RESULTS OF A NEUTRAL PH CLEANER THAT REMOVES COMPLEX FOULING AND METALS FROM MEMBRANES

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Abstract

Fifty years after the commercialisation and widespread use of membranes for water treatment the biggest single unresolved operational issue is fouling. The topic is well researched and the major components of fouling have been identified. There have been fewer studies on complex foulants which contain multiple components including metals. The metals present in the feed water to the membranes come from various sources. They can be dissolved or as a suspension in the originating body of sea water, well water or surface water. Metal impurities can be present as a direct result of chemical addition of coagulants and pH control chemicals and as a by-product of corrosion. Multi component foulants with metals are very difficult to remove and require multiple cleaning procedures at varying pH. The extremes of acid and alkaline conditions can have a detrimental effect on the membrane reducing lifespan and salt rejection.

The authors have conducted over 1200 membrane autopsies in the last decade. The autopsy identifies the nature of foulants and cleaning tests establish the best chemistry and protocols for foulant removal. This paper uses the data collected to demonstrate the detrimental effect of metal foulants on membrane performance and integrity. The effectiveness of cleaning procedures on removing complex multi component foulants containing metals is reviewed. The results of cleaning procedures using a new non-hazardous, pH neutral, organic, non EDTA, chelating cleaner will be presented. The neutral pH cleaner is less aggressive to the membrane and is a significant addition to cleaning pH sensitive cellulose acetate membranes that have strict pH limitations.

I. INTRODUCTION

Membrane fouling is one of the major challenges for an efficient operation of water treatment facilities, including sea water and brackish desalination plants, industrial plants and waste water reuse/tertiary facilities [1,2,3]. Main consequence of fouling phenomena on membrane systems is an increase in operational costs, mainly related to increased energy demand, additional labor for maintenance, chemical cleaning and reductions in membrane life [4].
The different fouling types affecting membrane systems are well known [5]: these include biological fouling, particulate/colloidal matter, inorganic fouling/scaling, and organic fouling,

Although fouling by metals could be included in inorganic fouling category, it is important to distinguish them so as to identify their source and because in some cases they may cause some additional effects on membrane surface.

Elemental metals such as iron and manganese are quite common in water and can oxidize from soluble to insoluble forms within a membrane and precipitate on the surface. In other cases, the presence of metals can be related to operational practices such as the use of iron and aluminum salts when used as coagulants to pretreat RO feedwater. Both ferric chloride and alum are sometimes overdosed and can carry over to post-precipitate and foul a membrane as a suspended solid [6].

There are also water treatment plants involved in industrial and mining processes in which presence of metals in the feed source is very significant.

The presence of metals at the membranes surface is not only important when they are the main fouling component. Both RO and UF membranes commonly show presence of metals as secondary component of fouling and this secondary component is in many cases the cause of poor cleanings by conventional techniques [7]. Additionally, when metallic particles from corrosion deposits (usually iron) from feed system metallurgy reach the membranes they can affect membrane integrity by abrasion.

Apart from the problems related to fouling, the ability of the transition metals such as iron, manganese, copper, zinc, etc. to change the valence states catalyzing and increasing the oxidation potential of oxidizing agents has been reported by several authors [8, 9].

For these reasons an in-depth study of how metals on membranes surface may affect plant performance and how to remove them from membrane surface to recover membranes performance is considered of importance. This study includes data from autopsies with significant presence of metals and covers details as membrane performance, failures, cleaning procedures, etc.

II. RESULTS AND DISCUSSION

II.1. PRESENCE OF METALS ON MEMBRANES SURFACE

Autopsies are the main tool to determinate the cause of a membrane failure, to identify fouling nature and source and to establish if there is any possibility to recover membrane performance. Considering the work done for previous papers presented at international conferences in the past [7, 10], data obtained from autopsied membranes carried out by authors (both RO and UF) were used to verify that the presence of metals as main component of fouling is approximately 10%.

Besides main fouling component, it is also well known that presence of secondary components is very important to obtain a good performance during cleaning procedures. During the mentioned previous studies based on autopsies results, it was demonstrated also that presence of metals is a very common secondary component on RO membranes, mainly when main fouling is organic [7].

For UF membranes, metals appeared also as a common secondary component for each type of main fouling, although it was especially usual when main fouling is composed of aluminosilicates/colloidal matter [10]. In any case, presence of metals on UF membranes shouldn't be observed as a problem but as an effect of these membranes effectivity since they are used to retain this kind of components.

Thus, most of the results related to membrane performance and failures related to metals included at this paper, will be focused on RO membranes which are those suffering a higher effect from metals presence.

Considering the data obtained from the autopsies carried out by the authors, main types of metals detected on RO membranes surface are: iron, aluminium and manganese. Following figure 1 shows the percentage of membranes which showed these and other metals as main component of fouling.

When studying different components of fouling on RO membranes it is important to point out that, apart from main and secondary components, it is very common to detect small presence of metals, especially iron (both as iron oxide particles or as part of aluminosilicates/clays) and also particles from corrosion drags (Fe-Cr-Ni).

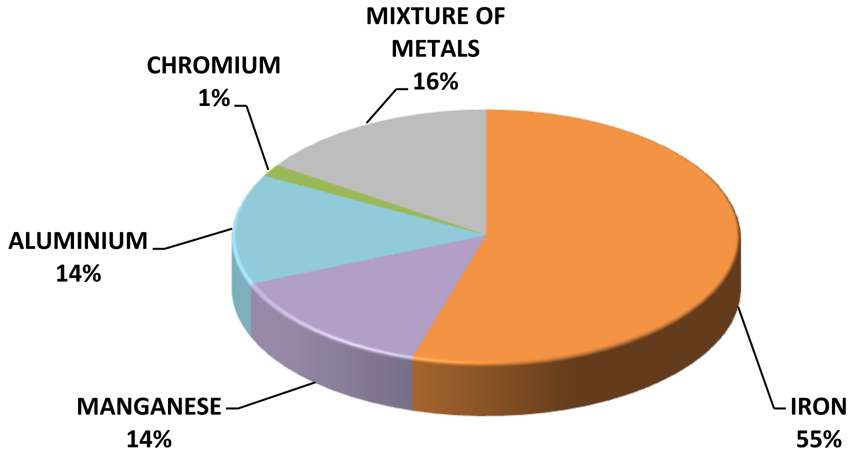


Figure 1.- Main metals detected during autopsies

It is almost impossible to find a fouling only composed of metals but, in any case, they commonly achieve a very characteristic color to fouling. On the other side, metals are very easily detected by analytical techniques like SEM-EDX and they also show some specific characteristics when they are studied by this technique.

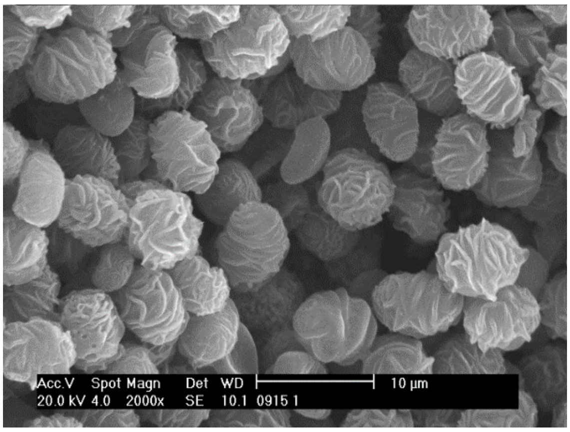
Table 1.- Characteristic of main metals fouling detected during autopsies and SEM-EDX analyses.

	Fouling characteristics - Visual	Fouling characteristics – SEM-EDX
Iron (as oxide)	Dark orange fouling	Amorphous structure It appears completely mixed with the rest of fouling components, although it shows a greater brightness.
Iron (from corrosion drags)	Sometimes particles can be visually detected, showing a dark/black color	They appear as very bright particles. It is commonly detected with chromium and nickel at small percentages.
Aluminium	No specific color	It commonly appears associated to an organic component, so it doesn't show any specific structure or special brightness.
Manganese	Dark brown color	Manganese appears as bright spherical structures.
Other metals	The rest of metals detected during autopsies appear as minor components, so they don't contribute to color.	Commonly they appear as small particles with greater brightness than rest of fouling components.

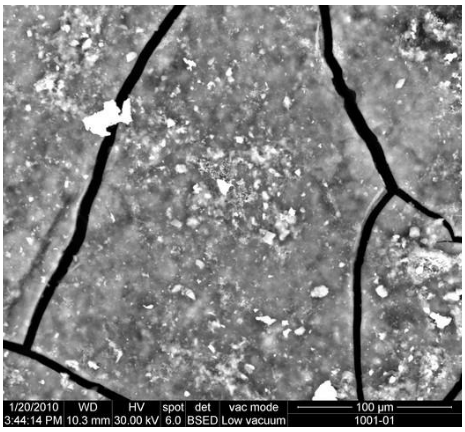
Some examples are included at the following photographs.

