A STUDY OF THE PHYSICAL AND CHEMICAL DAMAGE ON REVERSE OSMOSIS MEMBRANES DETECTED BY AUTOPSIES

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Abstract

Water treatment by reverse osmosis technology has as main aim to reject the maximum percentage of ions from raw water, giving as much treated water flow as possible. When there is a loss in these two parameters performance, it is essential to find the source of the failure, in order to use the necessary tools for its recovery. At this point, membrane autopsies are a very valuable source of information in order to understand the mechanisms that may have produced membrane capabilities loss.
Genesys Membrane Products (GMP) laboratory has developed during last decade more than 600 autopsies of membranes from all over the world. Therefore all the data obtained from these autopsies are a very valuable source of information about membrane failures. These membranes studies have shown that in almost the 75% of the cases, fouling is the main cause of membrane failures and this is one of the reasons because there is a broad research developed in fouling mechanisms understanding. The data obtained from these autopsies, have demonstrated also that the worst and main impact of fouling on membranes performance is the damage of polyamide layer and on rejection capabilities (1).

During the performance of reverse osmosis membranes in plants, there are many different processes that can damage the membrane surface: increases in differential pressure, backpressure phenomena, abrasion processes from fouling, massive or micro damages from scaling, oxidation processes or even degradation with time or cleanings. These damages, are commonly related to an increase in flow rate permeate and in a salt rejection decrease.
A well knowledge of membrane damage is very important considering that in more than the 30% of the membranes autopsied in GMP this phenomenon was found severe. These phenomena study is important also because, in many cases, damage is hidden by fouling and autopsies are the only way to detect a first step damage that could be prevented in plant if appropriated remedies are applied. GMP autopsies results demonstrate that almost the 80% of the studied membranes show slight signals of damage on the membrane surface, which were probably not detected in plant considering only performance failures.

In this study, statistical analysis from autopsies data will be used to check membrane damages, considering plants performance, membrane position, kind of fouling, feed water type, etc.
From the results obtained during the autopsies carried out on GMP laboratory and some preliminary tests carried out with some new techniques, the author intends to do also a review of the different analytical tools available for membrane damages detection and to check their advantages and disadvantages.

I. INTRODUCTION

Treatment of water by reversed osmosis is nowadays a well known and broadly used technology that still needs much research on new composite compositions and study in order to avoid membrane lacks and failures. Membrane autopsies are one of the main tools for the determination of membrane failures and for getting an accurate identification of membrane fouling.

All the different steps followed during the autopsy process and the different tests carried out, give a relevant number of data that achieve a valuable source of information about membranes integrity, fouling and performance. Then, although there is a lot of bibliography about RO technology, most of the studies and research developed is mainly theoretical or based on real data from only one site. At this point, the data obtained from the 600 membranes autopsies carried out in GMP laboratories during last ten years give information about many different sites, types of membranes, water, pre-treatment, failures, etc. that can be considered representative enough of RO technology.

As it was already established in previous papers based on GMP laboratory autopsies results (1), main causes of membrane failures are presence of fouling, chemical damages (oxidation processes) and physical damages.
Figure 1 shows the data obtained from 600 autopsied membranes, and demonstrates again that the main causes of failure on RO membranes performance is fouling. As we demonstrated before by the study of fouling impact on RO membranes [1] the main and worse consequence of the presence of fouling on the membrane surface is the damage that polyamide material may suffer. As figure 1 demonstrates, although it is more common to find mild and slight physical damages on membranes surface it is very important to know the extent of membrane damage in order to determinate if membrane rejection capabilities can be recovered. On the other side, chemical damage is detected also as mild and slight extent on a similar percentage of membranes and it is important to distinguish both phenomena in order to get an accurate diagnostic of the RO system failure.

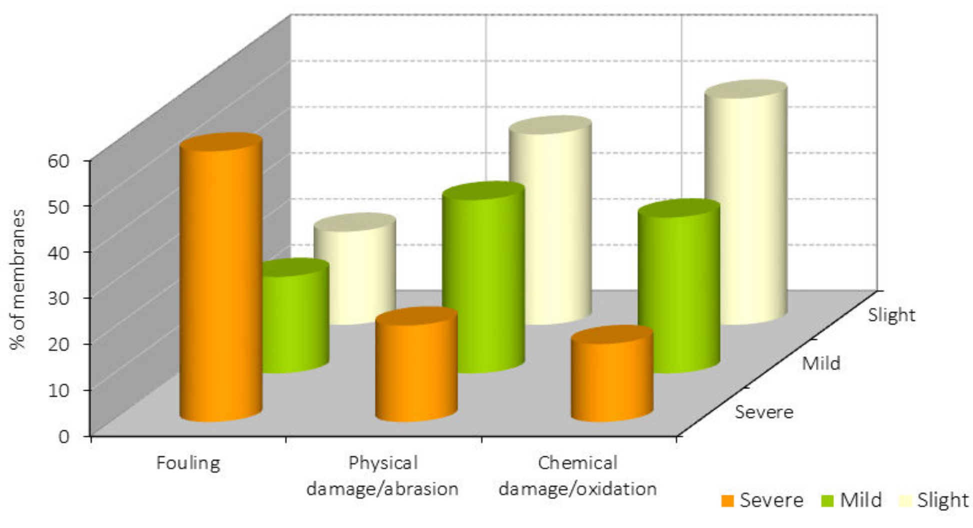


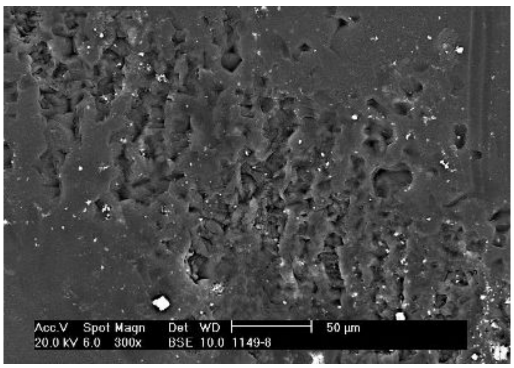
Figure 1.- Main membrane failures detected from membrane autopsies (n=600)

There are many sources of damages on membranes surfaces. Next table include some of the most common types of damages that can be detected on membranes.

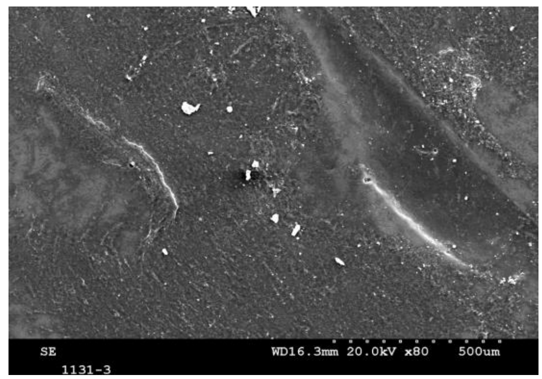
Table 1. Main damages detected on membranes surface

Physical damage	Chemical damage
• Abrasion marks from fouling nature • Marks from spacer protrusion • Marks from spacer material • Polyamide layer damages due to a massive presence of fouling (mainly due to scaling processes). • Polyamide bubbles (permeate overpressure) • Telescoping • Compacted membranes*	• Dosage of oxidant agents (mainly chlorine on polyamide-polysulphone membranes) • Use of aggressive cleaners*. • Use of extreme pHs*. *Non detected on GMP autopsies

The physical damages can be mainly due to leaks in the pre-treatment, the presence of fouling or to operational problems.
Next photographs show some examples of these damages, found during the autopsies carried out in our labs.

