MEMBRANE CLEANING PROCEDURES: PERFORMANCE OF COMMODITIES VS FORMULATED CLEANERS

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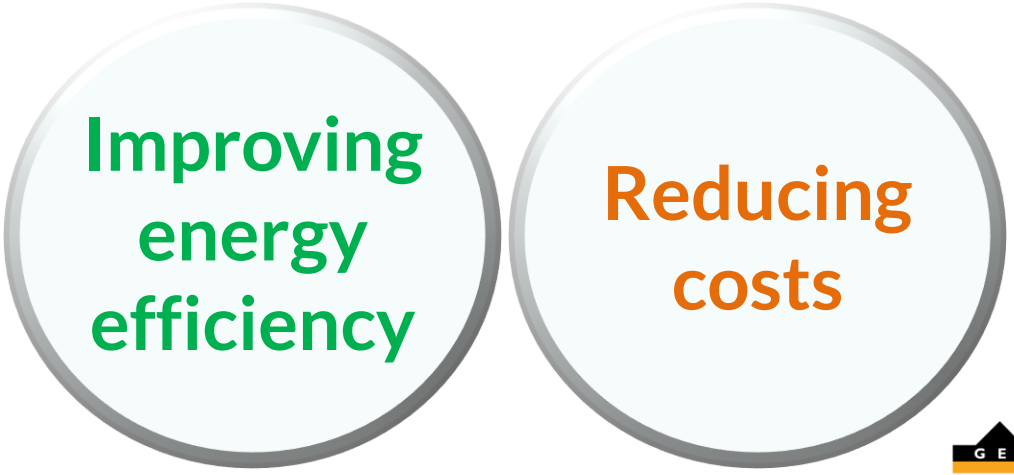
Development of membranes technology:

- ✓ Recovery of energy.
- ✓ New materials
- ✓ New membranes morphologies



FOULANT

Energy consumption
Affects plant efficiency

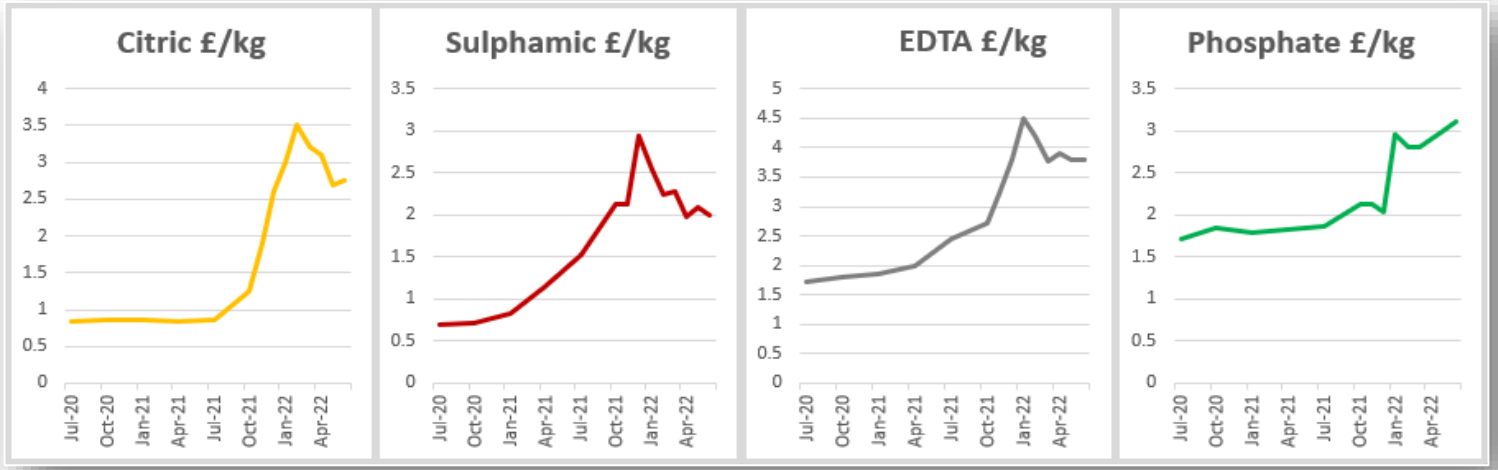
Cleaning procedures must be applied to restore membrane performance.