Photograph 1.- RO membrane surface with main presence of iron (as iron oxide)

Photograph 2.- Detail of fouling with main presence of iron (iron oxide).
It commonly shows a dark orange color

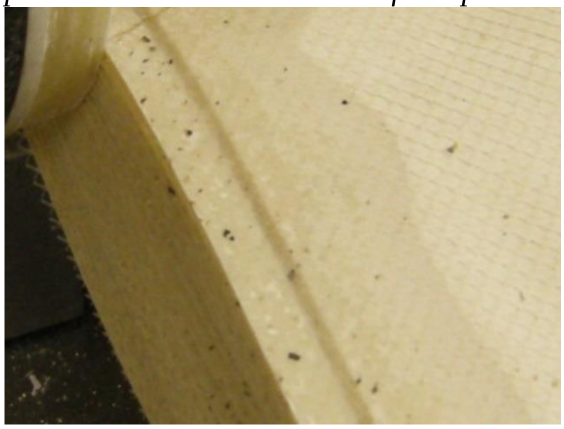


Photograph 3.- Detail of iron particles Granular shape



Photograph 4.- Detail of fouling with iron, which corresponds to the brighter component. Iron commonly appears at SEM as very bright and tiny particles mixed with the rest of components

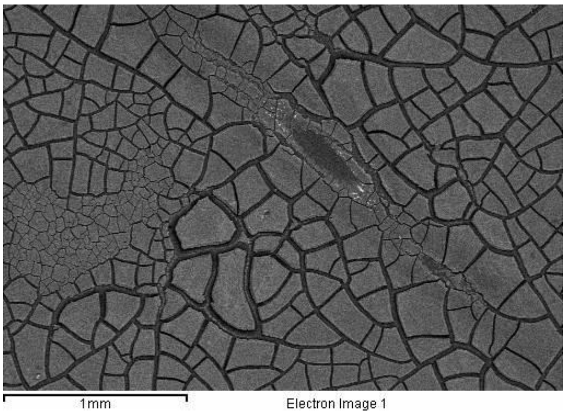
Photograph 5.- Massive presence of corrosion drags at membrane feed end



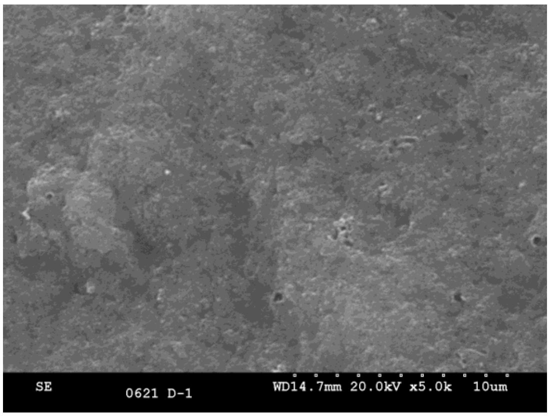
Photograph 6.- Presence of corrosion drags on membrane surface - feed side

Photograph 7.- RO membrane surface with main presence of aluminium. It doesn't show any specific color different than the rest of fouling components.

Photograph 8.- Detail of fouling with main presence of aluminium. It commonly appears mixed with organic matter and shows the color of the mixture.



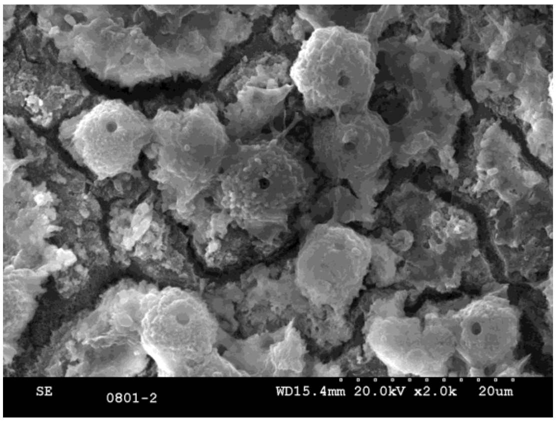
Photograph 9.- Detail of membrane surface with main presence of aluminium fouling. A cracked and thick fouling is characteristic of aluminium fouling.



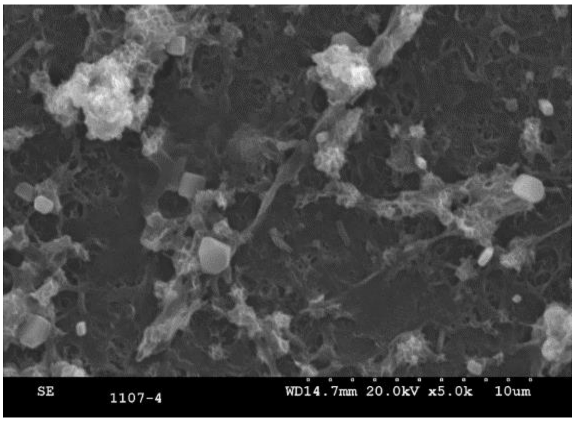
Photograph 10.- Detail of fouling with aluminium. It shows a very unspecific shape since it appears mixed with organic matter. It doesn't show bright intensity as other metals.

Photograph 11.- RO membrane surface with main presence of manganese fouling

Photograph 12.- Detail of fouling with manganese: very dark brown color (MnO_2)

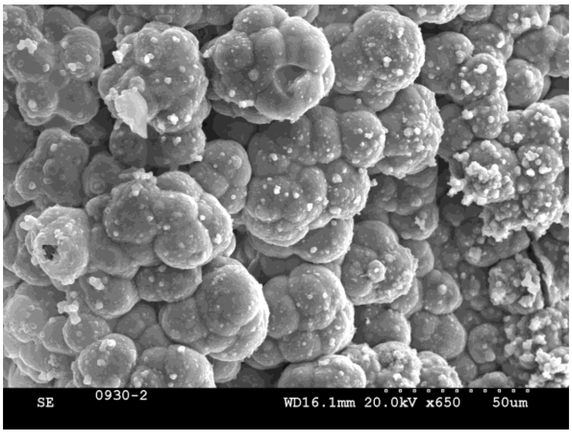


Photograph 13.- Detail of manganese fouling Manganese commonly shows very characteristic spherical structures mixed with the rest of fouling components



Photograph 14.- Detail of membrane surface with manganese fouling. It is common to find manganese structures dispersed on membrane surface.

Photograph 15.- RO membrane surface with presence of chromium: green color



Photograph 16.- Detail of chromium fouling

Fouling by metals is expected on lead elements of 1st stage and it is common to detect a rapid increase in dp, feed pressure and salt passage on membranes. Thus, during the autopsies, it was more common to detect presence of metals as main component at first positions, but they were also detected in the last positions in 27% of the autopsied membranes.

Considering autopsied membranes performance, when there is presence of fouling on RO membranes surface, a lower permeate flux would be expected. But when successful cleaning procedures are not applied in time and membranes keep operating with presence of fouling on the surface, an irreversible damage is commonly produced. Thus, figure 2 shows how during the autopsies included at this study, some membranes showed a permeate flux equal than reference and around a 25% a flux lower than reference, but the 47% of the membranes with a main presence of metals gave a higher flux than reference. This behavior is characteristic of damaged membranes. On the other side, most of the membranes with metals as main component of fouling showed a lower salt rejection than reference (see figure 3).

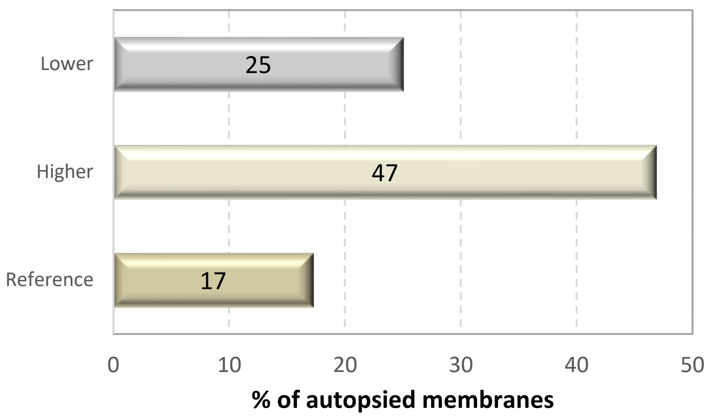


Figure 2.- Permeate flux performance of membranes with metals as main fouling component.

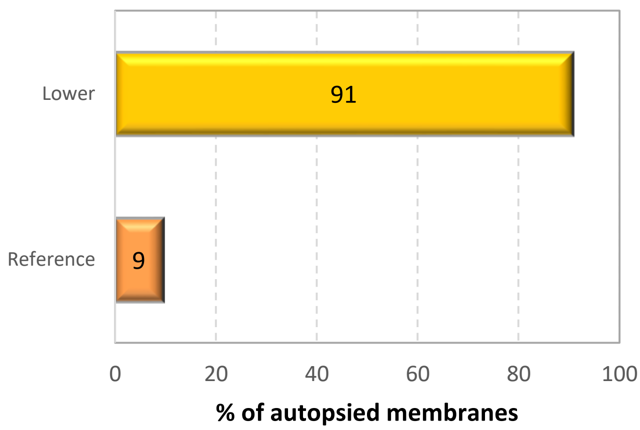


Figure 3.-Salt rejection performance of membranes with metals as main fouling component.

Autopsies are carried out on membranes that already show significant failures in plant but, in any case, these results demonstrate how membranes fouled with metals commonly show damage. Considering the results obtained during autopsies (figure 4), it seems that the observed damage is more related to a physical damage (86% of the membranes) than to chemical damage (23% of the membranes).