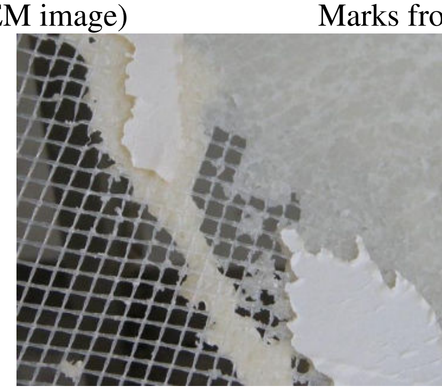


Abrasion marks from fouling (SEM image)

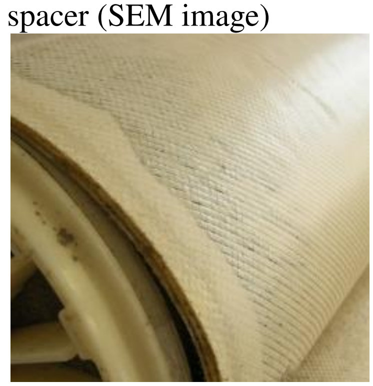


Marks from spacer (SEM image)

Spacer protrusion



Polyamide layer damages due to fouling



Polyamide bubbles/delamination

Concerning chemical damage, both chlorination and chemical cleaning are used effectively to decrease membrane fouling and recover membranes performance in use. The performance decline of polyamide membranes seems to be from the loss of structural integrity of constituent polymers.
Although there are different sources of chemicals that can produce damages, oxidation by chlorine is the most common and the one chosen for the studies included in this work.

Oxidation of polyamide-polysulphone membranes by chlorine is one of the most extended research lines in RO technologies. Due also to the extended application of chlorine in RO plants and its known damage to polyamide membranes, there are many papers about membranes oxidation by chlorine, where the reaction mechanism is well explained [2, 3].

II. METHODOLOGY

As explained already, the results shown in this paper are based on the studies developed during the autopsies carried out in Genesys Membrane Products S.L. laboratories.
A membrane autopsy implies the different steps explained in next diagram. The different tests and analytical tools used during autopsies will be thoroughly described during the paper.

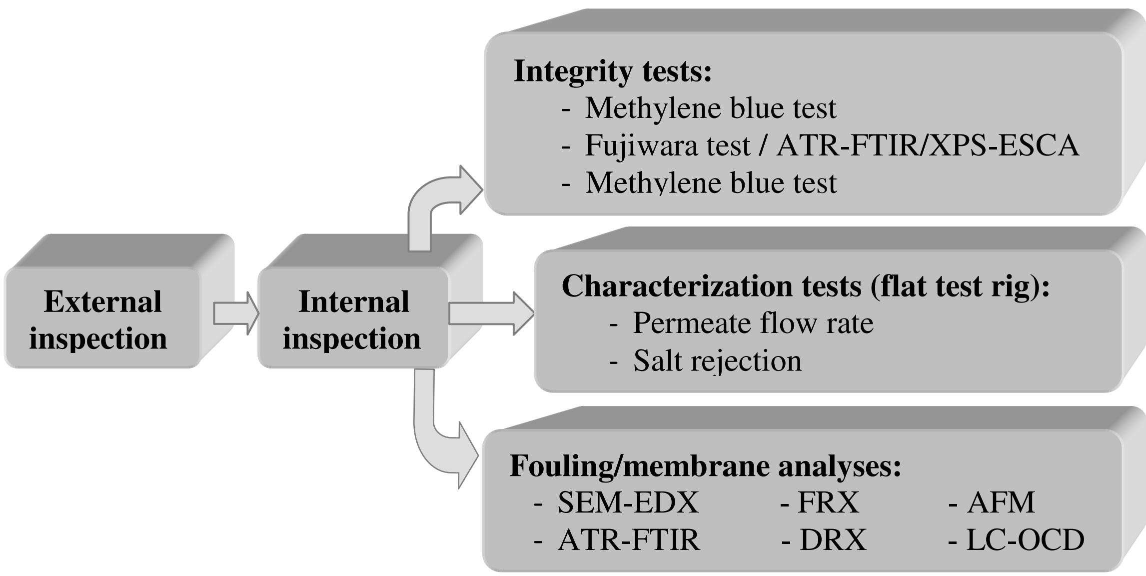


Diagram 1.- Schematic description of main analysis carried out during membrane autopsies

Besides the results obtained during autopsies, some additional tests were carried out on one membrane blank sample in order to do complementary tests by different techniques. Damage on these samples was verified measuring membrane performance parameters, although the main parameter considered for damage verification was salt rejection.
Next table includes the conditions of these samples and the references that will be used during the paper:

Reference	Details
Blank membrane	KOCH MEMBRANE SYSTEMS – Model HR
Mild chemical damage	Blank membrane + 100 ppm free chlorine pH: 7.00, 24 hours contact
Severe chemical damage	Blank membrane + 500 ppm free chlorine pH: 3.00, 24 hours contact
Physical damage	KOCH HR after real operation-Abrasion marks due to calcium sulphate

III. RESULTS

3.1. Damaged membranes performance.

One of the most clears signs of damages on an RO membrane is the lack of salt rejection capabilities and very often an increase on permeate flow rate. Next figures 2 and 3 show the performance of membranes with mild and severe damages depending on the kind of damage detected during autopsies.

As it can be observed in this figures the behaviour of membranes performance with the damages are very similar, and it would be impossible to distinguish the kind of damage on the membrane considering these parameters.

As expected, these figures demonstrate that, in most of the studied membranes, flow rate was higher than design and salt rejection was lower than expected for a membrane in good conditions.

But the conclusion that should be remarked from these graphs is that, despite the damage observed on some of the membranes, there is around a 30% of membranes giving a flow rate lower than design and more than a 10% of membranes that gave a flux similar to the reference values established by manufactures. This behaviour is mainly due to the presence of fouling and therefore in many cases it is not possible to detect membrane damages on site after fouling is removed.

