mai (1), Mohammed Rakib (1), Isabelle Deguerry (2), Romain Severac (2), Martial Pabon (3)

- (1) Laboratoire de Génie des Procédés et matériaux, École Centrale Paris, Grande Voie des Vignes, 92295 Châtenay-Malabry, France
- (2) DuPont de Nemours France SAS, allée de Chantereine, F-78711 Mantes la Ville, France
- (3) DuPont de Nemours International, 2 Chemin du Pavillon, 1218 Geneva, Switzerland

\*[estelle.couallier@ecp.fr](mailto:estelle.couallier@ecp.fr)

**Abstract:** (Your abstract must use **Normal style** and must fit in this box. The abstract should be written in English and should be around 1000 words long, i.e., 2 pages excluding title, authors & affiliations, keywords and references. Authors are encouraged to show important figures/tables etc in the abstract so as to make a full presentation.)

Pay attention that this draft needs final approval by DuPont before publication (eventual minor revision).

Large class B fires — i.e. polar or non polar burning liquids — can occur in places like refineries, airports or chemical plants. Such fires can be put out with the help of fire fighting foams prepared from specific aqueous formulations, called foam concentrates diluted in water to 1-6% and applied with a nozzle under the form of foam. Foam concentrates usually contain hydrocarbon surfactants or protein hydrolysates (synthetic or proteinic concentrate), and one or several fluorinated surfactants in case of high performance foam concentrates. During industrial solvent fires large amounts of water and foam are used: several cubic meters per minute during several days. Resulting water consists of either water from the foam and water used to protect equipment and persons from the heat of the fire. Therefore its composition is expected to be somehow close to diluted foaming solution.

Surfactants are amphiphilic molecules able to lower interfacial tension. These compounds have the particularity to self-aggregate when their concentration reaches the critical micelle concentration. Fluorinated surfactants are a particular class of surfactants which can dramatically lower the water surface tension. This ability plays a key role in the efficiency of firefighting waters. In addition, fluorinated surfactants are highly resistant to thermal and chemical attacks. The current treatment for firefighting waters is therefore incineration in halogen resistant incinerators, which is not economically viable and not convenient on a logistical point of view.

A previous paper aimed at proposing a process for purifying firefighting water containing fluorinated surfactants [1]. Experimental results indicated that electrocoagulation and filtration followed by reverse osmosis efficiently treated the water from fire extinguishment.

In this work we focused on the reverse osmosis step.

Polyamide and cellulose acetate membrane materials were screened in a flat sheet cell with model solutions representative of synthetic fire fighting foams. The most appropriate membrane considering rejection was a smooth anti foulant thin film polyamide SG membrane, designed for brackish water. However, because of membrane fouling, there was a trade-off between high rejection and low flux decline. The SG membrane showed even better rejection properties in spiral-wound module with both real and model pretreated firefighting waters. Though the flux decline was high, it seemed to tend to an asymptote with the increasing concentration. The stabilities of rejection and flux decline were confirmed during longer tests on an industrial pilot with

another fouling resistant thin film polyamide membrane for brackish water, a RE2540-FE membrane.

The flux decline caused by the surfactant mixtures was found linked to adsorption. The flux decline seemed mainly due to the adsorption of the anionic surfactant which showed the highest adsorption density in concentrated solutions (figure 1). This surfactant also showed lowest rejection properties. However, selective removal of this compound for purpose of flux enhancement, if desired, should be carefully studied. Indeed, with little or no anionic surfactant in the solutions, there would be more “free room” for the hydrophobic adsorption of the other surfactants on the membrane, which could decrease their rejections. A model was proposed to describe the flux decline as function of the fluorinated surfactant concentration, somehow representing the global surfactant concentration.

This model combined the resistance-in-series model to a Langmuir adsorption model by expressing the adsorption resistance as function of the retentate concentration (figure 2). Though this model would require to be tuned on the basis of extended experimental data, it adequately described the flux decline with retentate concentration of the model pretreated firefighting water. Further work could be done on the subject *via* membrane surface characterization, and study of mixed adsorption as well as mixed micellization of surfactant mixtures.

