

UF MEMBRANES AUTOPSIES: AN APPROACH TO HOLLOW FIBER MEMBRANES SURFACE

Authors: Nuria Peña García^a, Javier Rodríguez^a, Fernando del Vigo^a, Stephen Chesters^b

^a Genesys Membrane Products, C/Londres 38, Oficina 204, Las Rozas, 28232, Madrid, Spain

^b Genesys International Ltd., 3A Aston Way, Middlewich, CW10 OHS, Cheshire, UK

Presenter: Nuria Peña García
Laboratory Manager – Genesys Membrane Products S.L. – Spain
npena@genesysro.es

Abstract

Genesys Membrane Products S.L. (GMP) laboratory has demonstrated a broad experience in the development of membranes autopsies, which have been more than 900 during the last decade [1]. Although most of these autopsies correspond to reversed osmosis (RO) membranes, during last years a relevant increase on ultrafiltration (UF) autopsies requirements has been observed. The study of a membrane surface during an autopsy, involves different analytical techniques that will provide the needed information for a final diagnostic. In this work the author intends to show the utility of these autopsies in the diagnosis of UF membranes failures.

Besides, data from the autopsies developed in GMP laboratory will demonstrate the usefulness of these techniques for the study of hollow fiber membranes surface. Based on these studies, different UF configurations and compositions are reviewed and some examples and statistics about UF fibers fouling are also included.

I. INTRODUCTION

First UF polymeric membranes were developed in the 30s, but real efforts for membranes manufacturing didn't start until early 60's when first RO membranes were developed for practical applications. Due to the need to improve flow performance of these asymmetric membranes there was a research which ended in the development of UF membranes [2]. Ultrafiltration membranes and their molecular weight cutoff from 200 to 500,000 Da retain polymers, sugars and viruses that make that they can be used for concentration, purification and fractionation in many industries as food, medical pharmaceutical, medical, biotechnological and air filtration [3].

Besides, a growing application of UF membranes technology is in the areas of water and wastewater treatment. Surface water sources can be very efficiently treated by UF membranes and they are also used as a pretreatment, generally before nanofiltration or reverse osmosis membrane process [3].

The majority of UF membranes in service are polymeric: cellulose acetate, polyvinylidene fluoride, polyacrylonitrile and polysulfone are used to manufacture UF membranes. The base polymer surface chemistry can be modified to alter hydrophilicity of these polymers and different structures, filtration senses and applications are achieved [4].



The productivity of a membrane system will normally decrease with time as the membrane densifies (compacts) under the applied transmembrane pressure [4]. On the other side, a common problem in the application of ultrafiltration membranes in separations is the decline of permeate flux. Fouling phenomena are frequently observed due to solute accumulation at the membrane solution interface and solute adsorption onto membrane pores, which determine the surface properties and porosity of membrane and can result in irreversible flux loss [5]. Additionally, chemical compatibility in a specific application, pH, solvent and temperature resistance may affect these membranes performance [6]. When there is a failure on a UF module performance that it is operating in a real plant, the best tool to determinate the cause of failure is to carry out an autopsy. An autopsy is a complex process of tests and analyses carried out with the aim to achieve a diagnosis about membrane failure.

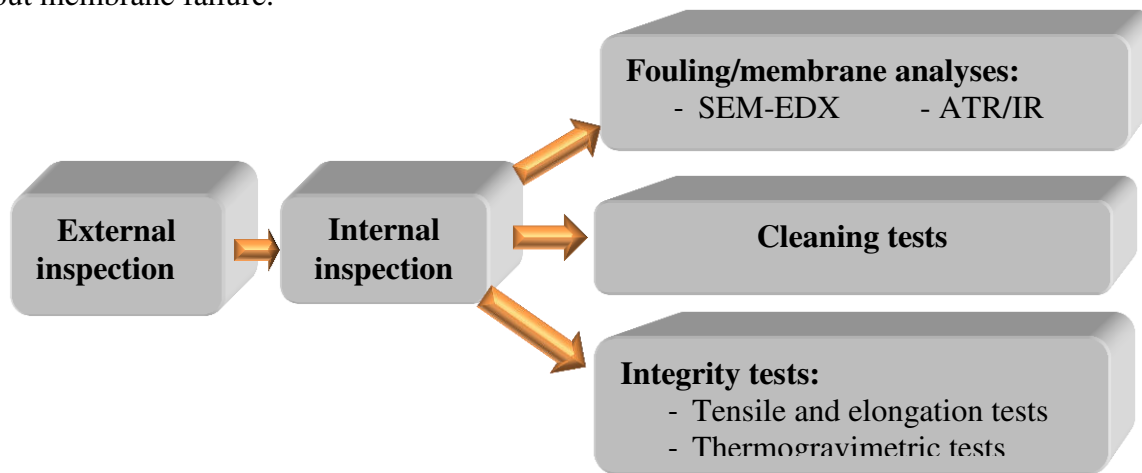


Diagram 1.- Schematic description of main analysis carried out in membrane autopsies

Some of the most powerful analytical techniques used during UF autopsies are:

- *Scanning Electron Microscopy – Energy Dispersive X-ray Analysis (SEM-EDX)* is used to study the membrane surface and to verify the elemental composition of fouling if detected. Elemental determination with the SEM-EDX system is based on analysis of X-rays produced via electron beam excitation of a sample area. This technique allows analysis of a sample in selective areas. The limited depth of analysis (typically a few microns), and the possibility to select the area of interest under the electron beam, allows for local analysis to reveal differences in composition. The identification and measurement of individual peak intensities in the X-ray spectrum is done with a computerized multichannel analyzer. This technique doesn't allow to determinate how the elements detected are related.

- *Internal Reflection Spectrometry or Attenuated Total Reflectance Infrared (ATR/IR) Spectrometry* can provide valuable information related to the chemical structure of membrane or characterize the fouling layer that may be present on the membrane surface.

In the mid-infrared, absorption of radiation is related to fundamental vibrations of the chemical bonds. Internal reflection spectrometry provides information related to the presence or absence of specific functional groups. Shifts in the frequency of absorption bands and changes in relative band intensities indicate changes in the chemical structure or changes on the membrane surface.

-*Thermogravimetric analysis (TGA)* is one of the members of the family of thermal analysis techniques used to characterize a wide variety of materials. TGA provides complimentary and supplementary characterization information to the most commonly used thermal technique, DSC.

TGA measures the amount and rate (velocity) of change in the mass of a sample as a function of temperature or time in a controlled atmosphere.

The measurements are used primarily to determine the thermal and/or oxidative stabilities of materials as well as their compositional properties. The technique can analyse materials that exhibit either mass loss or gain due to decomposition, oxidation or loss of volatiles (such as moisture).

-*Tensile stress-strain curves* are obtained by applying a tensile load. From these curves, as a function of the material, we can obtain the following parameters:

Young's modulus: slope of the curve in the initial linear (elastic) region

Yield strength: Stress value where elastic to plastic deformation occurs

Tensile strength: Stress value where the curve is maximum

Stress at break: Stress value where fracture occurs

Percent Elongation: Deformation at break of the material (a measure of the ductility)

Main application of these techniques during UF autopsies are described in table 1. Although it is common to use these techniques for membranes characterization and there are many papers based on this technics in theoretical studies [7], this study will demonstrate their utility on membranes that have been used in real water treatment sites.

Table 1: Analytical techniques used for UF membranes autopsy

	Fouling	Membrane integrity
<i>SEM-EDX</i>	<ul style="list-style-type: none"> ✓ Elementary identification of fouling components ✓ Elementary detection of membrane composition components ✓ Visual inspection of membrane surface: porous blocking, covering, etc. ✓ Efficiency of fouling removal in cleaning tests. 	<ul style="list-style-type: none"> ✓ Detection of abrasion marks ✓ Failures on membrane surface ✓ Porous size
<i>FTIR-ATR</i>	<ul style="list-style-type: none"> ✓ Identification of fouling components ✓ Identification of membrane composition ✓ Efficiency of fouling removal in cleaning tests. 	
<i>Tensile tests</i>		Modification of tensile parameters can have an important impact in the performance of hollow fiber membranes.
<i>Thermogravimetric analyses</i>		Transition temperatures will give information about chemical integrity.

II. TYPES OF MEMBRANES

UF membranes have different morphologies depending on their applications and characteristics of the influent to be treated. From the different configurations of UF membranes that are available in the market, the most common samples that are autopsied in our labs are hollow fiber membranes (see figure 1).