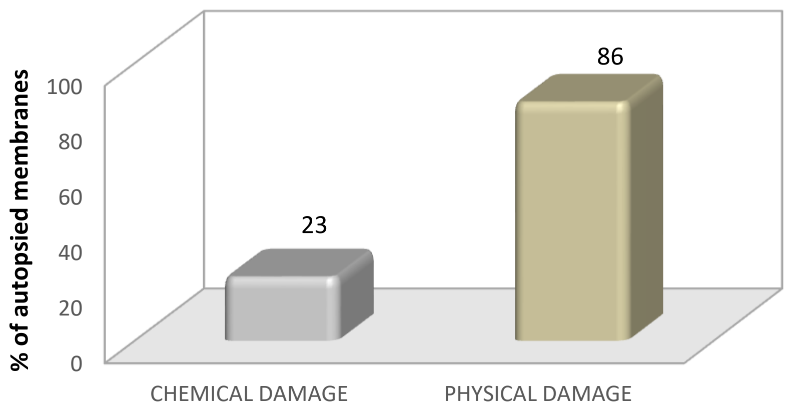
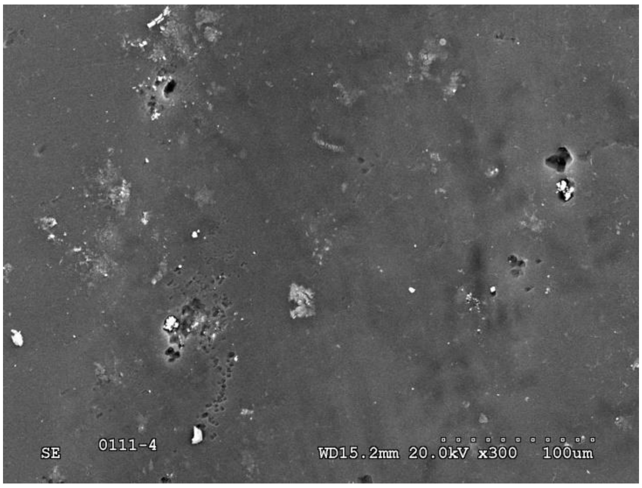


Figure 4.-Damage detected on membranes fouled with metals

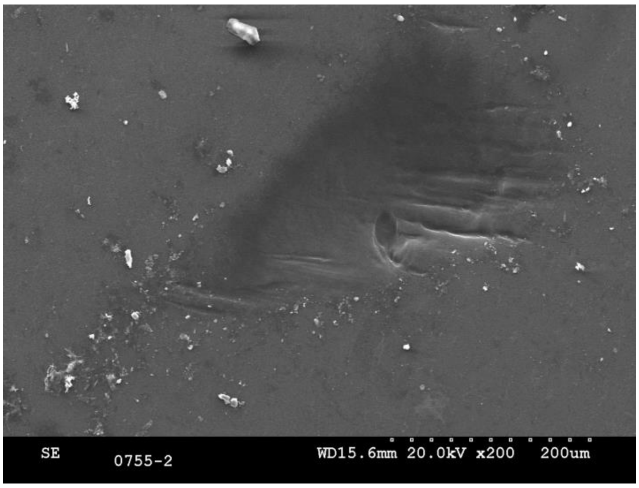
Physical damage on membranes with metals may have different sources. Since it is difficult to find only metal presence, composite nature of fouling will produce different kinds of damage:

- Metals commonly settle on membrane surface as oxides. These deposits combined with other components will produce increases in dp which will mainly produce damage on spacer support areas.
- When metals are present as corrosion drags, they show a sharp shape which will produce significant abrasion marks on membrane surface.

Following photographs show examples of abrasion marks produced by presence of corrosion drags on membranes surface (SEM images).



Photograph 17.- Abrasion marks from corrosion drags on membrane surface



Photograph 18.- Abrasion marks from corrosion drags on membrane surface

On the other side, although only a small percentage of membranes showed oxidation when metals were main components of fouling, it is broadly known that a small content of metals like iron, manganese, copper, etc. may catalyze oxidation reactions on membrane surface [8,9]. During autopsies it is almost impossible to detect if the presence of a metal played some role during an oxidation process, so no experimental data are available from real plants. In any case, the experience from many plants with oxidation episodes in presence of metals makes it necessary to be warned about.

All the reviewed data demonstrate that, even when metals are not the main component of fouling, it is very important to take into account that their presence may produce some irreversible damage on membrane surfaces. Thus, it is indispensable to consider presence of metals for the optimization of plant performance and for establishing a successful cleaning protocol.

II.2. CLEANING PROCEDURES FOR METALS REMOVAL

For metals removal, most membrane manufacturers recommend a cleaning procedure based on acids. Following table include some recommendations from some membrane manufacturers. Cleaning recommendations for UF membranes are very similar.

Table 2.- Cleaning recommendations for metals removal from membranes surface

Membrane manufacturer *	RO membranes Recommended cleaner	UF membranes Recommended cleaner
DOW FILMTEC	1.0% $Na_2S_2O_4$ (pH:5, 30ºC) 2.0% Citric acid 0,5% H_3PO_4 1.0% sulfamic acid	Citric acid, HCl, oxalic acid, sulphuric acid pH= 2
HYDRANAUTICS	2.0% Citric acid 1.0% $Na_2S_2O_4$ (pH: 4-6)	Citric acid or HCl
TORAY	Citric acid 1 – 2 %, adjust with ammonia (NH_3), pH: 2-4	---
LG NANO H_2O	2.0% Citric acid, pH: 2.5-4	---
INGE	---	pH= 1
PENTAIR	---	1% citric acid, 1% oxalic acid, 0,25% ascorbic acid

*Manufacturers technical manuals

These cleaning recommendations would achieve a successful metals removal if they were the only component of fouling. But due to composite nature of fouling on membranes surface, in most of the cases it is necessary to apply different cleaning steps for a complete removal of all the components.

As explained by some membrane manufacturers at their technical manuals, it is recommended to apply alkaline cleaning as the first cleaning step. Acid cleaning should only be applied as the first cleaning step if it is known that only calcium carbonate or iron oxide/hydroxide is present on the membrane elements. This is because acid cleaners typically react with silica, organics (for instance humic acids) and biofilm present on the membrane surface which may cause a further decline of the membrane performance. Sometimes, an alkaline cleaning may restore this decline that was caused by the acid cleaner, but often an extreme cleaning would be necessary.

If the RO system suffers from colloidal, organic fouling or biofouling in combination with calcium carbonate, then a two- step cleaning program will be needed: alkaline cleaning followed by an acid cleaning. The acid cleaning may be performed when the alkaline cleaning has effectively removed the organic fouling, colloidal fouling and biofouling. During multi-step cleaning procedures, and especially during acid cleanings, pH changes sometimes affect salt rejection capabilities and it is necessary to apply a third alkaline step to recover this parameter.

A new neutral cleaner has recently been developed. This product breaks down complex fouling matrices that incorporate organics, biofilm, and clay with metals such as iron, manganese and other transition metals. The chelating effect destabilizes the foulant matrix allowing surfactant and detergents molecules to penetrate the foulant layer and aid removal.
Membrane manufacturers specify strict parameters for membrane cleaning chemicals, pH, temperature and methodology. Extremes of alkaline pH and temperature can result in hydrolysis of the polyamide or cellulose acetate membrane rejection layer. Cellulose acetate membranes are extremely sensitive to pH with general recommendations of between pH 3 and 9 (depending on manufacturer) for cleaning. These limitations of pH and temperature make the removal of complex foulants combining organics, biofilm, clay and metals difficult to remove. Neutral cleaner has been formulated to enhance removal of complex foulants from membranes at pH of 7.0-7.8. This will also limit damage caused to membranes by the repeated use of high & low pH cleaning solutions.

The product comprises three main active components:

1. Complexing Agent Chelant: it dissolves iron oxides and calcium based deposits. The chelating agent forms chemical complexes with metallic ions (Fe, Cu, Al etc) "mobilizing" them from within the foulant layer.

Iron oxides found in natural RO feed waters rarely occur as pure oxides but instead contain significant amounts of other elements, forming Fe-Ca (-C-organic) – rich colloids. In first stage membrane fouling Iron and other metal deposits are not present as a single ion but as a colloidal complex. The action of the chelating component on metallic structures aids removal of complexed organic compounds from the membrane surface.

2. Polymer – when present in the membrane cleaning solution at neutral pH it is an anionic polymer. Side chains of the molecule lose protons and become negatively charged, in addition they become able to absorb and retain water and their structure swells. The compound also has dispersant properties that improves the separation of particles and prevents settling or clumping on the membrane surface during the soak phase, this action keeps removed foulants in the bulk CIP liquid. This negatively charged molecule also helps repel negatively charged organic foulants keeping them mobile.

The combination of water absorbance and dispersive properties aids chemical penetration into the foulant layer, once inside the deposits the molecule absorbs water and swells significantly which further disrupts the foulant and prevents reformation on the membrane surface.

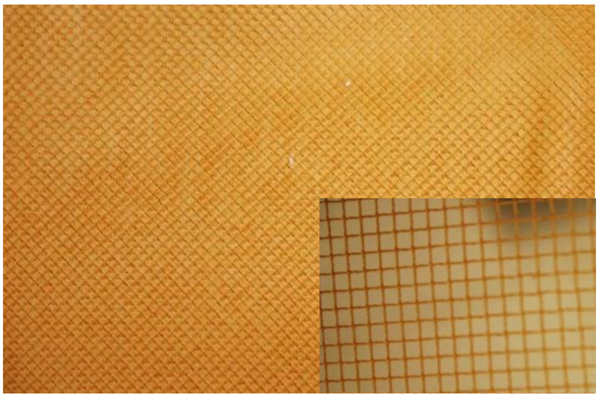
3. Reducing Agent: the main function of this component is to reduce ferric Fe^{3+} to ferrous Fe^{2+}, this soluble iron can then be removed in the bulk CIP liquid preventing refouling on the membrane surface.