In this work, solid data was gathered, such as the average rejection of the fluorinated surfactant in the industrial pilot which was 99.95%, and the permeability of the membrane of  $0.5 L h m^{-2} bar^{-1}$  with model solution representing pretreated firefighting water concentrated by a factor 20. This could allow the calculation of the area required for the mobile unit.

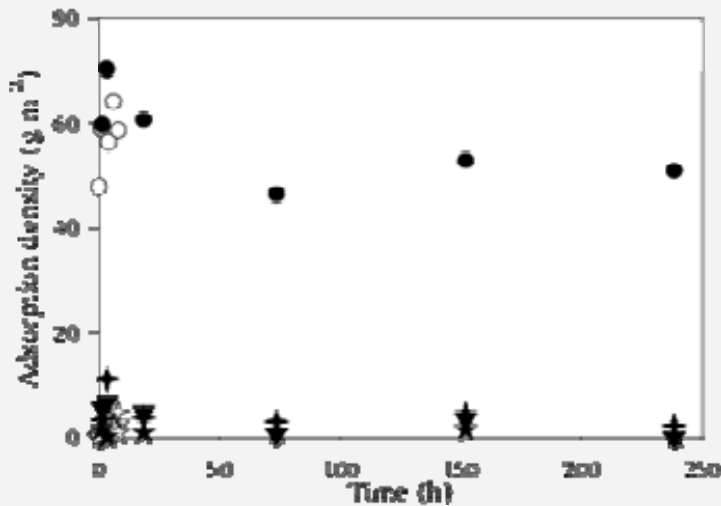


Figure 1: Surfactants adsorption density during reverse osmosis in the Polymem pilot of 40 L of CF20 solution, at 30 bar, and cross-flow velocity of  $0.095 m s^{-1}$ .

Test 1: ○: SOS; ▽: Tegotens; ☆: Simulsol, ☆: fluorinated surfactant.

Test 2: ●: SOS; ▼: Tegotens; ★: Simulsol, ★: fluorinated surfactant.

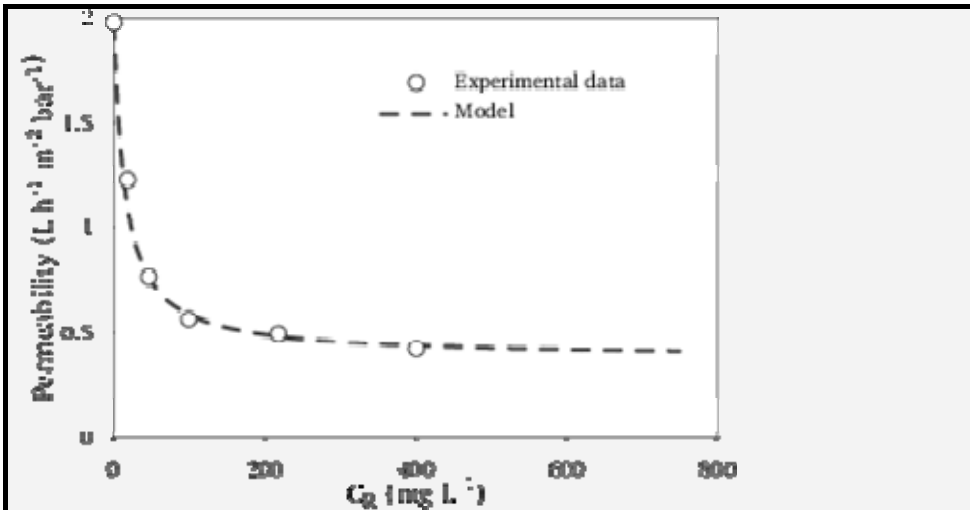


Figure 2: Model and experimental data for the permeability versus retentate concentration of the fluorinated surfactant, during reverse osmosis of model pretreated firefighting water in the Millipore pilot, at 20 bar, with a spiral-wound SG membrane. The concentration of the fluorinated surfactant is an indicator of the global concentration of other surfactants also present.

#### references

- [1] C. Baudequin, E. Couallier, M. Rakib, I. Deguerry, R. Severac, M. Pabon, Purification of firefighting water containing a fluorinated surfactant by reverse osmosis coupled to electrocoagulation-filtration, Separation and Purification Technology 76 (2011) 275-282