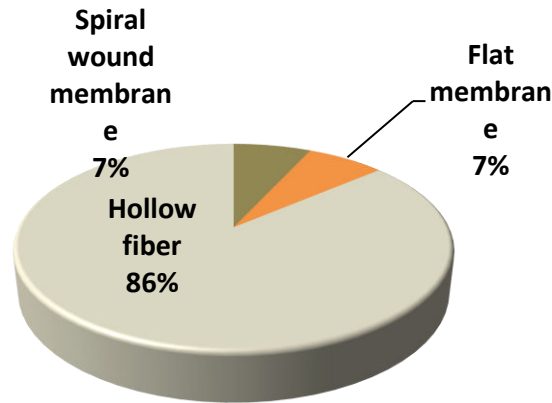


Figure 1.- Different configurations of autopsied UF membranes

The visual inspection of these fibers during autopsies mainly allows checking if there is presence of fouling on module ends, any relevant failure on fibers integrity, if there is a homogeneous or heterogeneous presence of fouling along the length of fibers, etc.



Module end



Blocked fibers



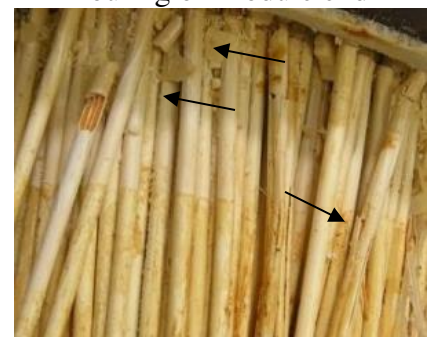
Fouling on module end



Presence of fouling



Module configuration



Damages on fibers

UF hollow fibers membranes have different composition and configuration. The following photographs show some of the different configurations, structures and types of UF hollow fiber samples commonly analyzed in our laboratories.



From the different composition available in the market, the most popular autopsied membranes are:

- PES (52%). Inside-outside filtration sense.
- PVDF (33%). Outside-inside filtration sense for most of them, although depending on additional components of these fibers composition, this sense of filtration may change.

Both SEM-EDX and ATR/IR allow to verify and to check membranes composition and configuration. Following figures include some IR spectra obtained from different hollow fiber composition. By this technic is possible to verify fibers composition, but also if there is any additional component.

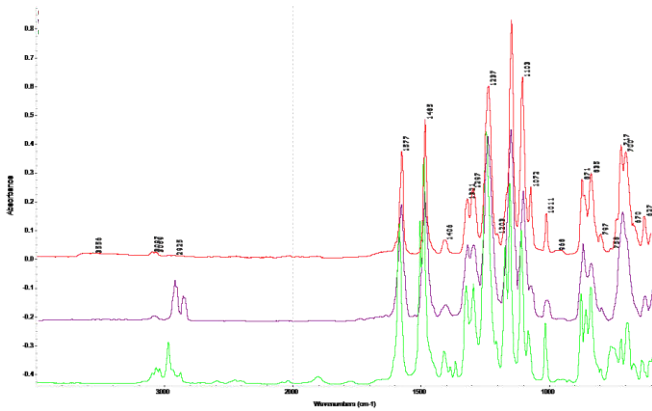


Figure 2. Characteristic PES IR spectra

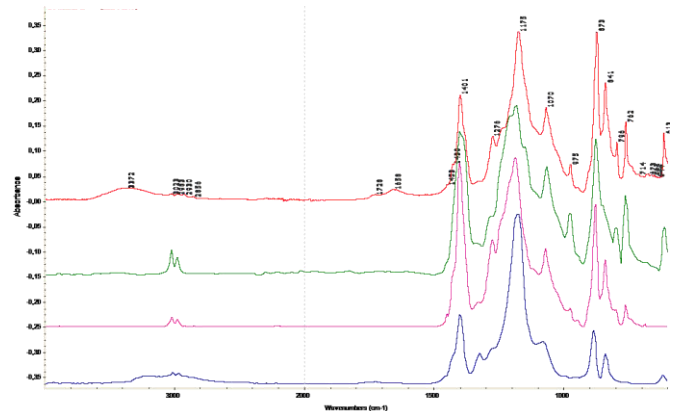
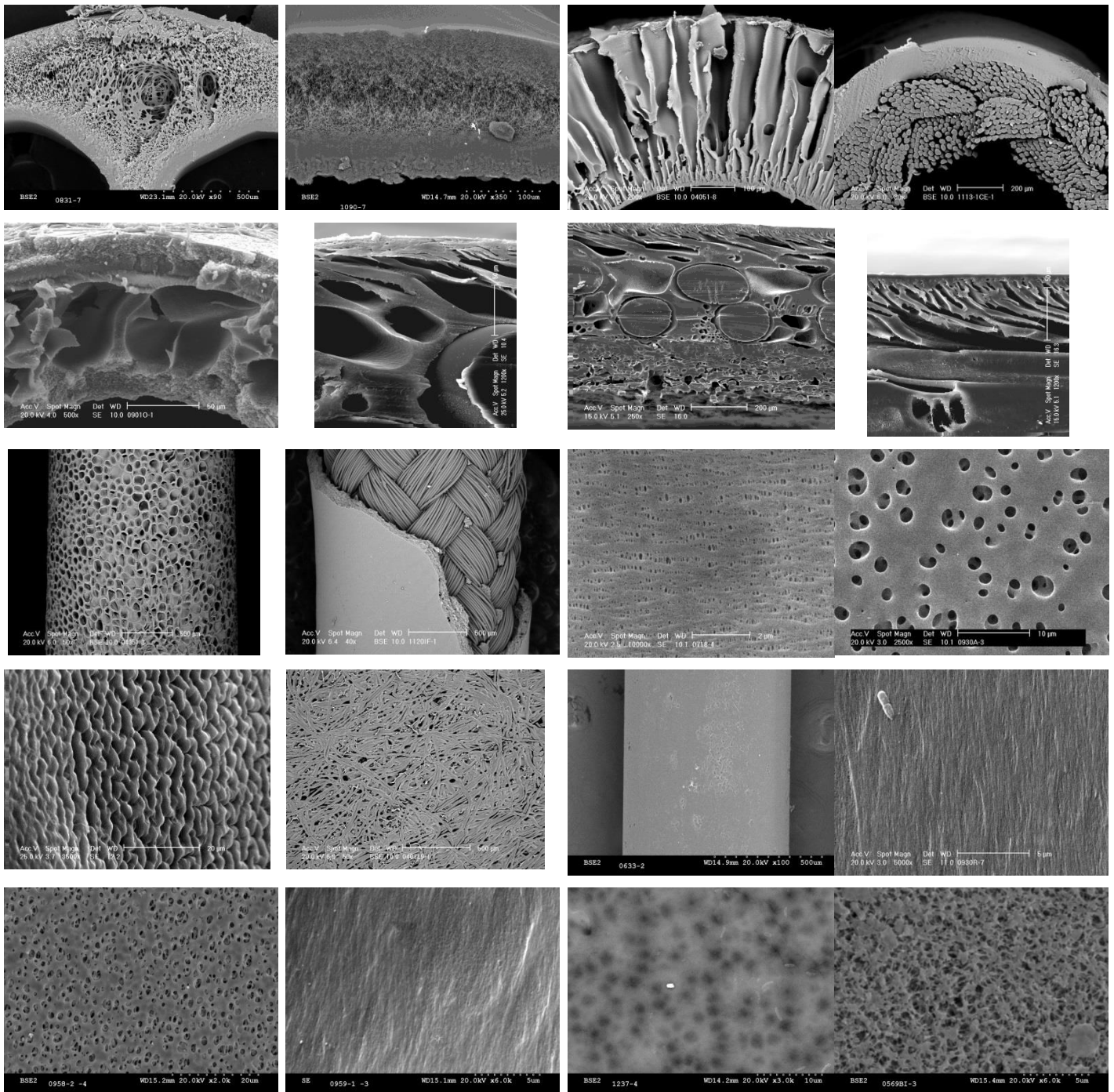


Figure 3. Characteristic PVDF IR spectra

The other common technique used for autopsies, SEM-EDX, cannot identify organic components, but it is very useful for a characterization of membrane structure.

Following microphotographs show different cross section of different UF hollow fibers where different distribution of its components can be distinguished.



Different morphologies and structures of UF hollow fibers obtained by SEM

III. FAILURES ON UF MEMBRANES

As already explained, it is normal that UF hollow fiber membranes suffer a decline in permeate flux. The best tool to have an accurate diagnosis of membrane failure is a membrane autopsy. Considering the results obtained from 90 autopsies, the following figure 4 shows that most common reason of failure in this kind of membranes is fouling. In this percentage of membranes with fouling, the 63% showed a relevant covering.