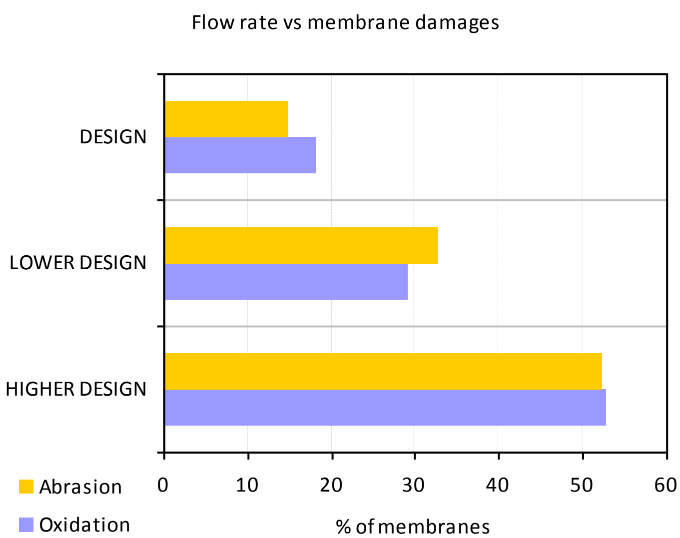


Figure 2.- Permeate flow rate from damaged membranes

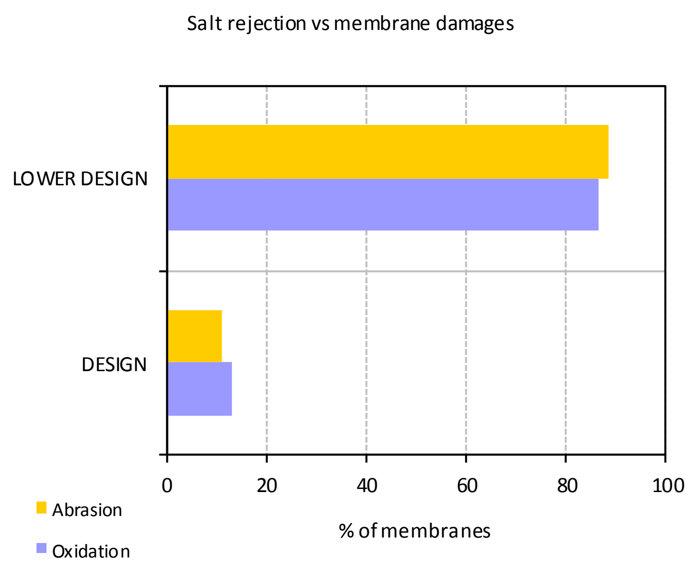


Figure 3.- Salt rejection from damaged membranes

3.2. Damages vs fouling.

As already mentioned, fouling is one of the main membrane failures and its presence may finally produce physical and irreversible damages on the membrane surface. The nature of the fouling may produce a different damage depending on its composition. Next table compiles different damages that can be observed on membranes surface depending on the nature of the fouling. These are the expected damages from each fouling, but for the study of damages on membranes, it is important to consider the composite nature of fouling since it is almost impossible to find a pure fouling (1). This table includes also the percentage of membranes detected for each kind of fouling.

Table 2.- Main fouling compositions detected on membrane autopsies

FOULING GROUP	Expected membrane failures	Expected damages
Biofilm / organic matter 31%	**↑ΔP, ↓Flux, Salt passage**	Increases in differential pressure commonly produces damages on the membrane surface due to that spacer material exerts pressure on the polyamide layer and that produces severe damages on the membrane surface.
Other organic - 8%		
Colloidal matter - 29%	**↑ΔP, ↓Flux**	Besides damages produced from the spacer material marks due to increases in **ΔP**, this kind of fouling produces abrasion marks on the membrane surface.
Scales - 22%	**↓Salt rejection, ↓Flux**	Scaling produces characteristic abrasion damages due to its crystalline shape.
Metals - 10%	**↓Flux**	Depending on the nature of metals, damages may be produced in different ways. When metals come from corrosion drags they produce severe abrasion marks.

As figure 4 shows, when just the main nature of the fouling is considered, the number of membranes with chemical damages is quite similar for organic and inorganic fouling. However, when physical damages are considered, they are more common when the fouling is mainly inorganic.

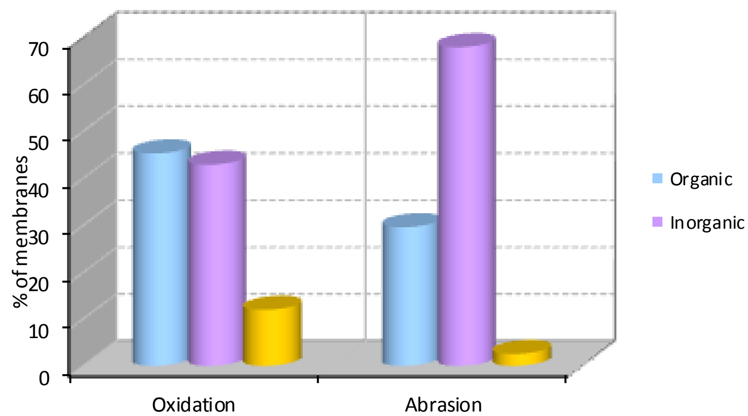


Figure 4.- Damages depending on the nature of fouling

After considering these organic and inorganic nature of the fouling, figure 5 includes the percentage of membranes with chemical and physical damage depending on the composition of fouling. These data only considered the main fouling found on the membrane surface, although most of them were composed of composite fouling.

As it can be observed on this figure, when the main damage is physical, the main percentage of membranes was fouled with colloidal matter and scaling.

On the other side, although in most of the cases presence of fouling produces physical damage, chemical damage is observed also on fouled membranes. Figure 5 shows how the most common fouling observed on chemically damaged membranes is biofilm. The use of oxidant agents is broadly used for disinfection of the water before it comes into the membranes, and so it is easier that these systems are in a higher risk of oxidation. By the way, this figure demonstrates that oxidation process may occur in presence of any kind of fouling, although the lowest percentage of chemically damaged membranes was found on scaled surfaces.

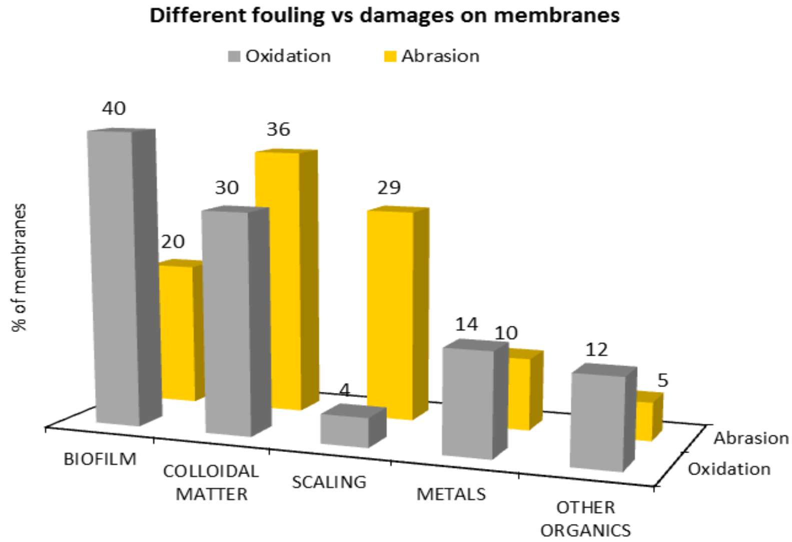


Figure 5.- Damages depending on the composition of fouling

Quite related to the composition of the fouling, it is interesting to consider the position of the membranes and the damages observed on them (figure 6). As this figure shows, although both physical and chemical damages can be detected on all the studied positions, abrasion is more common on first positions and oxidation processes on last positions.