The features of this cleaner make it very suitable for metals removal. Then, in order to test the efficiency of this Neutral cleaner for metals removal, RO membranes fouled with the three main metals detected during autopsies (iron, aluminium and manganese) were chosen. During these studies, performance of the cleaner was compared to acid cleaners and also to procedures based on alkaline-Neutral cleaner and conventional cleanings based on alkaline-acid-alkaline steps.
To check neutral cleaner efficiency, permeate flux and salt rejection were tested at the flat test rig. Besides, SEM-EDX analyses were carried out before and after cleaning procedures. As complement to conventional analysis mapping images were carried out in order to identify better presence/absence of the studied metal.

II.2.1. Cleanings on RO membranes

II.2.1.1. Iron fouling

Following photographs show a general view of a membrane surface with a main presence of iron as iron oxide. As usual, not only iron was detected on this membrane and presence of aluminosilicates/colloidal matter was identified also (see EDX spectrum at figure 5).
As it can be observed, membrane shows characteristic orange color, which was impregnating also spacer material.



Photograph 19.- General view of membrane surface and spacer material with iron

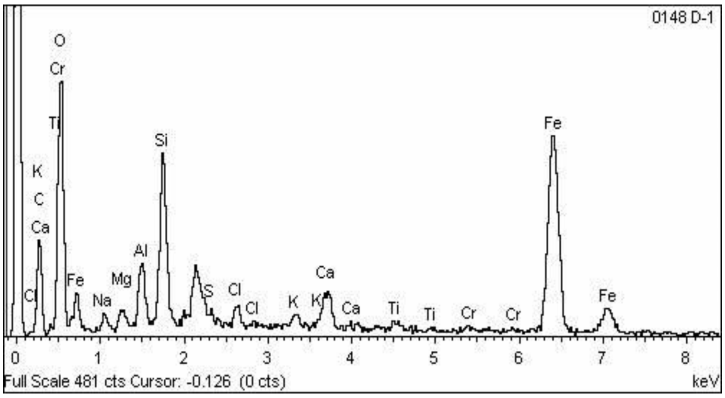


Figure 5. EDX results obtained from iron membrane fouling.

In order to check the removal of iron, some cleaning tests were carried out with membrane coupons on a flat test rig. For these tests, procedures recommended by membranes manufacturers were compared to neutral cleaner performance working at similar conditions.
Figure 6 corresponds to the graphical representation of permeate flux improvement percentage, which is directly related to fouling removal. Presence of aluminosilicates on membrane surface made it quite difficult to obtain a significant removal of iron but, in any case, they demonstrate that the neutral cleaner achieves a significant permeate flux increase and that it can be compared to other conventional cleaners performance which work at lower pH values.

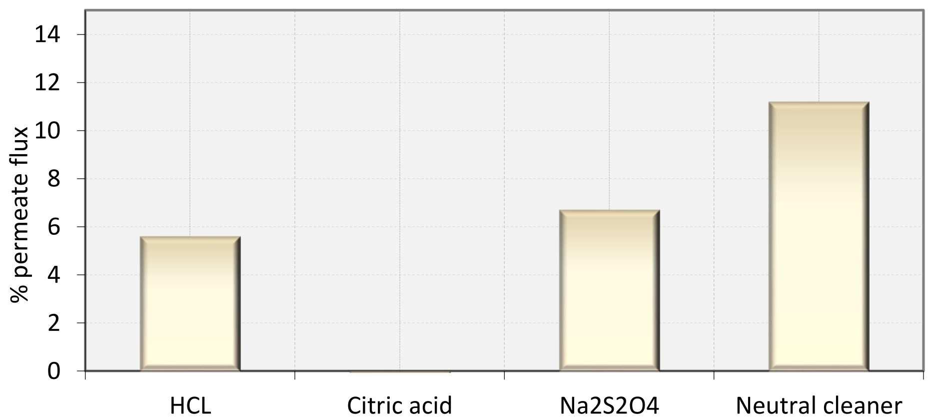
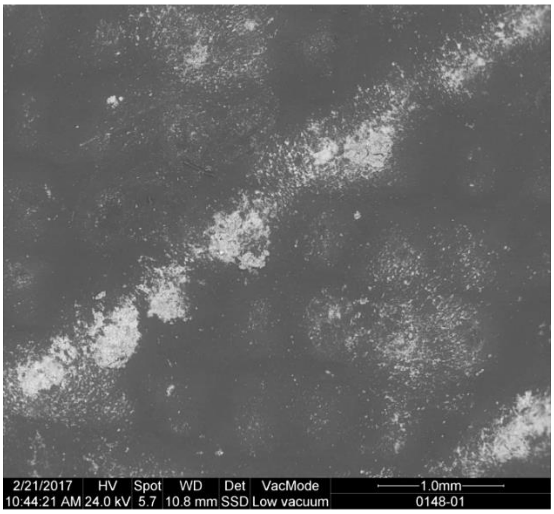


Figure 6. Permeate flux improvement percentage obtained during cleaning tests for iron removal.

As complement to these tests, some SEM-EDX were carried out on the membrane coupons obtained after cleaning with HCl and neutral cleaner. During these analyses a mapping in red color was applied to check iron distribution on membrane surface (figures 7 to 9).
These results indicate that neutral cleaner can be as effective for iron removal as a strong acid cleaner at low pH.



Photograph 20. Fouling composed of iron and aluminosilicates was concentrated on spacer support areas of membrane surface.

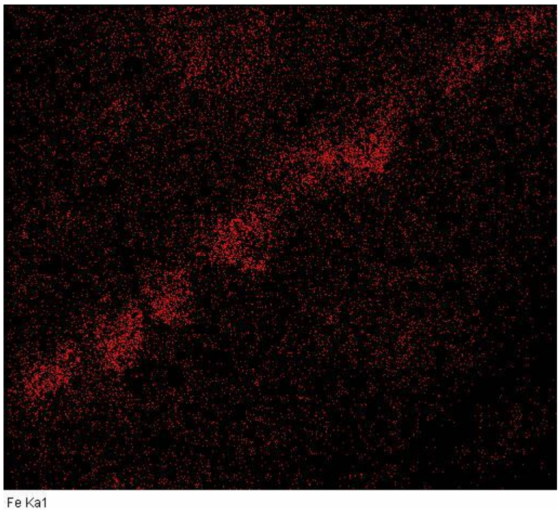


Figure 7. Distribution of iron on membrane surface

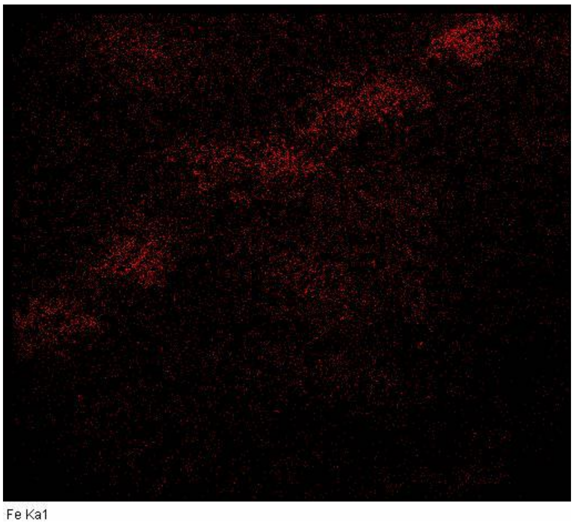


Figure 8. Distribution of iron after cleaning with HCl (strong acid)

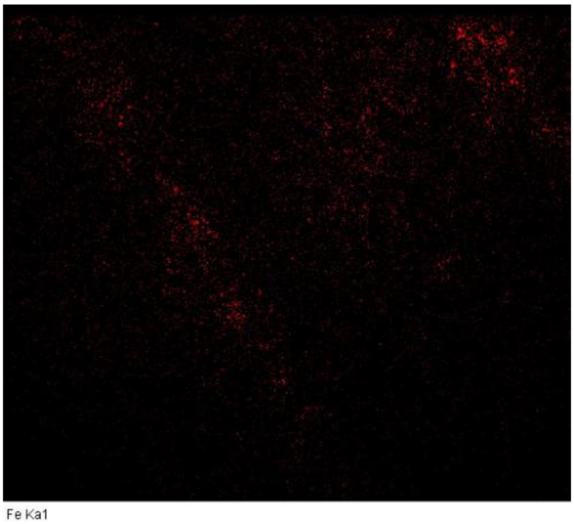


Figure 9. Distribution of iron after cleaning with neutral cleaner

II.2.1.2. Aluminium fouling

For this study, chosen membrane was from a pilot plant with dosing of a coagulant based in aluminium. Following photograph shows a general view of this membrane surface, which showed a significant presence of fouling composed of biofilm (56.6%) and around a 24% of the inorganic component as aluminium. Besides, presence of aluminosilicates and small percentages of other elements were detected also (see EDX spectrum at figure 10).