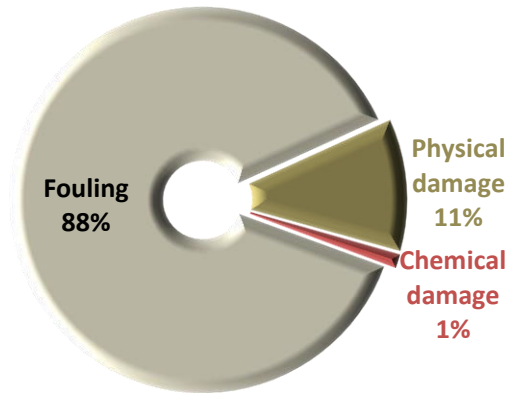


Figure 4.- Main failures detected on UF membranes during autopsies

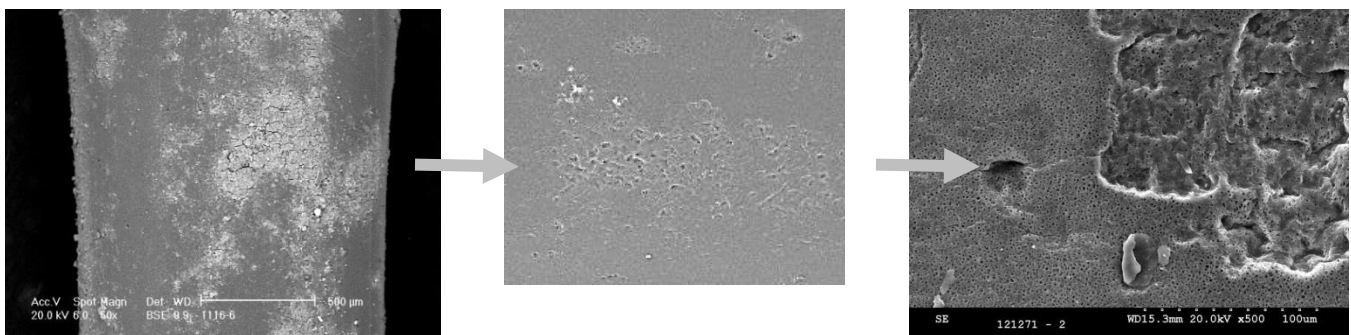
This presence of fouling is commonly reversible by cleanings, but it is very important to know the nature of the fouling in order to choose the most suitable cleaning procedure.

It is very important to have a very good characterization of UF influents, not only to expect the kind of fouling, but also to verify the compatibility of water components to UF membrane composition (mainly in process/industrial waters). In any case, the best way to assure and accurate identification of UF membranes is by an autopsy.

III.1. INTEGRITY

Although a loss of integrity is not the most common failure detected during autopsies, it is necessary to have analytical tools that check if fibers preserve most of their original integrity.

An easy way to check if there is any loss of integrity on hollow fiber membranes is by SEM. Following microphotographs show how a removal of fouling from fiber surface reveals the presence of relevant abrasion marks on its surface. These marks can produce not only failures on product quality, but also a decrease on fiber integrity.



Another important characteristic that reveals a loss in hollow fiber integrity is tensile strength. As an example, following table shows some results obtained from a fiber which didn't show relevant presence of fouling, but a lack in performance. As it can be observed, this fiber had suffered significant changes on tensile parameters when it was compared to a blank membrane which verified that membrane failure was due to these changes on fiber properties.

Table 2 . Mechanical – tensile tests

Sample	Peak load N	Modulus N/mm ²	Load at break N	Strain at break %	Stress at break N/mm ²
Blank	35,030	51,427	35,030	43,563	2,703
Sample	24,671	60,077	24,671	4,731	1,904

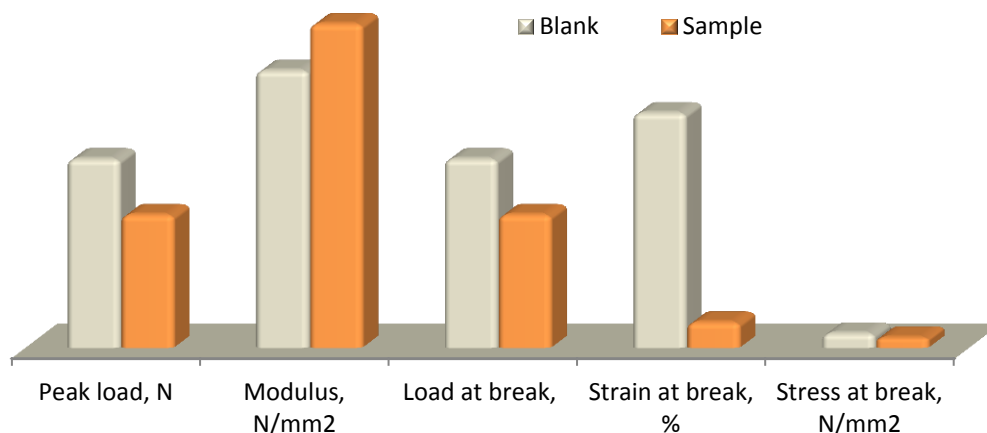


Figure 5. Mechanical properties of a damaged membrane compared to a membrane blank

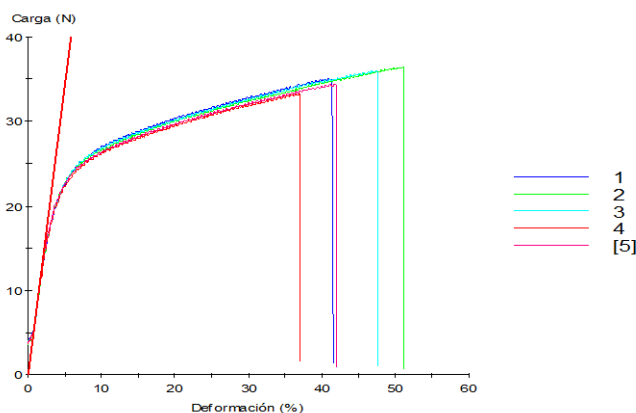


Figure 6. Blank fiber tensile tests

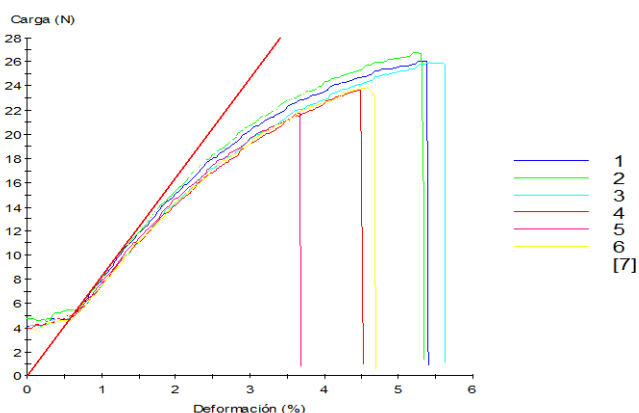


Figure 7. Sample fiber tensile tests

These changes on mechanical properties may be due to different factors. Besides a loss due to compaction or even to abrasion problems due to fouling presence, chemical integrity of hollow fiber membranes can change also. Although chemical solutions are widely employed for cleaning and disinfecting UF membranes, contact with chemicals may play an important role in membrane ageing [7, 8, 9].

When there is a loss of integrity on UF hollow fiber membranes, it is important to verify chemical integrity. As described during introduction, there are some techniques for testing UF hollow fiber membranes compositional properties as thermogravimetical analyses (TGA). Next figure 8 represents the differences between a membrane with some integrity problems (green line) and a membrane blank (brown line). As it can be observed, membrane sample showed some changes on thermal properties related to changes on fiber chemistry.

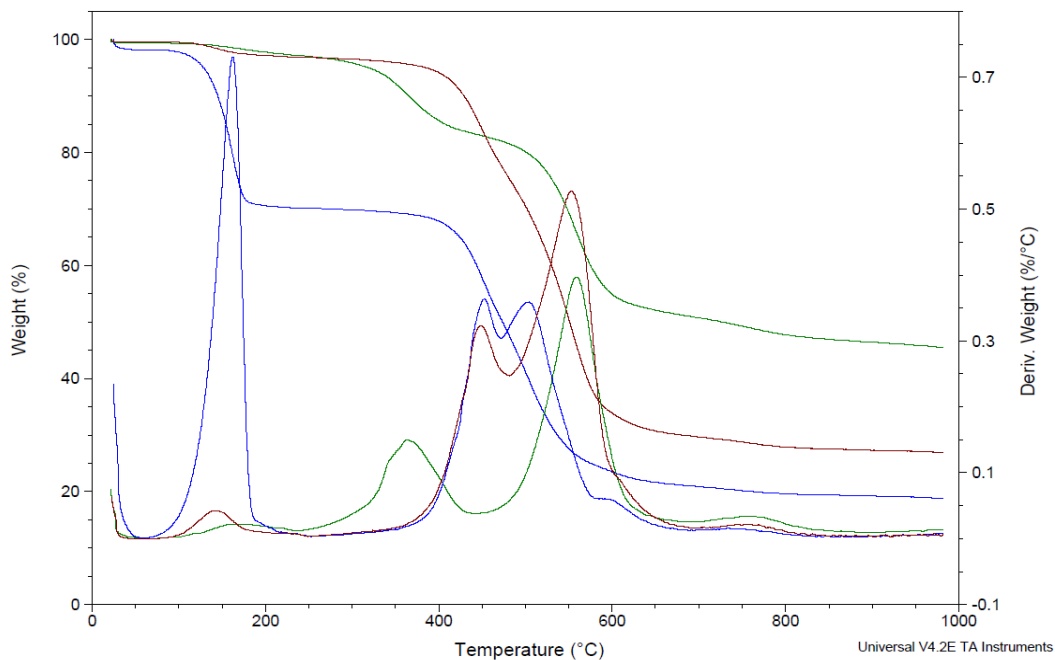


Figure 8.- Comparison of curves obtained from the TGA analyses of membrane blank
 Green line-Sample
 Blue line-Membrane blank 1 Brown line-Membrane blank 2

As these results demonstrate, both mechanical and thermal properties can be useful tools for determining UF hollow fibers integrity.