The most common types of fouling that are detected on membranes (biofilms and colloidal matter) are commonly related to first positions and, thus it is reasonable to find a higher percentage of damages on first positions. Concerning chemical damages, the first contact of any chemical is with the first position, but once again if we consider that the most common fouling are mostly found on the first positions, the chemicals would damage in a less extent the membranes with less presence of fouling.

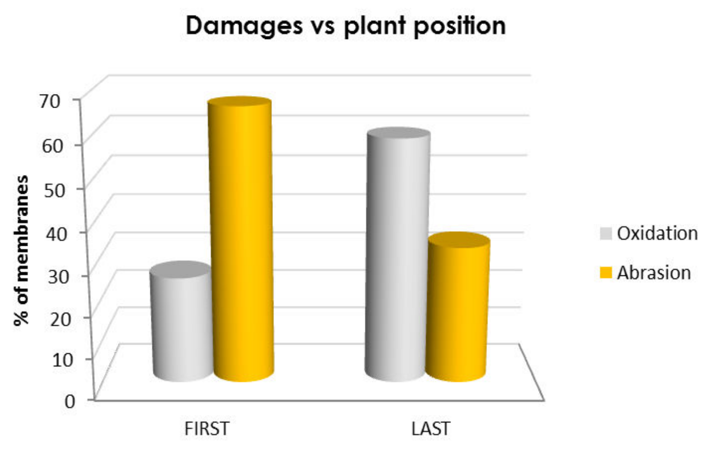


Figure 6.- Damages detected on autopsied membranes depending on site position

Another interesting data to be considered in the study of membrane damages is the type of water to be treated. Although RO membrane technology can work with many sources of water, the main two types of water to be considered are sea water and brackish water. The percentage of membranes with damages was higher for brackish water elements, but brackish water is also the most common type of membrane received in our laboratories and these data are not conclusive.

3.3. Analytical tests for damages detection

As explained before, autopsies use many different analytical tools for the identification of the different damages and foulings that can be observed and detected on a membrane surface.

The most extended tests that are carried for the determination of chemical damages are methylene blue test and Fujiwara test.

3.3.1. Methylene blue test

This test is based on the passage of a high molecular weight compound through the polyamide layer. When presence of this compound is detected on the permeate side of the membrane, it means that the polyamide layer is damaged. As figure 8 shows, methylene blue test was positive for almost the 80% of the membranes with chemical and physical damage. As this figure shows, membranes with oxidation show a higher percentage of membranes with a negative answer to the test and membranes with abrasion a higher percentage with a massive positive.

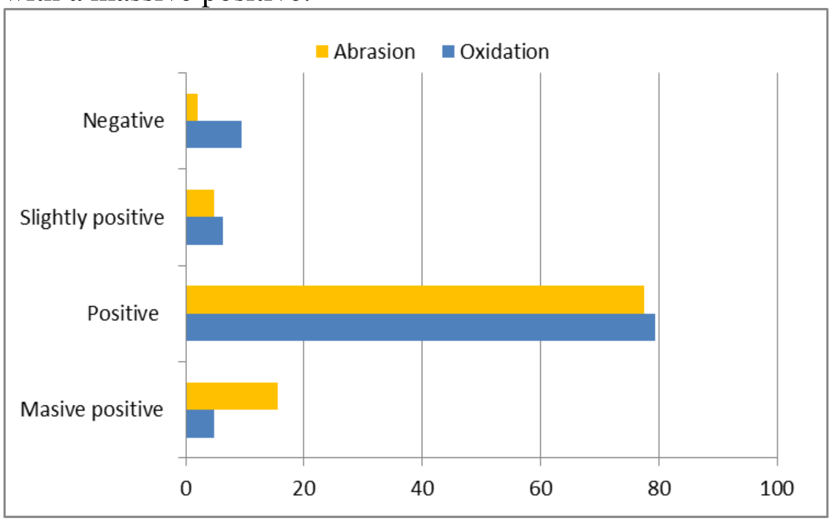
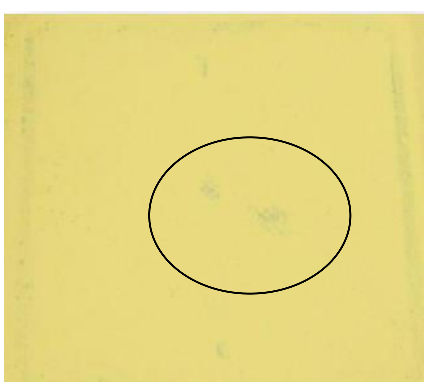
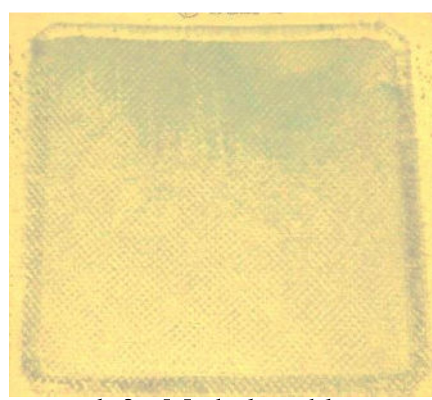


Figure 8.- Methylene blue tests on membrane autopsies.

For the demonstration of these conclusions, we did some tests on our labs and, as next photographs show we verified that even with a severe chemical damage, methylene blue test is not as positive as with a severe physical damage. Therefore, this test seems to be more sensitive to physical than to chemical damage.



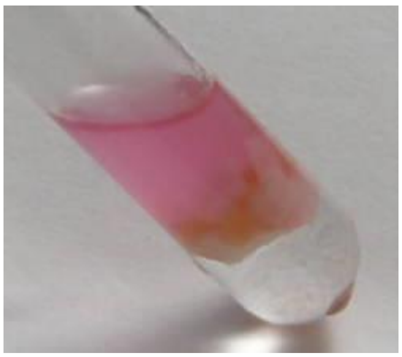
Photograph 1.- Methylene blue test on a membrane with a **severe chemical damage**



Photograph 2.- Methylene blue test on a membrane with a **severe physical damage**

3.3.2. Fujiwara Test (FJ)

FJ test detects significant levels of polyhalogen compounds so it will detect if the membrane is significantly oxidised. This is a colorimetric test in which a pink colour in the analytical solution, indicates organically bound halogens. Figure 8 shows the percentage of membranes with a positive Fujiwara test on membranes with oxidation and abrasion as main failures detected. As expected, Fujiwara test was positive on the 76 % of the membranes with clear signs of oxidation and on a 14% on membranes that showed also a relevant physical damage.