Photograph 21.- General view of membrane surface with significant presence aluminium

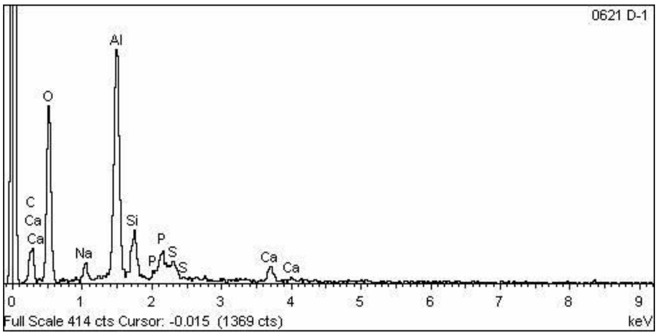


Figure 10. EDX results obtained from aluminium membrane fouling.

As for the previous example, some cleaning tests were carried out with membrane coupons on a flat test rig. Since aluminium commonly appears with organic matter/biofilm, for these tests a wider range of chemicals was tested.

Following figure 11 includes the results obtained during these tests. As it can be observed, permeate flux improvement was higher for alkaline cleaners and Neutral cleaner achieved also a higher permeate improvement than acid cleaners. Photographs 23 and 24 correspond to membrane coupons obtained after a three step cleaning (alkaline-acid-alkaline) and two step cleaning procedure (alkaline-neutral cleaner) respectively. As it can be observed, both membrane coupons show a significant fouling removal.

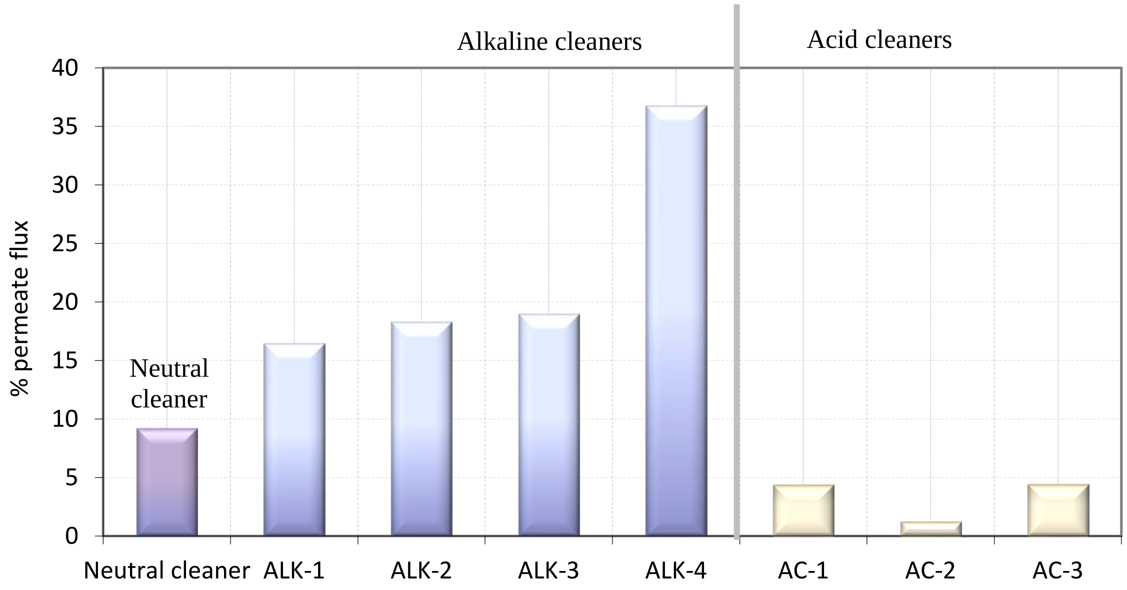
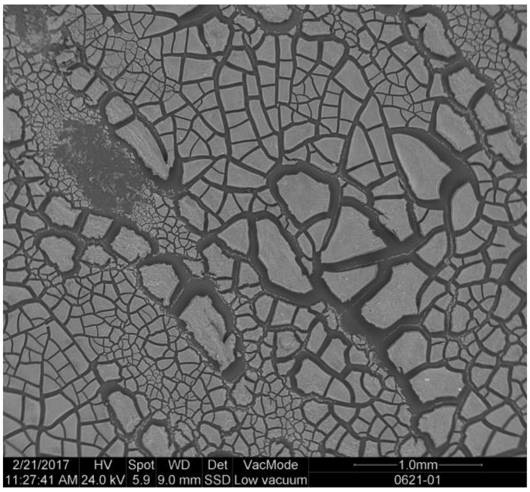


Figure 11. Permeate flux improvement percentage obtained during cleaning tests for aluminium removal

As for the previous sample, additional SEM-EDX analyses were carried out on the membrane coupons obtained after cleaning with neutral cleaner and with the recommended acid. During these analyses a mapping in pink color was applied to check aluminium distribution on membrane surface (figures 11 to 13). As it can be observed, a higher removal of aluminium was achieved with neutral cleaner than with the acid.



Photograph 22. General view of fouling on membrane surface

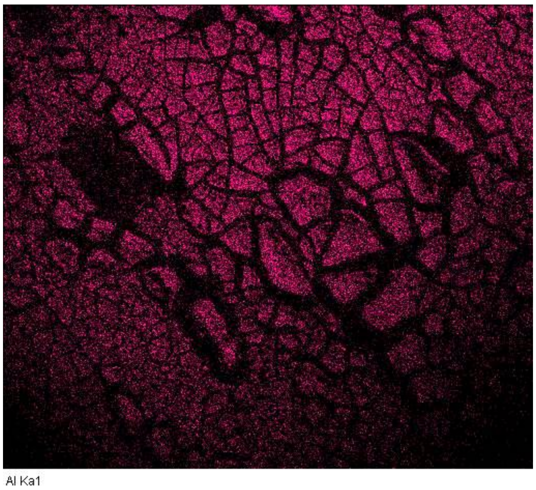


Figure 11. Distribution of aluminium on membrane surface

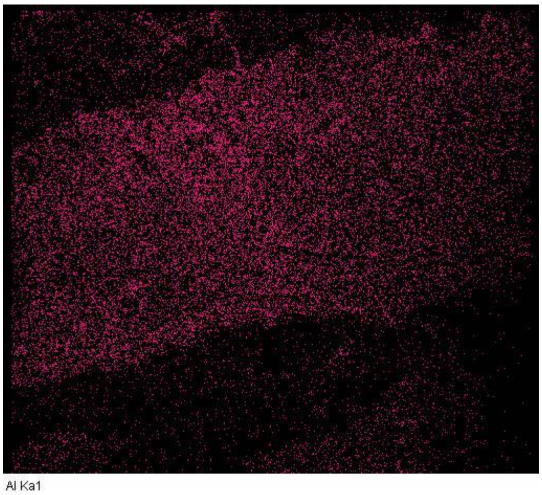


Figure 12. Distribution of aluminium on membrane surface after cleaning with AC-3 (mild acid)

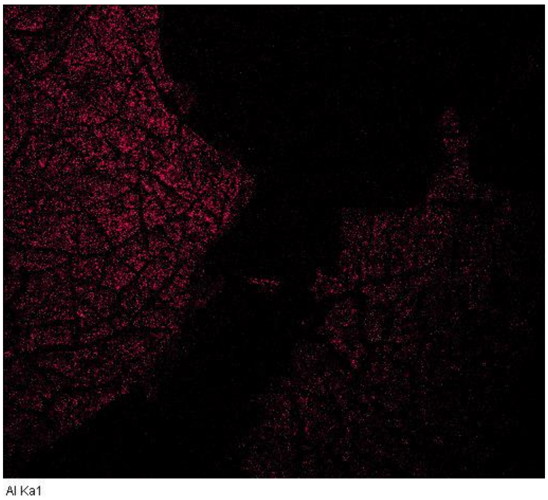
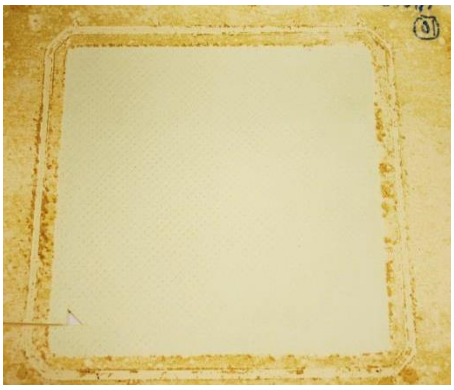


Figure 13. Distribution of aluminium on membrane surface after cleaning with neutral cleaner

Photograph 23.- Membrane coupon after three steps cleaning (alkaline-acid-alkaline)



Photograph 24.- Membrane coupon after two steps cleaning (alkaline-neutral cleaner)

II.2.1.3. Manganese fouling

Following photograph 25 shows a detail of the membrane surface chosen for manganese removal study. This membrane showed presence of fouling composed of biofilm (41,2%) and main presence of sodium chloride and manganese were detected at the inorganic component (see EDX spectrum at figure 14).