III.2. FOULING

As already explained during the introduction there are two main analytical techniques for fouling identification: SEM-EDX and ATR-FTIR.

Following spectra include some characteristic IR spectra of membrane fibers with presence of fouling.

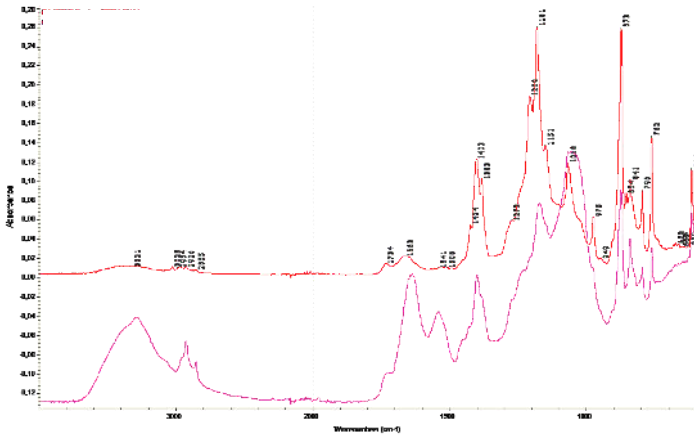


Figure 9. IR spectra of internal and external fiber surface – fouling on external surface

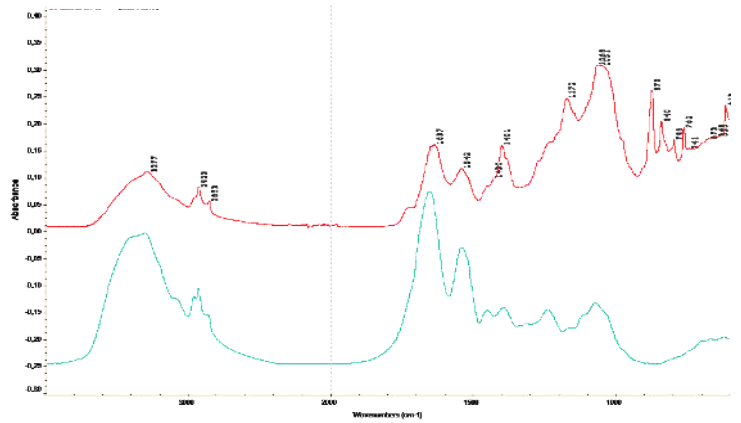


Figure 10. Characteristic biofilm IR spectra

Although IR achieves a good identification of fouling, mainly when it is organic, a microscopic inspection of fiber surface is essential for a good study of fouling presence.

Next microphotographs and spectra correspond to the analytical results obtained from both external and internal surface of a PES fiber autopsied. Although these fibers filter from inside to outside, presence of fouling (different composition) was detected on both sides.

As it can be observed, this fiber showed a relevant presence of fouling, which in any case allowed distinguishing any structure neither on external surface (support surface) nor on the internal surface (filtration surface).

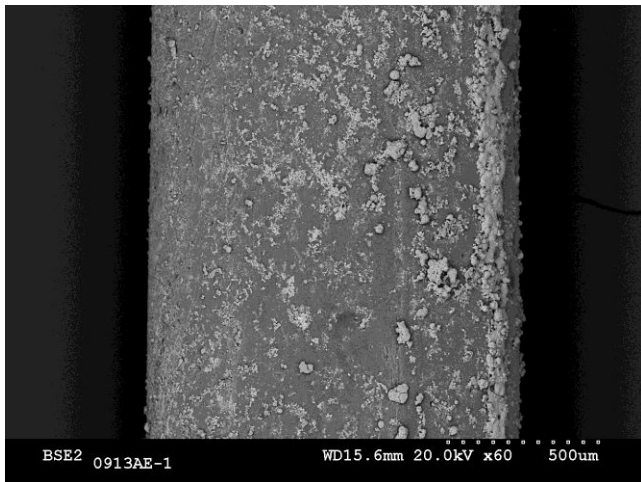


Figure 11. SEM image detail of UF hollow fiber external surface

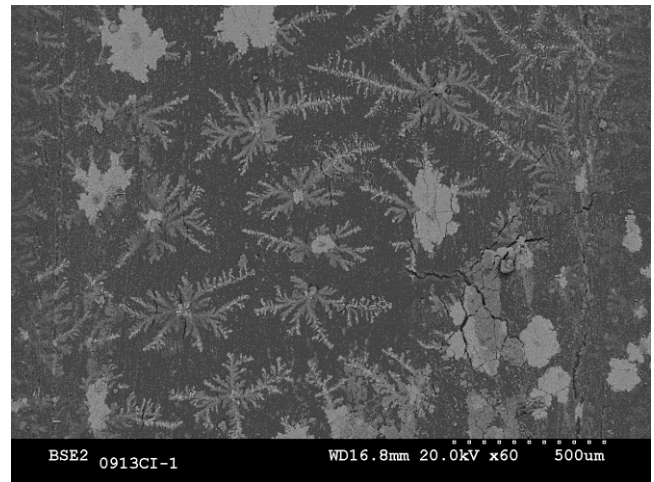


Figure 12. SEM image detail of UF hollow fiber internal surface

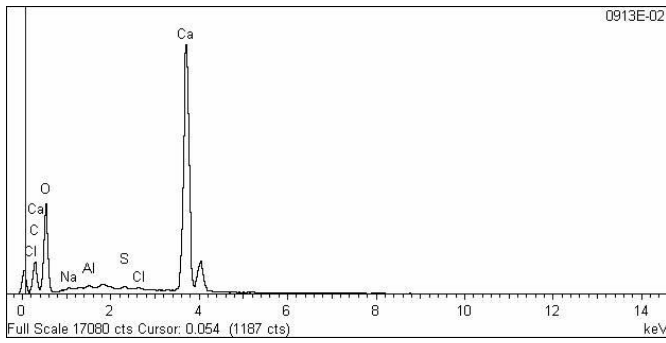


Figure 13. EDX analysis of UF hollow fiber external surface fouling

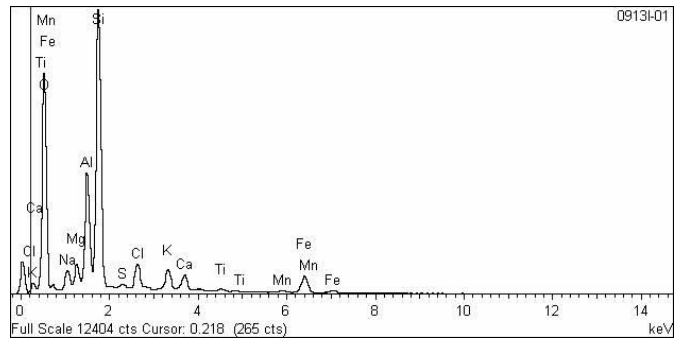


Figure 14. EDX Analysis of UF hollow fiber internal surface fouling

Besides the identification of fouling by this conventional analysis, SEM-EDX allows to get a distribution of each detected component by doing a mapping analysis of the surface. Following microphotographs distinguish the distribution of calcium and silicon as main components of the fouling on both external and internal surfaces.

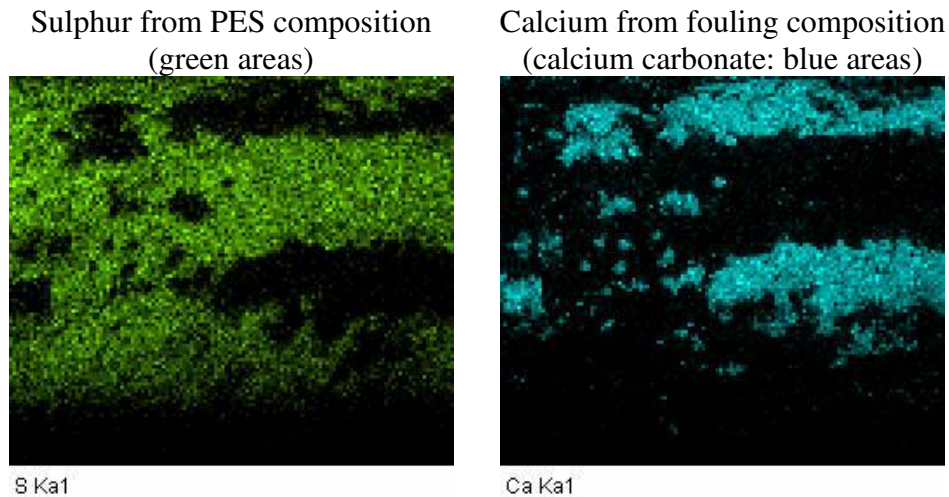


Figure 15. External surface main components distribution

Another very useful application of this analysis on UF hollow fiber membranes is to analyze cross section of fiber membrane.