Example of a positive Fujiwara test

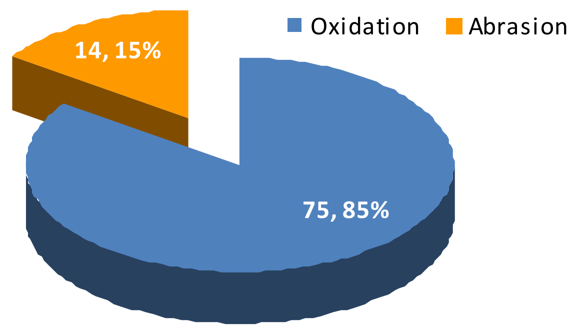


Figure 8.- Positive Fujiwara tests on membrane autopsies

Considering the performance of the membranes with a positive Fujiwara test, next figures 9 and 10 show how in more than the 60% of the membranes flow rate was lower or equal than design. On the other side, even with a positive answer on this test, the 20% of the membranes gave a good salt rejection. These results verify that Fujiwara test indicates that the membrane has been in contact to halogen, but does not confirm damage by oxidation.

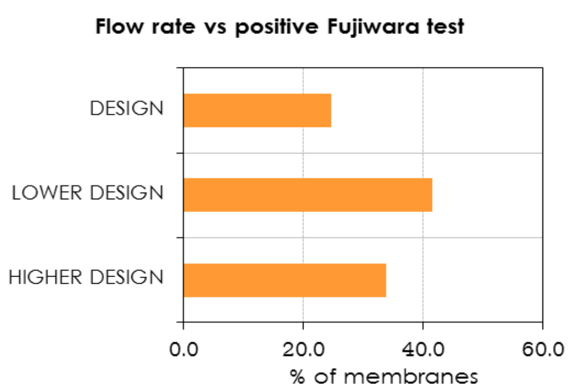


Figure 9.- Performance of membranes with positive Fujiwara test – flow rate

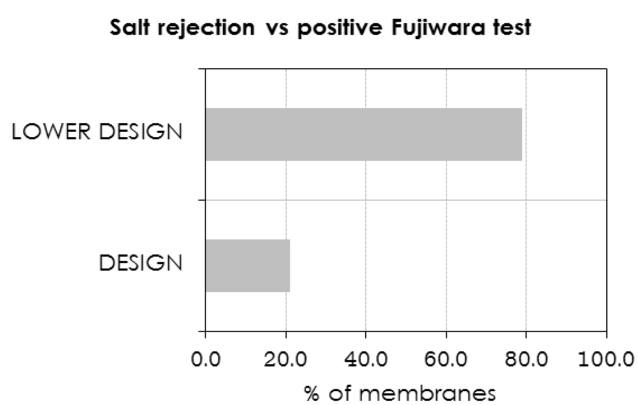


Figure 10.- Performance of membranes with positive Fujiwara test – salt rejection

The lacks in these traditional tests make necessary to use additional techniques that help to determinate the kind of damage that we have in RO membranes during autopsy. Thus, there are other analytical tools for oxidation identification that are commonly used these days as ATR/FTIR and XPS/ESCA.

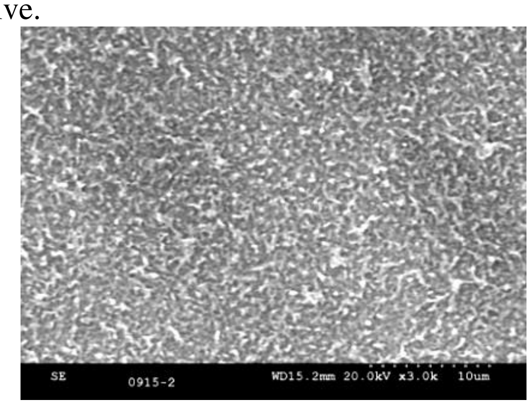
3.3.3. Scanning electron microscopy – Energy Dispersive X-ray Analysis (SEM-EDX)

This technique is used to study the membrane surface and to verify the elemental composition of its fouling and deposits detected. Elemental determination with the SEM-EDXA 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.

Scanning Electron Microscopy – Energy Dispersive X-ray Analysis (SEM-EDX) is one of the most powerful and basic tools used during membrane autopsies. The main damages that could be detected by this technique are physical: abrasion marks and marks from spacer.

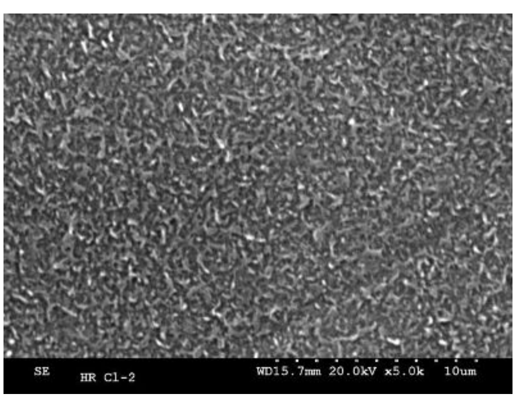
Concerning chemical damages, it is very difficult to detect them by this technique. Next images show the differences between a blank membrane and membranes with relevant physical damage and mild and severe chemical damage. As it can be observed, it is only possible to detect accurately physical damages by this technique, since even when chemical damage is very relevant, it wouldn't be possible to distinguish a damage that a fouling. On the EDX analyses of these examples (spectra 1 to 3) we could detect traces of the oxidant agent (chlorine), but in a real sample it would be impossible to verify if this chlorine could come from hypochlorite or from rests of sodium chloride, for example.

The detection of the oxidant agent would get more complicated on sea water samples, where the real oxidant agent is bromine, which is more difficult to detect by this technique. On those cases, it would be necessary to check the membrane by X-RAY FLUORESCENCE, for example which is much more sensitive.