Photograph 25.- General view of membrane surface with presence of manganese

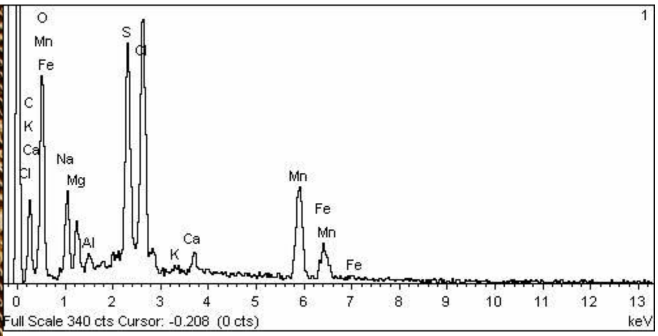


Figure 14. EDX results obtained from manganese membrane fouling.

Again, some cleaning tests were carried out with membrane coupons on a flat test rig. Since on this membrane manganese appeared also with organic matter/biofilm, both alkaline and the most suitable acid chemical were tested.

Following figure 15 includes the results obtained during these tests. As it can be observed, permeate flux improvement was higher again for alkaline cleaners and neutral cleaner achieved also a higher permeate improvement than acid cleaner. Photographs 27 and 28 correspond to membrane coupons obtained after a three step cleaning (alkaline-acid-alkaline) and two step cleaning procedure (alkaline-neutral cleaner) respectively. As it can be observed, both membrane coupons show also a significant fouling removal.

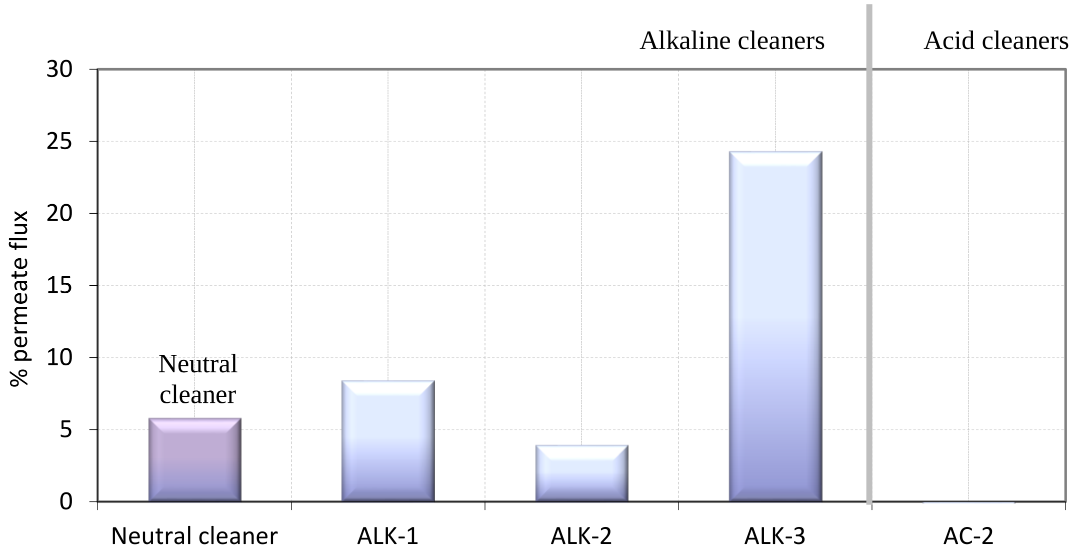
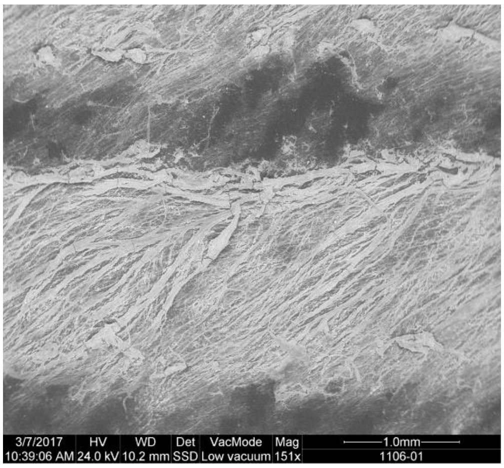


Figure 15. Permeate flux improvement percentage obtained during cleaning tests for manganese removal

As for the previous samples, additional SEM-EDX analyses were carried out on the membrane coupons obtained after cleaning with neutral cleaner and with the recommended acid. During these analyses a mapping in orange color was applied to check manganese distribution on membrane surface (figures 16 to 18). As it can be observed, a quite similar removal of manganese was achieved with neutral cleaner than with the acid.



Photograph 26. General view of fouling on membrane surface

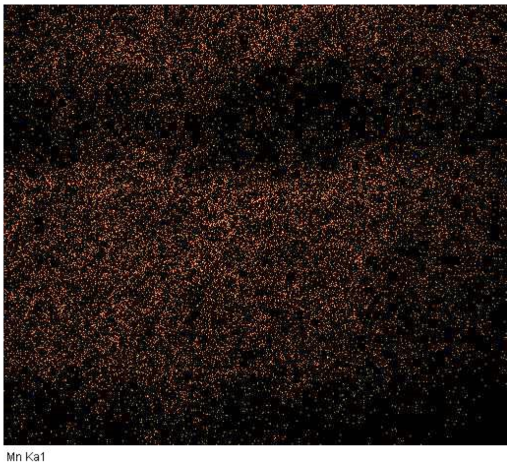


Figure 16. Distribution of manganese on membrane surface

Figure 17. Distribution of manganese on membrane surface after cleaning with AC-2 (mild acid)

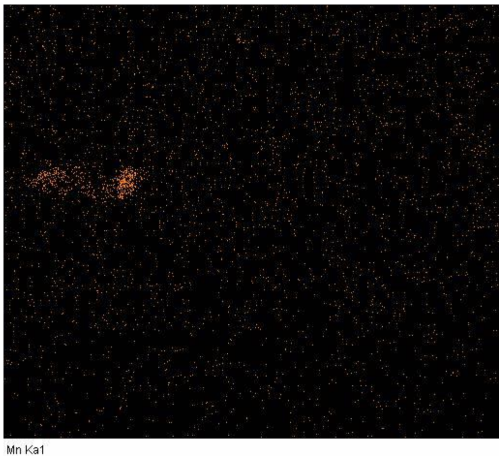


Figure 18. Distribution of manganese on membrane surface after cleaning with neutral cleaner

Photograph 27.- Membrane coupon after three steps cleaning (alkaline-acid-alkaline)

Photograph 28.- Membrane coupon after two steps cleaning (alkaline-neutral cleaner)

The results obtained during the tests carried out in our lab to check neutral cleaner efficiency for metals removal have demonstrated that it shows better performance than acids in terms of permeate flux improvement and similar metals removal.

Besides these parameters, some tests were carried out on full elements to check the effect of neutral cleaner in dp.
These tests were carried out on a plant with following characteristics and observed failures:

- 7,000m^3/day 2 stage BWRO (7 skids)
- 1st stage older membranes (5 years) – dP 3.5 bar after high pH cleaning
- ALK-4 (alkaline cleaner & Biocide) reduced dP to 3.5 – 3.4 bar at 1st stage.
- AC-1 (acid cleaner) didn't reduce dp at 2nd stage
- In 3-4 weeks of operation dp increased to 4 bar

Foulant: Combination of Iron/Manganese and Organics/Biofilm

Following graphs show the changes observed in dp on this plant stages. As figures 19 and 20 show how Neutral cleaner achieved a dp decrease that it wasn't reached with ALK-4 or AC-1 at the stages where they were applied.

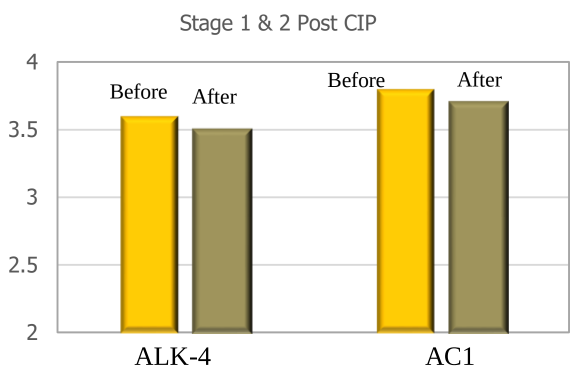


Figure 19.- Changes observed in dp after cleaning with ALK4 (stage 1) and AC-1 (stage 2)

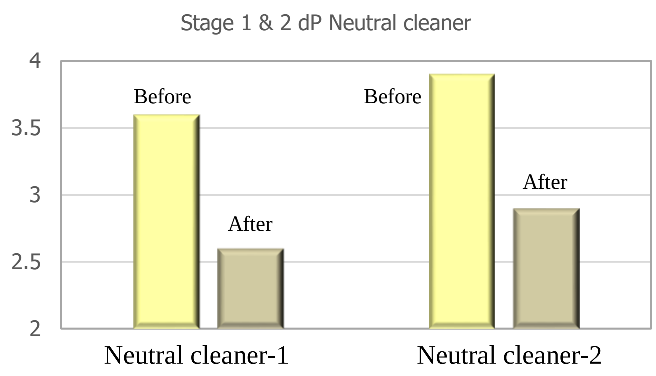


Figure 20.- Changes observed in dp after cleaning with neutral cleaner at stage 1 and 2

II.2.2. UF membranes cleaning

Besides RO membranes, UF autopsies have shown that Neutral cleaner is also a very suitable cleaner for UF membranes.