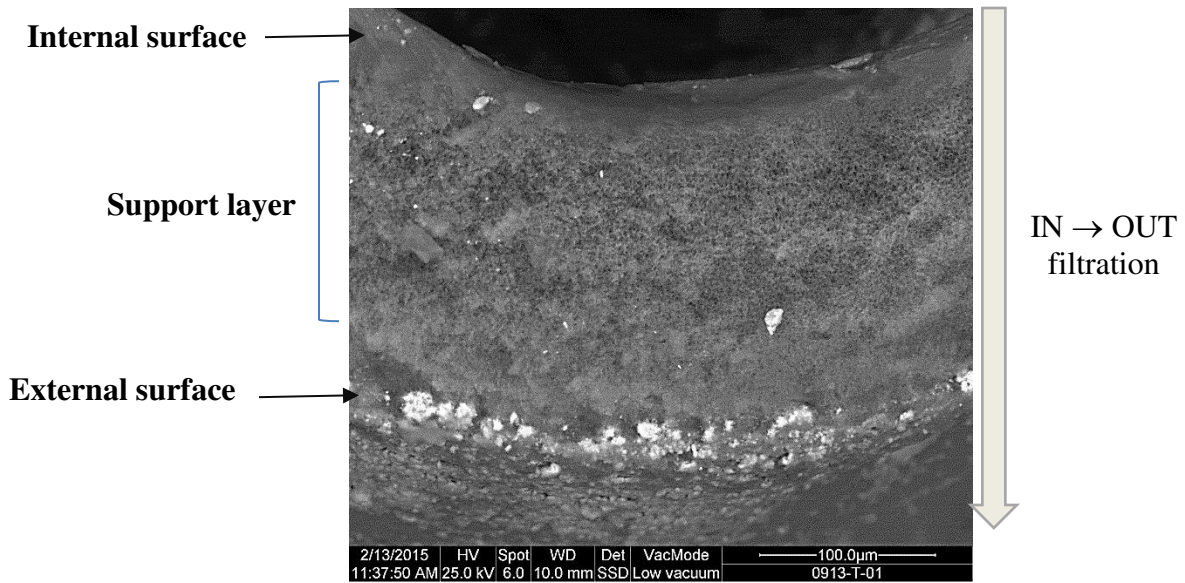
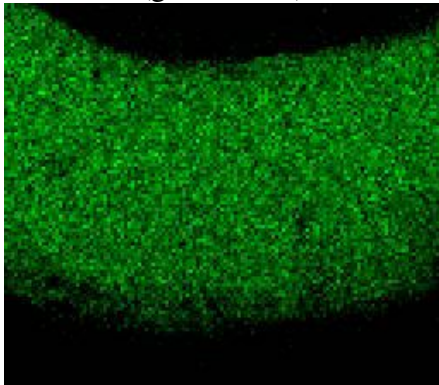


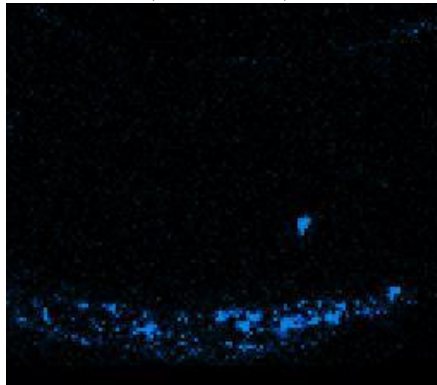
Figure 16. Detail of UF hollow fiber cross section

Sulphur from PES fiber composition
(green areas)



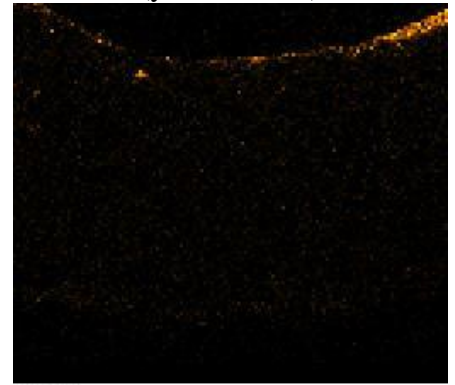
S Ka1

Calcium from calcium carbonate
(blue areas)



Ca Ka1

Silicon from aluminosilicates
(yellow areas)



Si Ka1

Figure 17. UF hollow fiber cross section main components distribution

This analysis is very useful when it is necessary to check if part of the fouling may come into the fiber support of hollow fiber membranes.

Besides, this visual distribution of main elements, SEM-EDX allows obtaining distribution curves of each element along the cross section.

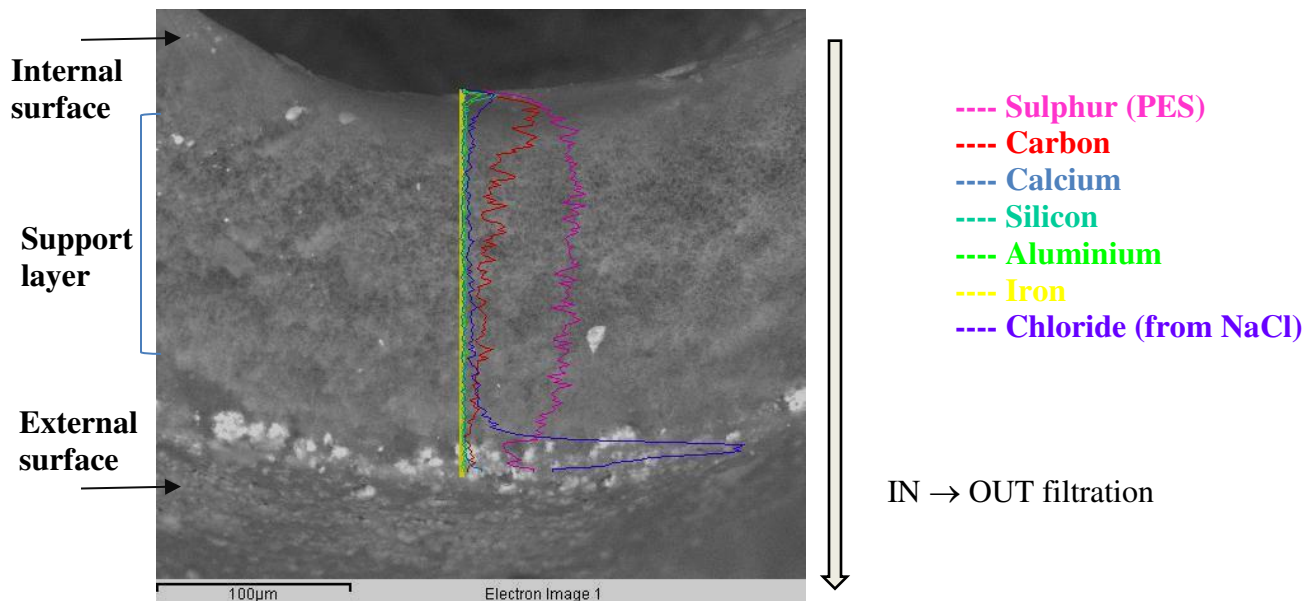


Figure 18. Elements distribution at UF hollow fiber cross section

As figure 17 and 18 verify composition of fouling on both sides of the fiber are different and they are localized on both external and internal fiber surface, but not in the fiber support.