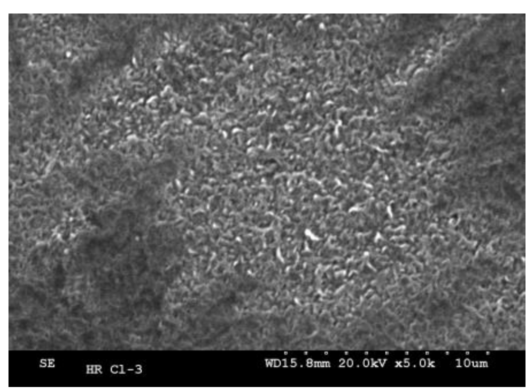


Blank membrane

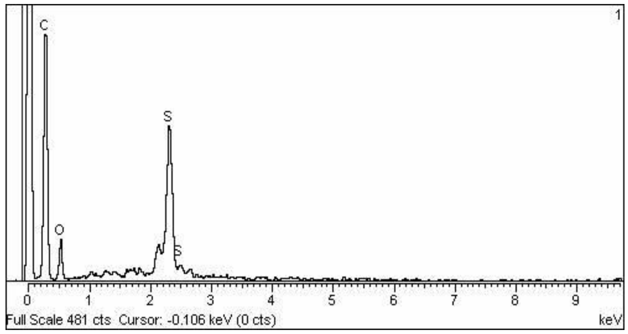
Severe physical damage



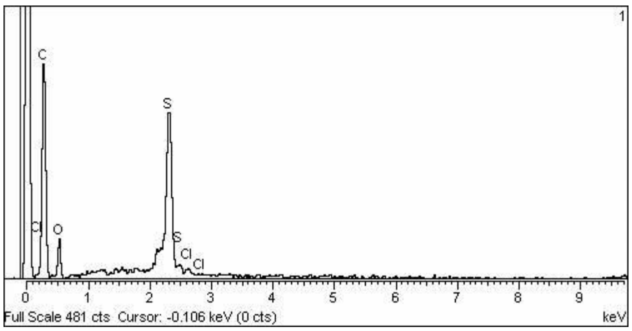
Mild chemical damage



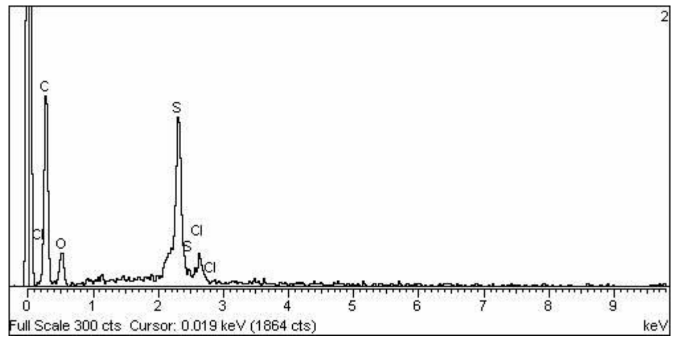
Severe chemical damage



EDX spectrum 1. Blank membrane



EDX spectrum 2. Mild chemical damage



EDX spectrum 3. Severe chemical damage

3.3.4. X-ray photoelectron spectroscopy (XPS) or Electron Spectroscopy for Chemical Analysis (ESCA)

XPS or ESCA is a quantitative spectroscopic technique that measures the empirical formula, chemical state and electronic state of the elements that exist within a material. XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and number of electrons that escape from the top 1 to 10 nm of the material being analyzed.
This technique is able to detect bromine and it can distinguish the oxidation state of the detected elements.
When the oxidant agent is sodium hypochlorite, this technique allows to distinguish between chloride (198,7 eV) and chlorine related to carbon by a quasicovalent bound (200 eV) [4,5]. Next table 3 shows how on membranes with demonstrated oxidation processes, the percentage of this element increases.
On the other side, if the analysis is carried out on a membrane without fouling, this technique would be able to detect any other oxidant agent different than chlorine on the membrane surface.
As happened for Fujiwara tests, this technique is able to detect presence of halogens on the membrane surface, but it doen’t show a possible damage of the membrane surface.

Table 3. Binding energies and atomic percentage of elements detected on membranes with physical and chemical damages.

Binding energy, eV	C1s	O1s	N1s	S2p	Na1s	Cl2p
Blank membrane	284.8 (81) 287.0 (19)	532.1	399.6	168.1	-	-
Physical damage	284.8 (74) 286.8 (26)	532.0	399.7	168.3	-	-
Mild chemical damage	284.8 (75) 286.9 (25)	532.1	399.8	168.1	-	200.2
Relevant chemidal damage	284.8 (77) 287.1 (23)	532.0	399.7	168.0	1071.3	200.2

Atomic %	C (%at)	O (%at)	N (%at)	S(%at)	Na (%at)	Cl(%at)
Blank membrane	71.3	22.9	5.2	0.1	-	-
Physical damage	71.2	22.9	5.5	0.2	-	-
Mild chemical damage	69.6	23.2	6.3	0.1	-	0.8
Relevant chemical damage	66.4	23.6	4.3	0.1	1.2	4.4

3.3.5. Attenuated Total Reflectance Infrared (ATR/IR)

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.

Then, by this technique we can be check polyamide layer bands and to check if there are any structural changes on it [6]. Comparing membranes with different damages to a membrane blank spectrum (see figures 11 to 13) it can be observed that there are no relevant changes on membranes with physical damages. On membranes with chemical damages, some slight changes can be observed on membranes with mild damages, but when oxidation processes are severe, these bands can even disappear.

The techniques that we have shown until now, are those commonly used during membranes autopsies [7].