II.2.2.1. PVDF membrane

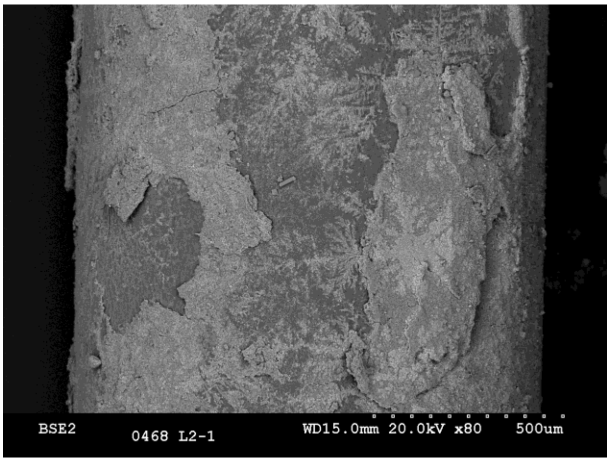
Flow path: Outside-in. This membrane was used to treat sea water.

Following photographs show how hollow fiber membrane surface showed a heterogeneous covering of fibers length by fouling.

Fibers from this membrane showed presence of an organic covering composed of protein derivatives related to organic matter/biofilm, with iron, aluminosilicates and magnesium and calcium compounds (calcium sulphate). When cleaning tests were carried out on these fibers, results showed that best fouling removal was observed with an acid cleaner (AC-2=photograph 32).

Photograph 29.- General view of PVDF module

Photograph 30.- Detail of PVDF fibers



Photograph 31.- General view of fouling on PVDF fiber on external surface

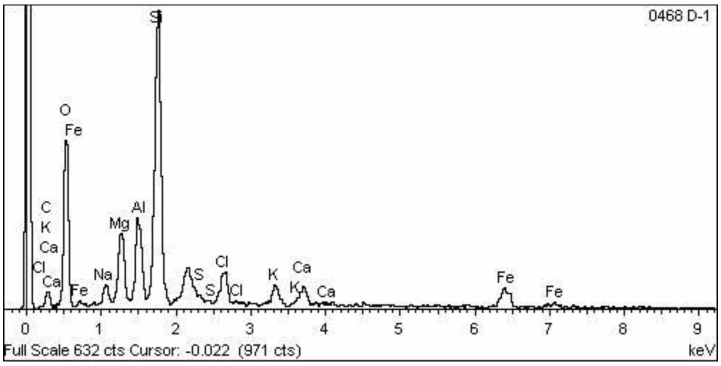


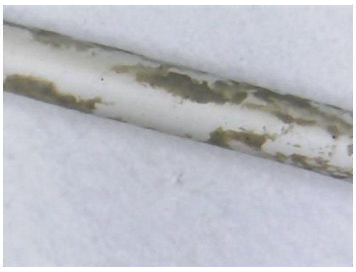
Figure 21. EDX results obtained from PVDF fiber fouling

End 2 surface after ALK-4

End 2 surface after ALK-3

End 2 surface after ALK-1

End 2 surface after **Neutral cleaner**



End 2 surface after NaOCl

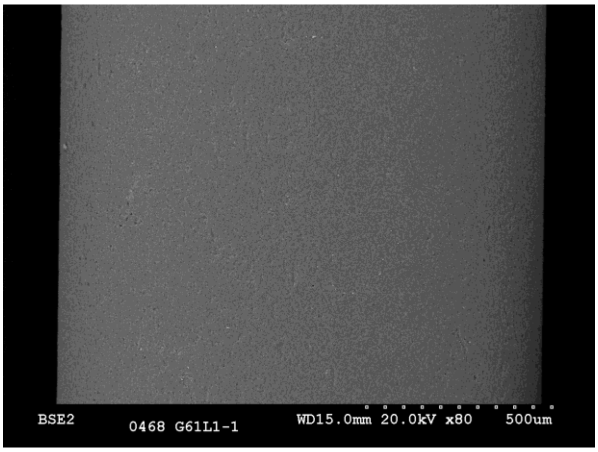
End 2 surface after NaOH

End 2 surface after AC-1

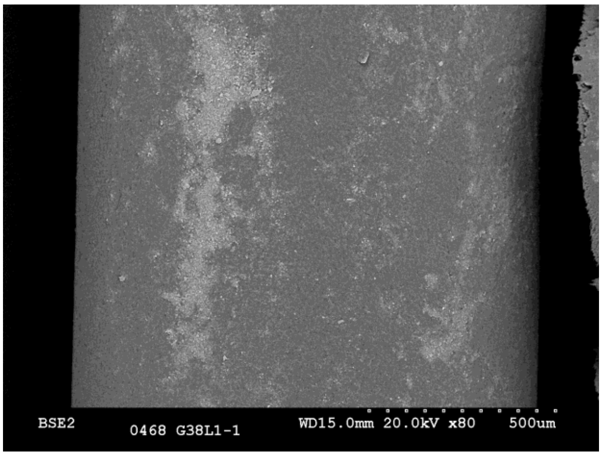
End 2 surface after AC-2

End 2 surface after citric acid

Photograph 32.- Cleaning tests carried out on PVDF fibers



Photograph 33.- Detail of PVDF fiber after cleaning with neutral cleaner



Photograph 34.- Detail of PVDF fiber after cleaning with AC-2 (acid cleaner)

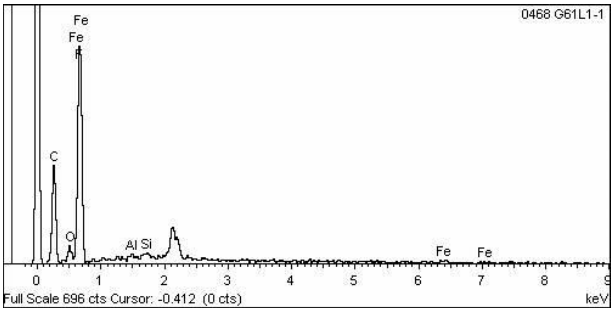


Figure 22. EDX results obtained from PVDF fiber after cleaning with neutral cleaner

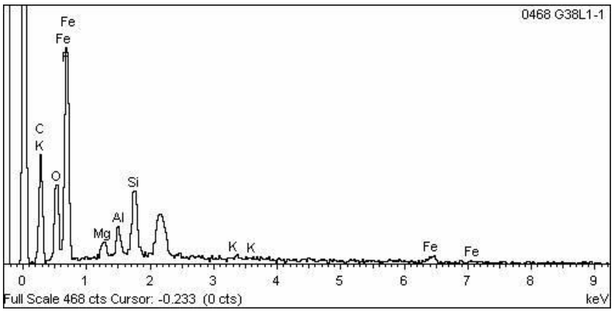


Figure 23. EDX results obtained from PVDF fiber after cleaning with AC-2

II.2.2.2. PES membrane

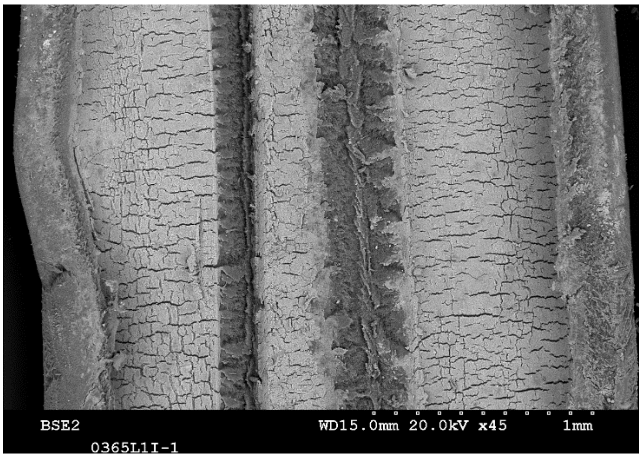
Flow path: Inside-out. This membrane was used also to treat sea water.

Following photographs show the fibers that compose this module. As it can be expected from UF fibers with inside-out flow path, main presence of fouling was observed on the internal surface of fibers. This fouling was mainly composed of an organic component (biofilm), sodium chloride, iron, phosphorus-zinc, calcium-magnesium and small percentages of other elements which could not be related.

In this case, cleaning tests showed the best removal of fouling with ALK-1 and neutral cleaner (see photographs 38, 39 and 40). Besides the results obtained by SEM-EDX, during this study it was possible to check fibers permeability and as figure 27 shows, best flux increase was obtained also with neutral cleaner.