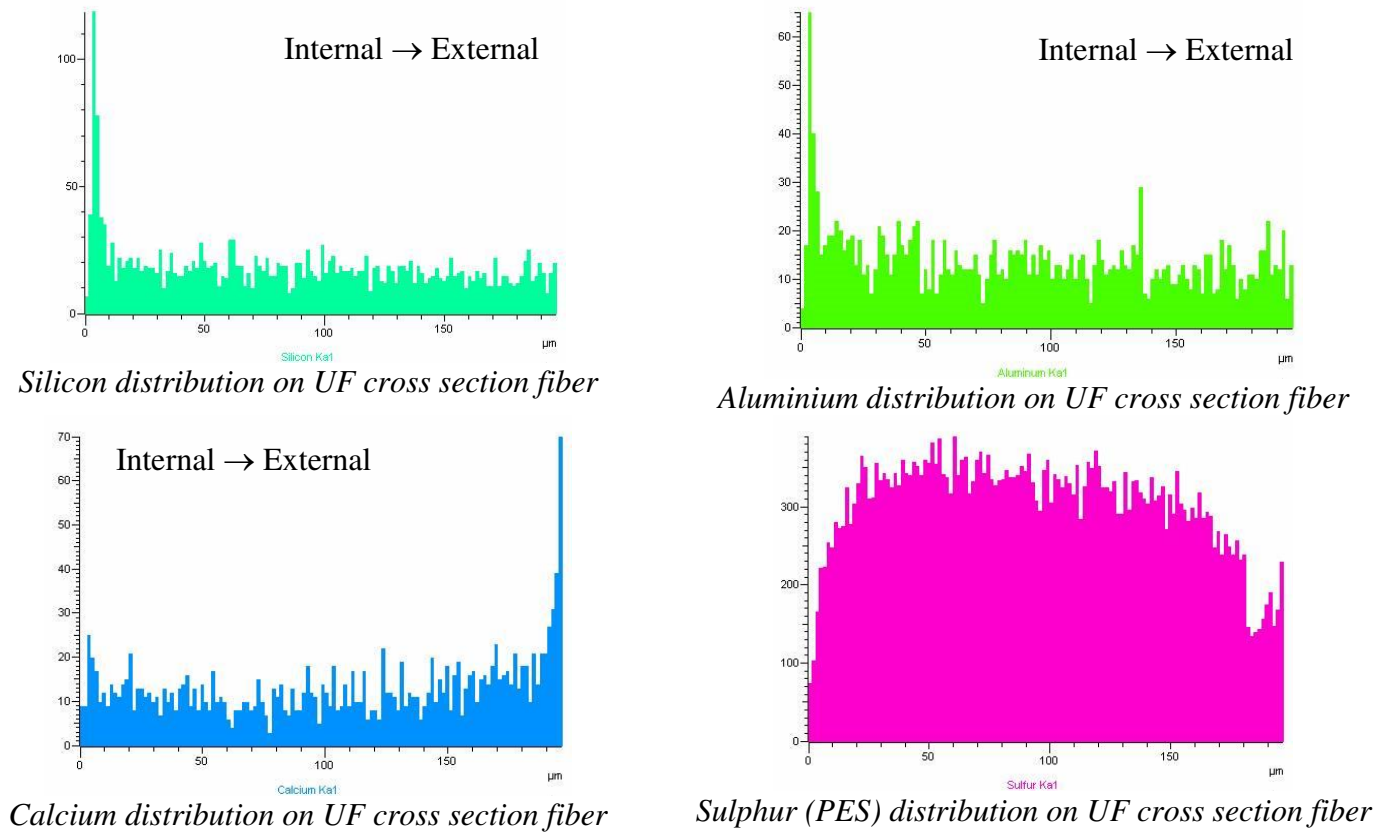
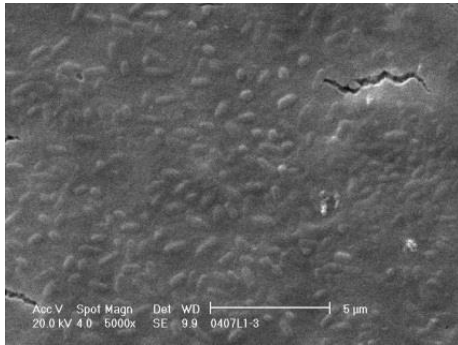


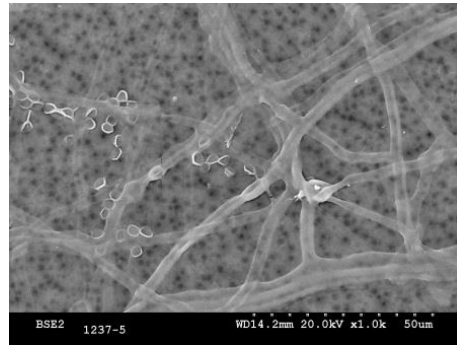
Figure 19. Elements distribution curves at UF hollow fiber cross section

As already explained, GMP laboratories has carried out a relevant number of UF autopsies based on these analytical techniques, which can be used as an important source of information about the different types of fouling that can be found on an UF membrane surface.

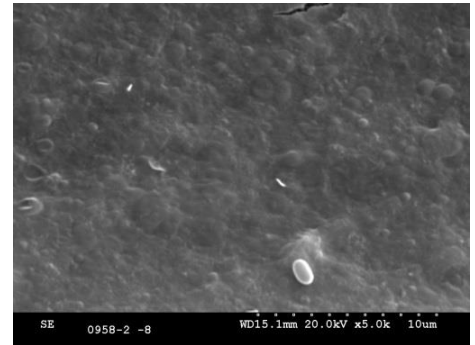
From the 90 autopsies data used for this study, nearly the 70% showed a fouling mainly organic. Besides this broad classification, figure 20 shows the different kinds of fouling detected as main component during these autopsies: biofilm and organic fouling, colloidal matter, metals (mainly iron and aluminium) and calcium carbonate. Some SEM images of the different types of fouling are included also.



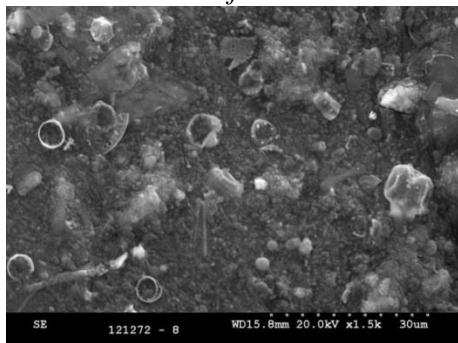
Biofilm



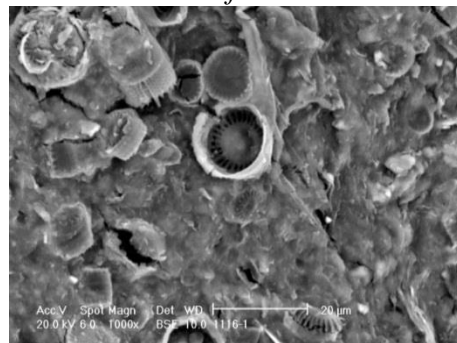
Biofilm



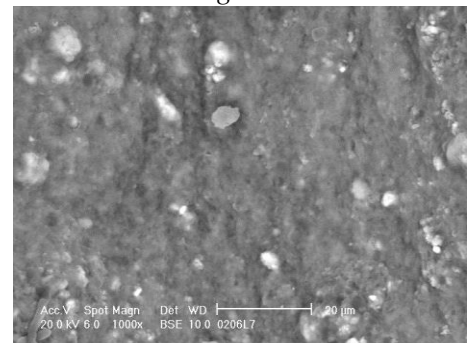
Organic



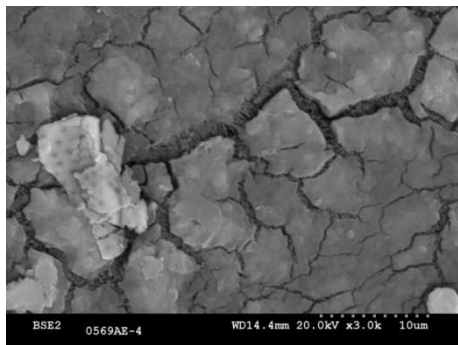
Colloidal matter



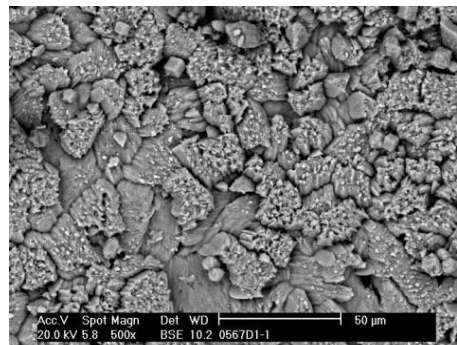
Aluminosilicates + diatoms



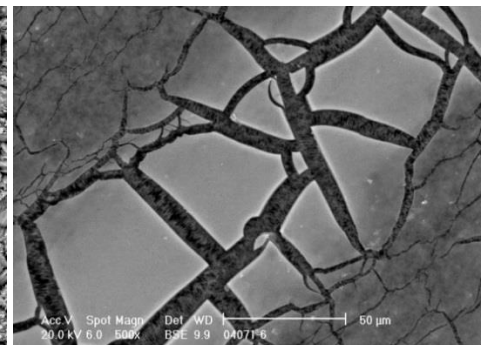
Iron



Aluminium



Calcium carbonate



Calcium phosphate

Fouling on UF membranes surface

UF process is a barrier, which is used for the retention of water components that must be removed. Then, biofilm, organic matter and colloidal matter should be expected as main fouling components. Concerning the presence of metals, they can be also present in water but it is more common that they come from coagulants dosage. If coagulation process is optimized, these metals shouldn't reach UF membrane surface but, since it is not always possible to control water variability, UF systems must guarantee a perfect retention of these compounds.