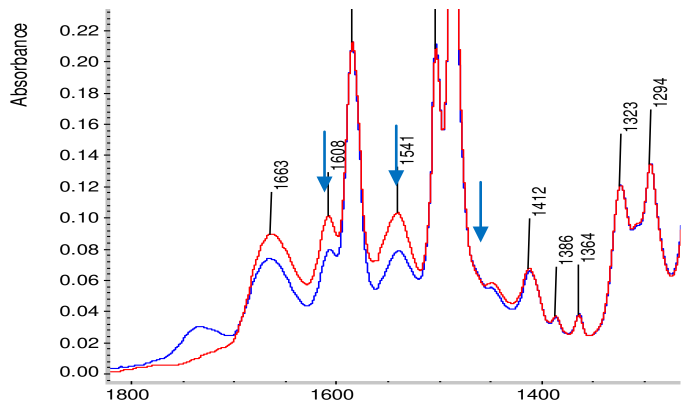


Figure 11. Severe Physical damage

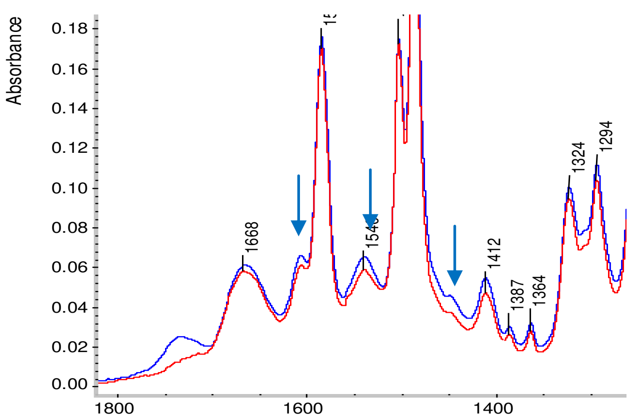


Figure 12. Mild chemical damage

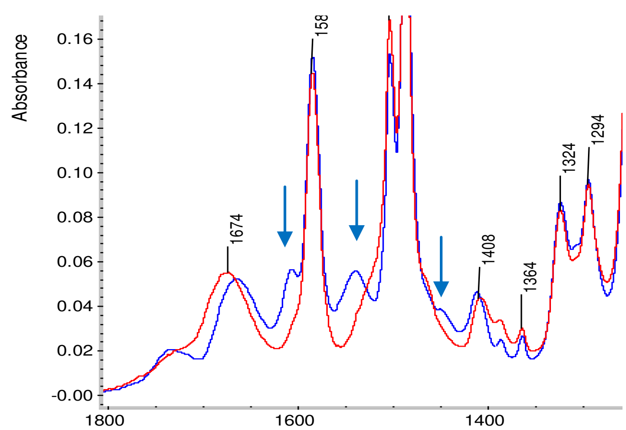


Figure 13. Severe chemical damage

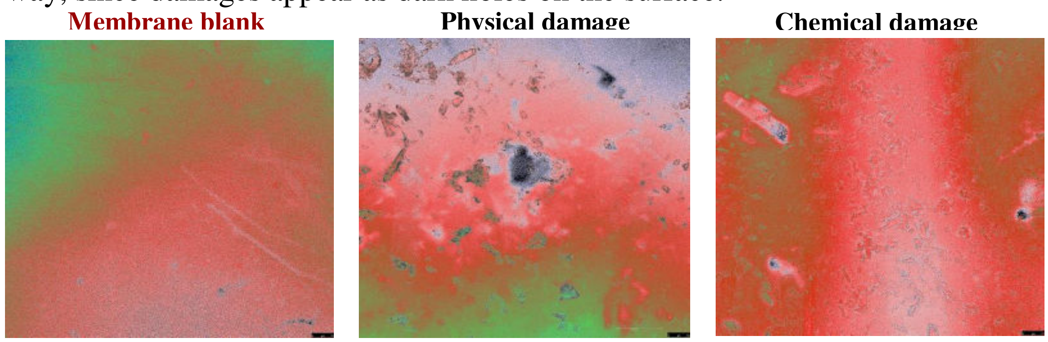
3.3.6. Complementary techniques. Preliminary tests

Although the results obtained from all the techniques explained before are good enough for the detection of membrane damages, it is necessary to search new and different techniques that could help on specific cases where no real clue about damage diagnosis is achieved.

Confocal microscopy

Confocal microscopy allows the study of samples with fluorescent properties or fluorescent marking, causing optical sections. This microscopy gives a dimensional study of the samples, including the interior, and in certain materials (like RO membranes) creates images from the surface through reflection [8].

Although this microscopy is more similar to an optical microscope and it doesn't allow to reach very high magnifications as SEM, these photographs show how it could help to distinguish physical damages in an easiest way, since damages appear as dark holes on the surface.



But the most interesting application of this microscopy in RO membranes, is that these equipments have spectral detection systems which allow to obtain autofluorescence curves and emission espectra.

Therefore, if we compare the spectra obtained with different laser sources on the study of one membrane blank and damaged membranes (figure 14), we can observe a decrease on the intensity of the spectrum maximum with the damages. Although the spectra changes with all the damages studied, this technique seems to be more sensitive to chemical than to physical damages.

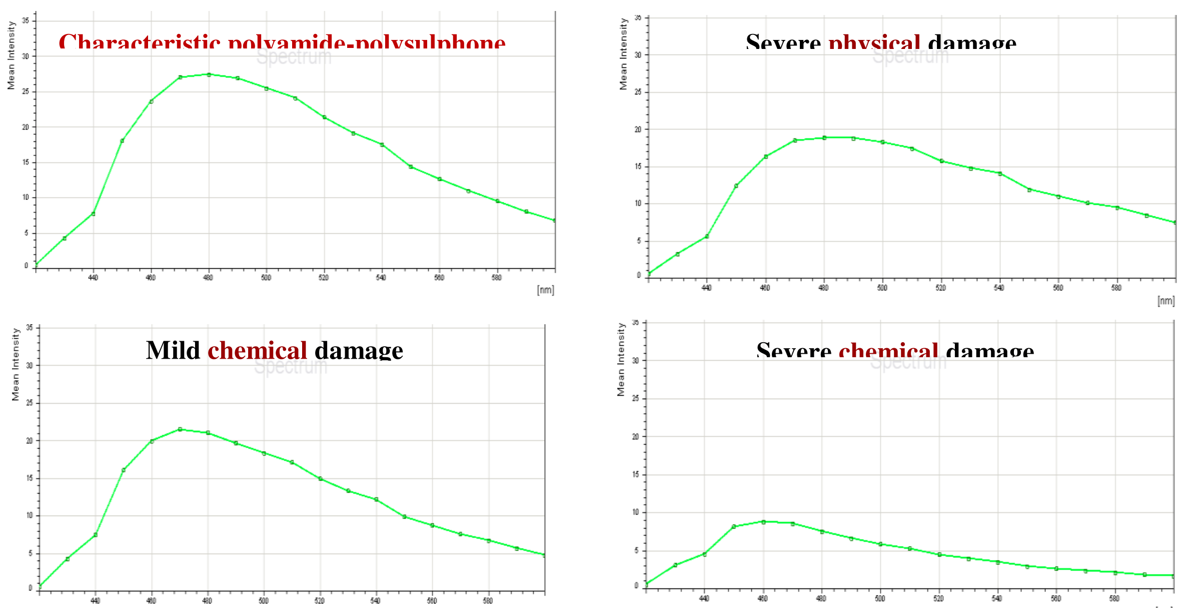
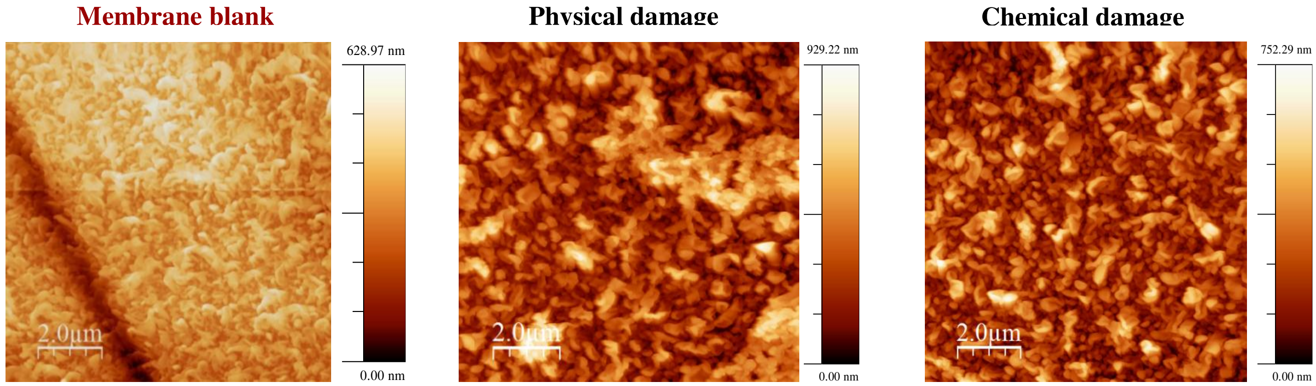


Figure 14. Emission spectra from different membrane damages obtained with a confocal microscope

Atomic force microscopy (AFM)

AFM or Scanning Probe Microscopy (SPM) provides a 3D profile of the surface on a nanoscale, by measuring *forces* between a sharp probe and surface at very short distance.