Photograph 35.- General view of PES module

Photograph 36.- Detail of PES fibers (external and internal surfaces)



Photograph 37.- General view of fouling on PES fiber-internal surface

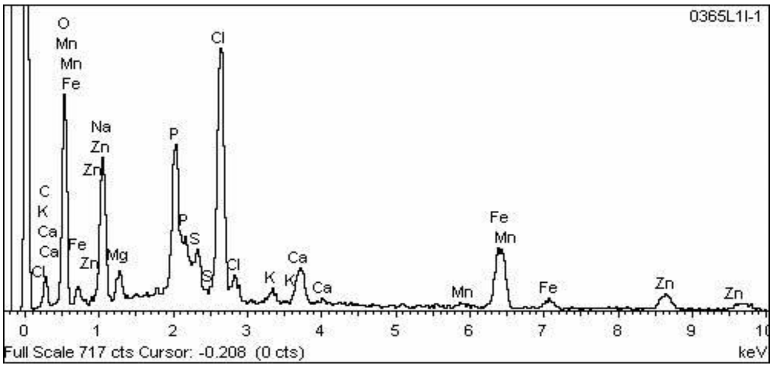
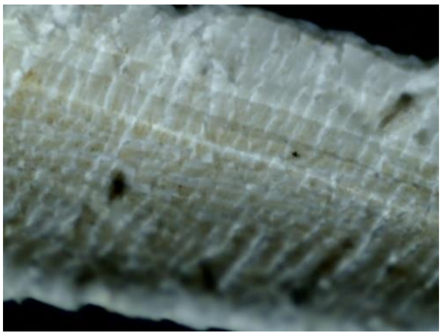
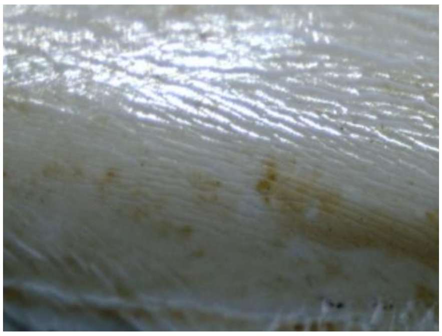
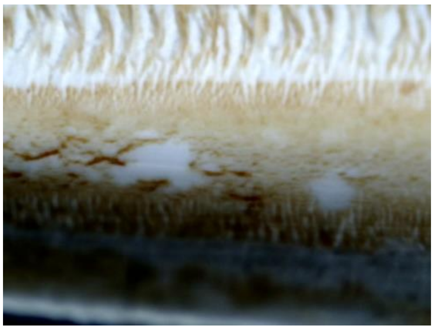


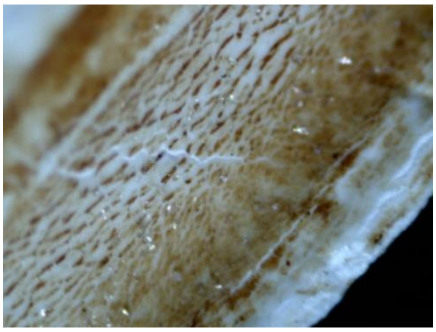
Figure 24. EDX results obtained from PES fiber fouling


PES internal Surface after cleaning with ALK-2

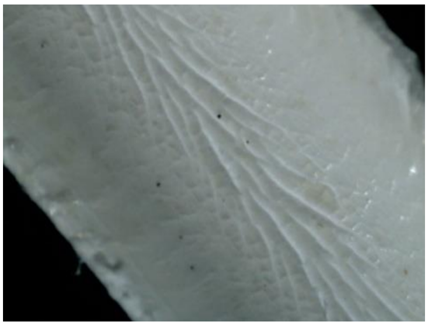

PES internal Surface after cleaning with ALK-1

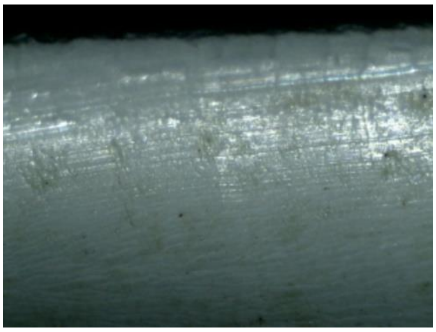

PES internal Surface after cleaning with ALK-3


PES internal Surface after cleaning with ALK-4


PES internal Surface after cleaning with NaOH

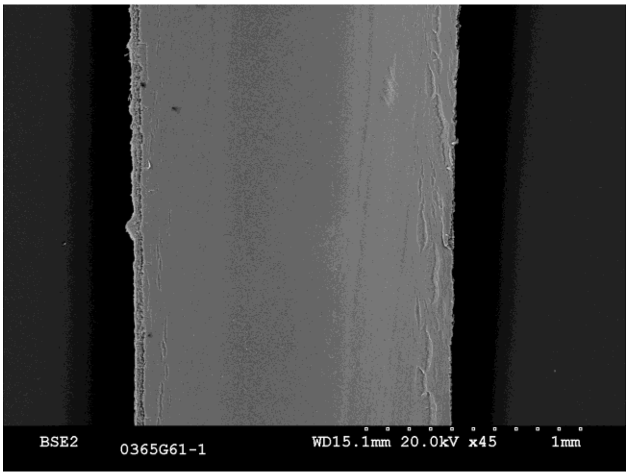

PES internal Surface after cleaning with **Neutral cleaner**


PES internal Surface after cleaning with AC-1

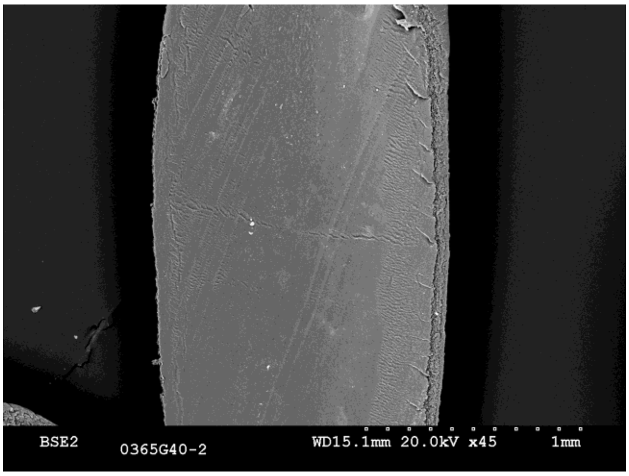

PES internal Surface after cleaning with AC-2


PES internal Surface after cleaning with AC-3

Photograph 38.- Cleaning tests carried out on PES fibers



Photograph 39.- Detail of PES fiber after cleaning with neutral cleaner



Photograph 40.- Detail of PES fiber after cleaning with ALK-1 (alkaline cleaner)

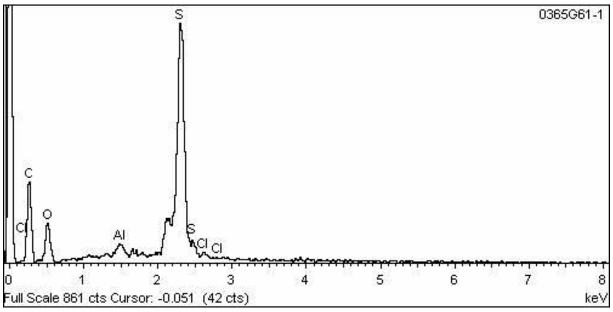


Figure 25. EDX results obtained from PES fiber after cleaning with neutral cleaner

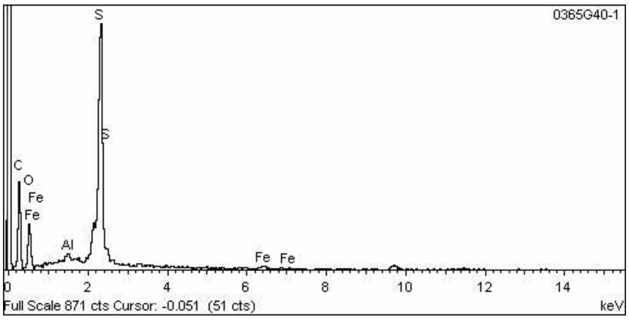


Figure 26. EDX results obtained from PES fiber after cleaning with ALK-1

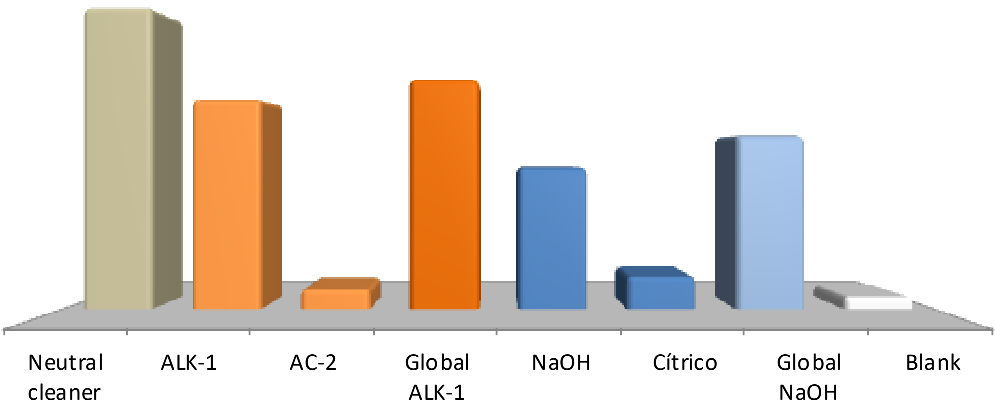


Figure 27.- Percentage flux increase obtained during cleaning tests carried out with PES fibers

CONCLUSIONS

- Presence of metals is very common on membrane surface after water treatment.
- Most common metals detected during autopsies are iron, manganese and aluminium.
- It is very common also that membranes with metal fouling are damaged, mostly due to a physical abrasion.
- The presence of metals on membranes surfaces, like other foulants, can affect membrane performance (low permeate flux and salt rejection). However, since they also commonly show physical damage, different performance results are expected.
- It is almost impossible to find a pure fouling of a single chemical component on a membrane surface and it is important to apply a suitable cleaning procedure which can remove as many fouling components as possible.
- The use of neutral multicomponent cleaners can be a suitable alternative to acid cleaners for metals fouling removal from both RO and UF membranes of different composition.
- The use of mild chemicals during membranes cleaning procedures will preserve membrane integrity for longer and it will be environmentally friendly.

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