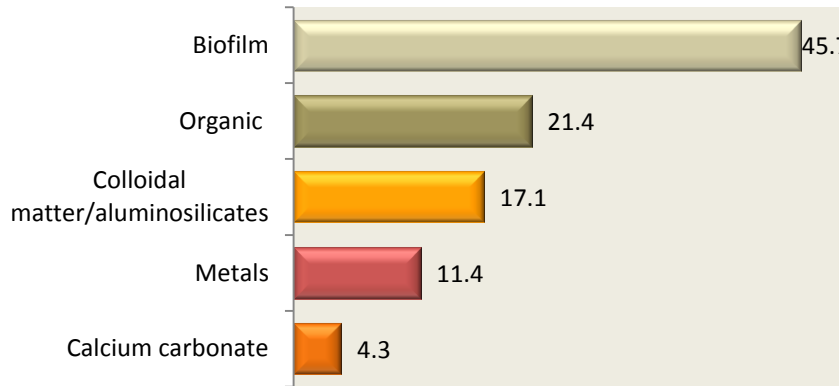


Figure 20. Main kind of fouling detected as main component during UF autopsies

Then, there are some main types of fouling that should be expected for an UF system but, as already explained in a previous paper about RO fouling [1], it is almost impossible to find a pure fouling. It is that secondary component of fouling the one that avoids in many cases the good effectivity of a cleaner and the recovery of membrane performance and that is why is so important to have a good characterization of fouling.

In order to help the understanding of the composite nature of fouling, figure 21 includes main secondary components detected for each kind of main fouling during autopsies.

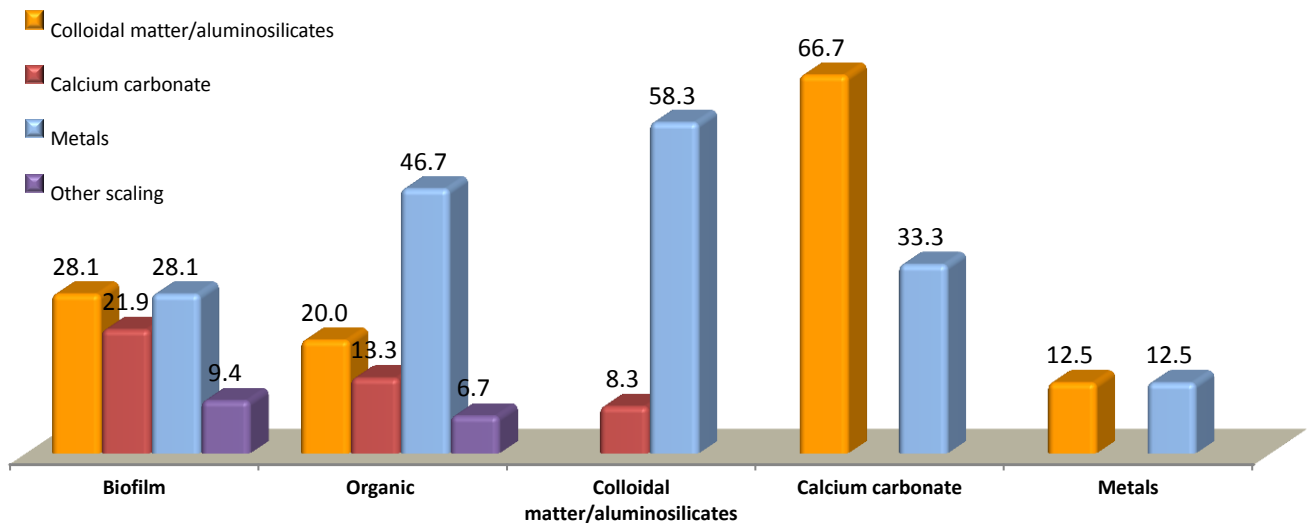


Figure 21. Secondary components of fouling detected during UF autopsies

As it can be observed in this figure, biofilm and organic fouling show more variety of secondary fouling composition. The most common secondary component of fouling is metals, followed by colloidal matter/aluminosilicates. Besides, for the main types of fouling (organic and colloidal matter) it is common to detect also calcium carbonate as secondary component and even other scaling different that carbonates.

At this point, it is important to remind that calcium carbonate is not a common component in the water to be treated by UF, but it can be developed in water due to some change in water characteristics, mainly in pH.

As already explained in introduction, UF hollow fiber membranes have different configuration and structure, which depends on the sense of filtration. As a media of filtration, the identification of fouling included in figures 20 and 21 was carried out on the filtration side. But the 37.5% of IN→OUT fibers and the 7.7% of OUT→IN membranes, presence of fouling was detected also on the support layer. In most of the cases, fouling was similar on both fiber surfaces filtration side, but more than the 20% of the fibers with relevant presence of fouling on the support component, showed presence of calcium carbonate (example included in figures 11 to 19).

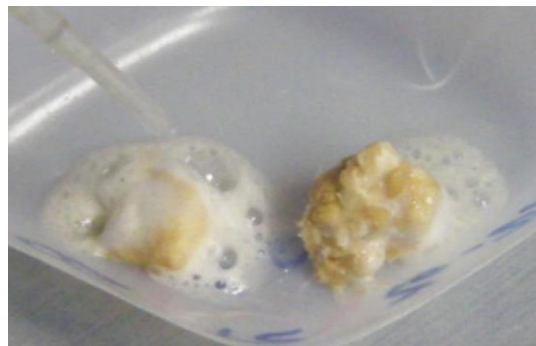
Considering these results, it has been demonstrated the common presence of calcium carbonate on hollow fiber UF membranes. This scaling presence on UF membranes must be a consequence of cleaning procedures, which commonly use product water with a relevant increase of pH (alkaline cleaners).

Presence of calcium carbonate can decrease efficiency of cleaning procedures and produce irreversible damages on fiber surface (abrasion marks, etc) and then a loss in integrity.

Another important factor to consider is that UF works in many systems as pretreatment for RO membranes. A scaling already formed during RO pretreatment avoids performance of antiscalant and the consequent scaling on RO system also (following photographs show a real example).



Scaling on UF support surface



Effervescence due to carbonates presence



Carbonates presence of RO feed side



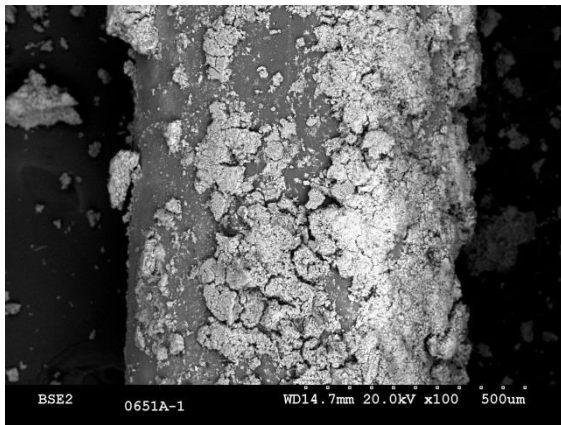
Scaling on first RO membrane position after scaled UF membrane

IV. CLEANING TESTS

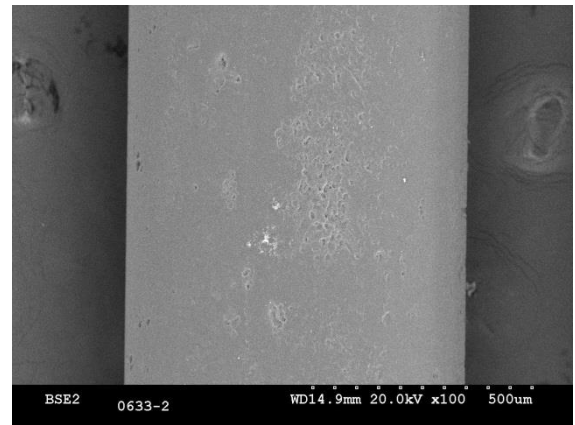
There are different cleaning procedures for UF hollow fiber membranes. When these cleanings are carried out with chemicals it is important to have an accurate identification of fouling. If a cleaning procedure is not effective, membrane will never recover original performance and fouling presence will increase very fast. During cleaning tests carried out for autopsies it is common to verify than formulated chemicals are more effective against fouling than commodity chemicals. This is mainly due to the presence of secondary components of fouling as explained in chapter III.2.

Besides the identification of fouling, UF membrane autopsies are very useful for the determination of the best cleaning procedure and chemicals.