AFM system is mainly used to characterize different surface properties, for example topographic properties (three-dimensional surface imaging, surface roughness, grain size, step height) [9].



If we check the three dimensional images of a membrane blank and damaged membranes and its relieves, we can observe that when the damage is physical, it seems that the difference between the maximum and valleys on the membrane are much higher that on the membrane blank, which looks more smooth. On the other side, the membrane with chemical damage has a relief more similar to the membrane blank, but the distance between the valleys and maximums is much higher and wide on the membrane chemically damaged.

Therefore the studies developed by this technique indicate that the membrane topography and roughness changes from both physical and chemical damage.

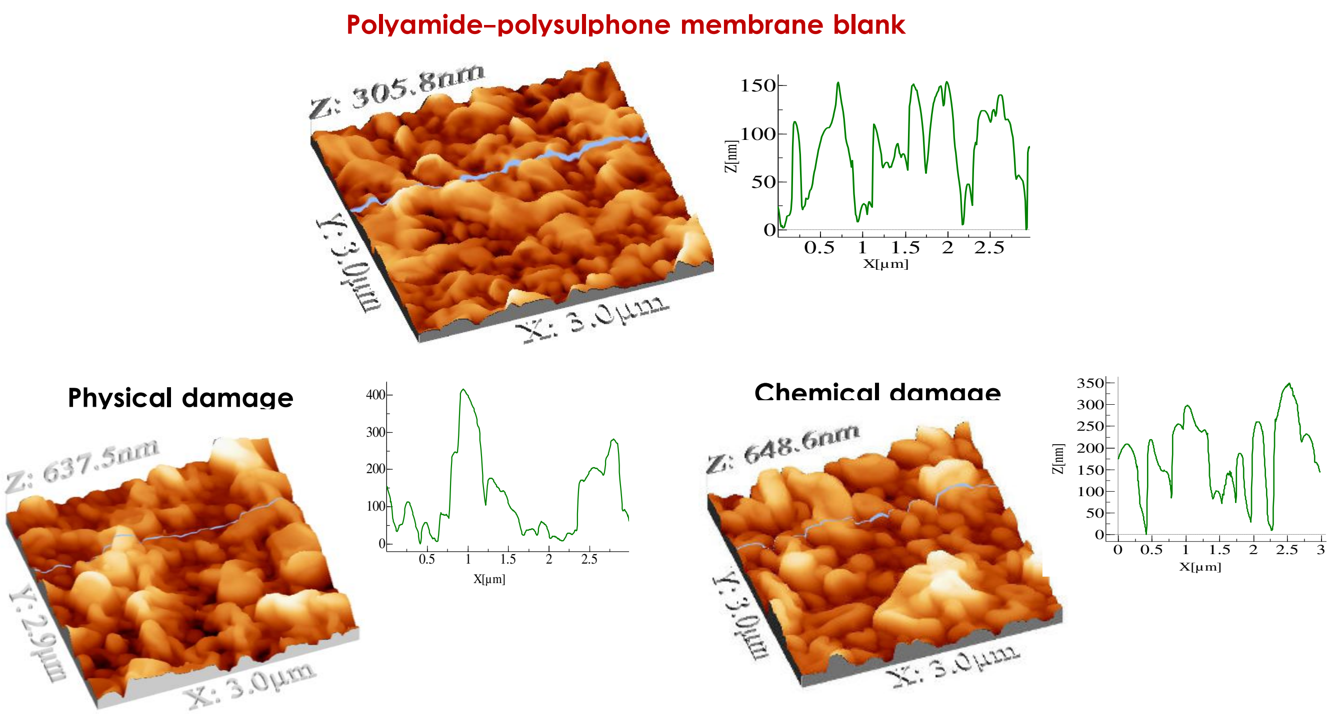


Figure 15. Images and topography of membrane with physical and chemical damage

Zeta-potential

The electrokinetic or zeta-potential is an important parameter of the electrical double layer and represents a characteristic of electrical properties of solid/liquid interfaces [10].

Measurements were carried out with NaCl solutions at different concentrations on the three membranes used as reference for checking during the previous tests for the evaluation of different analytical techniques.

Next figure 16 represents the measurements of zeta potential vs different sodium chloride concentrations. As it can be observed, chemically damaged membrane surface is slightly more electronegative than membrane blank. When the damage is physical, membrane surface shows an opposite effect and lower.

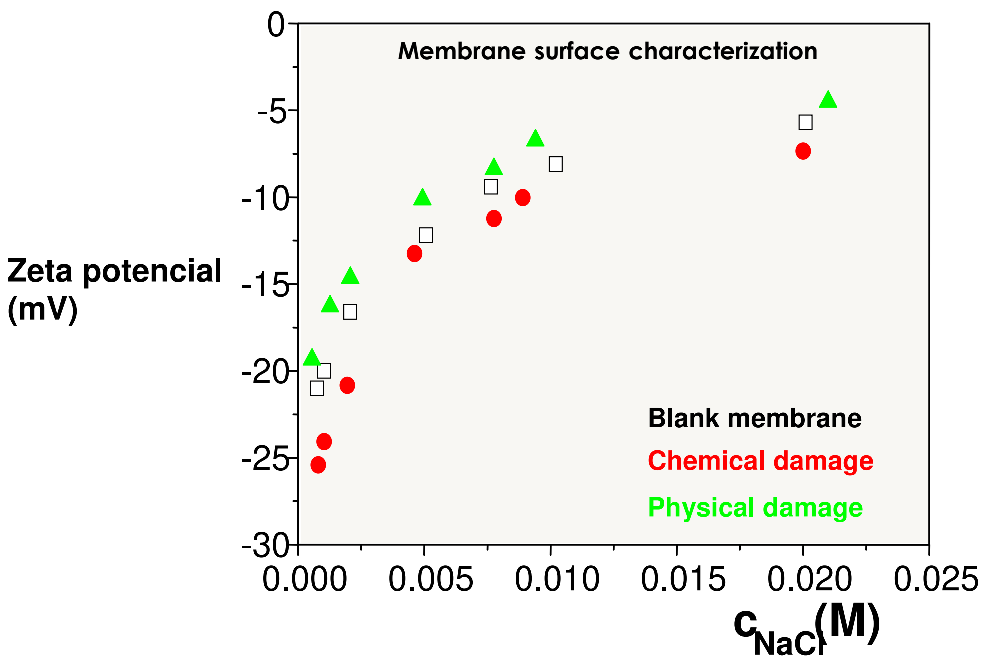


Figure 16. Zeta potential values obtained from membranes with physical and chemical damages

IV. CONCLUSIONS

- Main damages detected on membrane autopsies are physical, due to the presence of fouling.
- In many cases, the presence of this fouling may hide the presence of damage on the membrane and the real reason of membrane performance failure.
- It is necessary to consider different parameters and details from the membrane in study in order to determine the nature of the damage.
- Both physical and chemical damage produce changes on certain characteristics and properties of the membrane surface, which could be used as complementary analytical techniques.

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