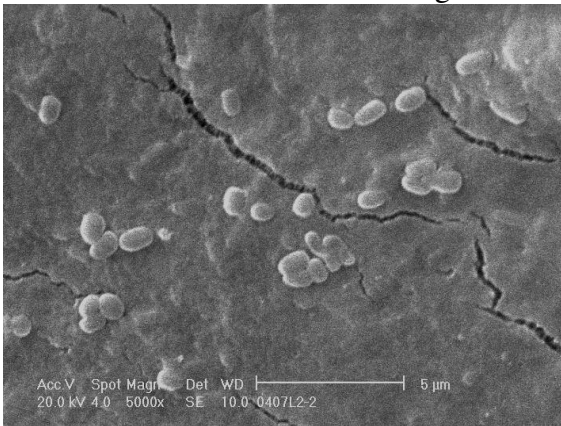
Following microphotographs show some examples of UF hollow fiber membranes after a cleaning procedure analyzed by SEM.



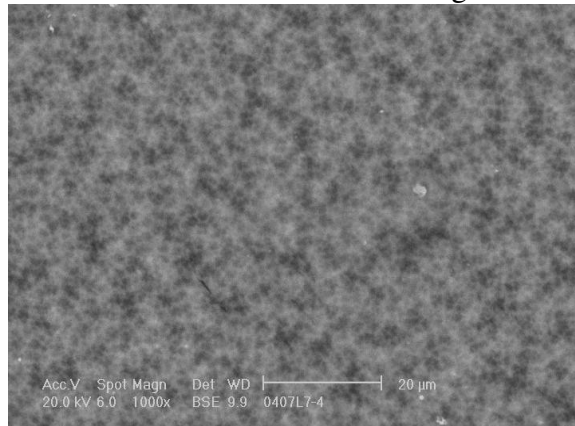
Fiber surface with scaling



Fiber surface after cleaning



Internal surface with fouling



Internal surface after cleaning

Besides the visual comparison of fiber surfaces, EDX analyses results allows to compare the percentage of elements detected during these analyses and to verify the removal of certain elements or the increase in main membrane components after cleaning process (see figure 22 as example).

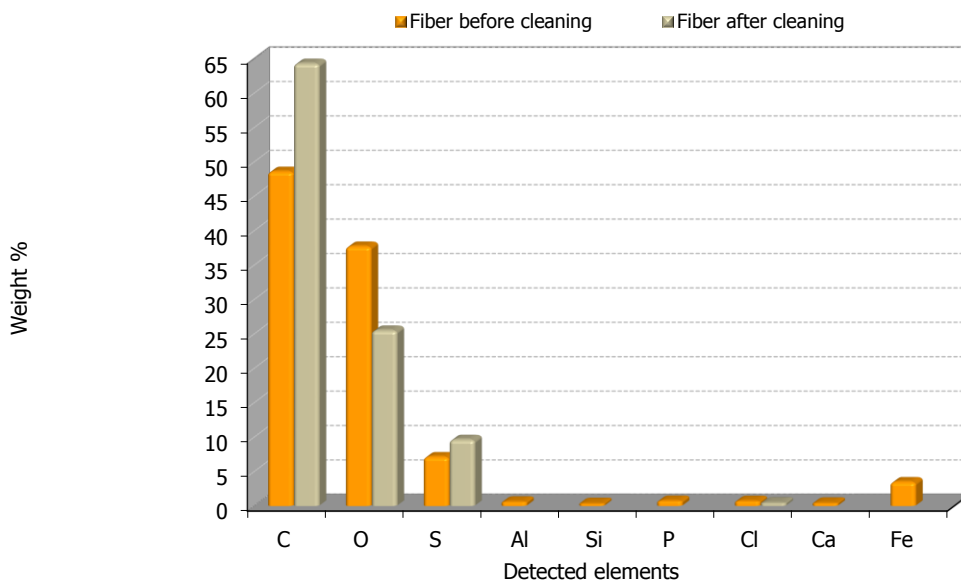


Figure 22. Comparison of EDX detected elements before and after cleaning procedures

As already demonstrated for membrane and fouling identification IR spectroscopy is another useful technique to verifying cleaning effectivity in fouling removal. Following figure shows IR spectra of a fiber internal surface before and after a cleaning procedure applied in field. These analyses demonstrate the effectivity of the cleaning procedure applied in this case.

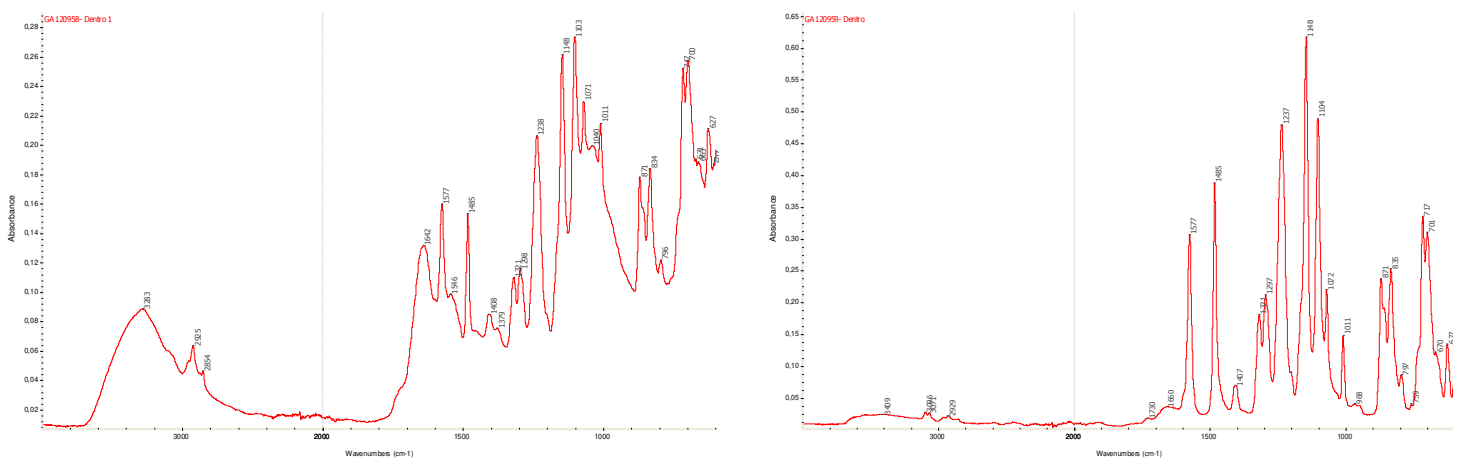


Figure 23. IR spectra of an internal UF hollow fiber Surface before (left spectrum) and after cleaning procedure (right spectrum)

V. CONCLUSIONS

- UF hollow fiber autopsies data demonstrate the usefulness of both SEM-EDX and ATR/FTIR for both membrane composition and fouling identification.
- Fouling identification obtained during autopsies has demonstrated that besides the retention of main water components, it is common to find calcium carbonate as consequence of cleaning procedures.
- Although fouling is the main failure detected on UF hollow fiber membranes, it is necessary to make additional effort in studying loss of integrity.
- In most of the cases a loss in integrity is due to presence of fouling, but chemical stability of membranes composition is also a possible cause of failure which is necessary to check.

VI. REFERENCES

- [1] N. Peña, S. Gallego, F. del Vigo & S.P. Chesters. Evaluating impact of fouling on reverse osmosis membranes performance, *Desalination and Water Treatment*, 51 (2013) 958-961.
- [2] C. Anselme and E.P. Jacobs. *Treatment of water by membrane processes*, Chapter 10. Ultrafiltration.
- [3] V. Chen, P. Le-Clech, *Hollow Fiber Technology*. Encyclopedia of Chemical Processing, Taylor and Francis, Dec 2007; 1253-1265.
- [4] G.R. Ziegler, *Membrane Structure*, Encyclopedia of Agricultural, Food and Biological Engineering, Second Edition, Taylor and Francis, Sept. 2010; 1031-1034.
- [5] I. Xiarchos, D. Doulia, V. Gekas, G. Trägårdh. Polymeric Ultrafiltration Membranes and Surfactants, *Separation & Purification Reviews*, 32:2, 215-278.
- [6] J. Pellegrino, *Filtration and Ultrafiltration Equipment and Techniques*, *Separation & Purification Reviews*, 29:1, 91-118.
- [7] E. Arkhangelsky, D. Kuzmenko, V. Gitis. Impact of chemical cleaning on properties and functioning of polyethersulfone membranes. *Journal of Membrane Science* 305 (2007) 176-184.
- [8] C. Causserand, S. Rouaix, J-P. Lafaille, P. Aimar. Ageing of polysulfone membranes in contact with bleach solution: Role of radical oxidation and of some dissolved metal ions. *Chemical Engineering and Processing* 47 (2008) 48-56.
- [9] S. Rouaix, C. Causserand, P. Aimar . Experimental study of the effects of hypochlorite on polysulphone membrane properties. *Journal of Membrane Science*. Volume 277, Issues 1-2 June 2006. 137-147.

VII. ACKNOWLEDGEMENT

Thanks to Victoria Velasco and Javier Rodriguez from Genesys Membrane Products S.L., who have been involved in the experimental work included in this work.