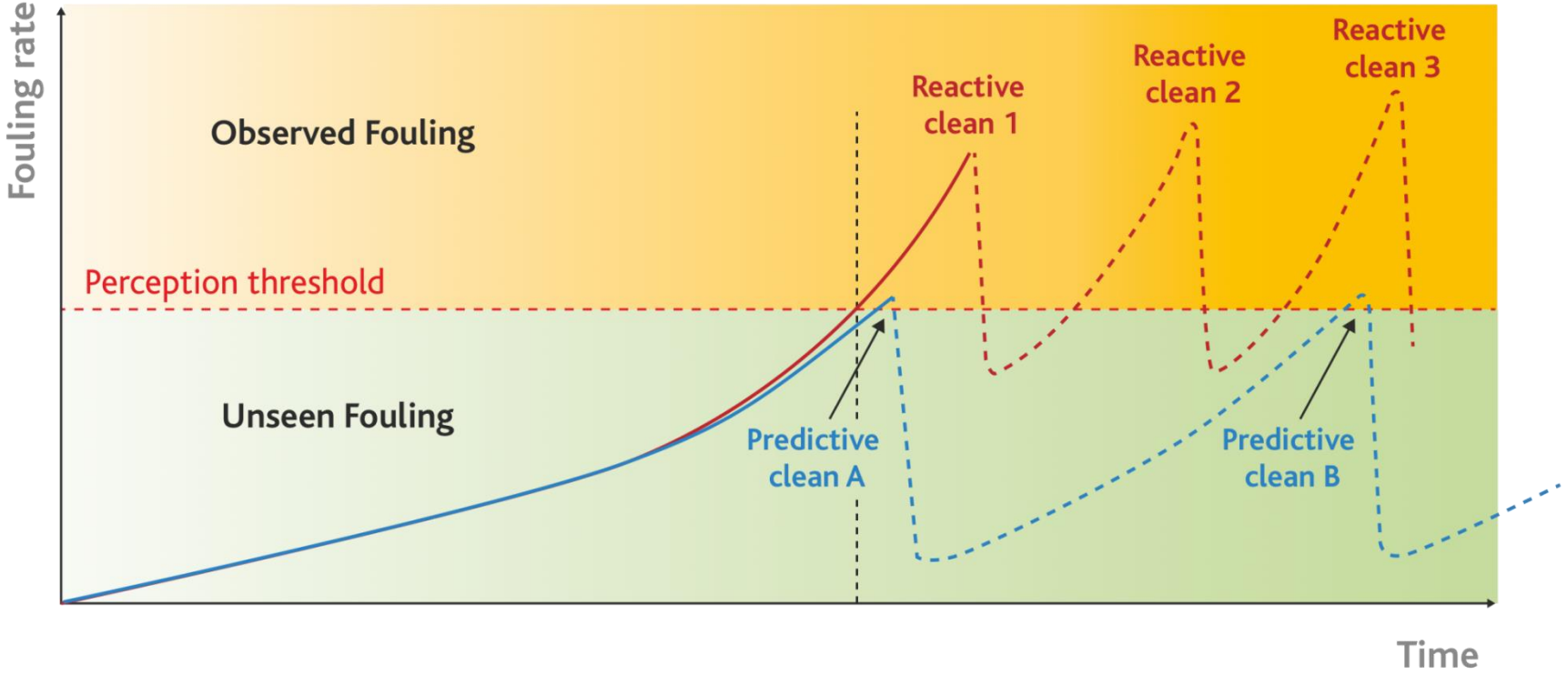
- Commodity cleaners
- Formulated cleaners

Commodity cleaners

- Some commodity chemical raw material prices have more than tripled in price since different factors have affected global supply chains.

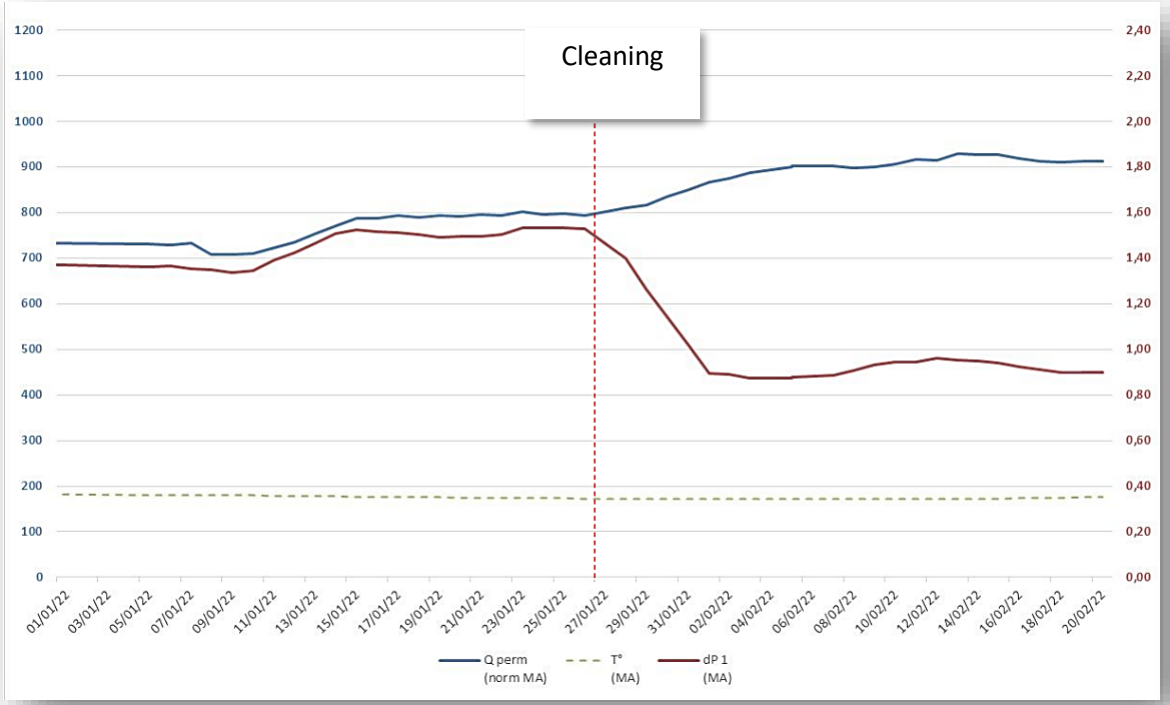
Price increases in Pounds/kg for very basic commodity chemicals that have had stable prices for years.





- ⇨ Preventive cleanings will preserve membrane integrity and reduce membrane replacement frequency,
- ⇨ Effective cleanings will decrease cleaning frequency

Energy saving



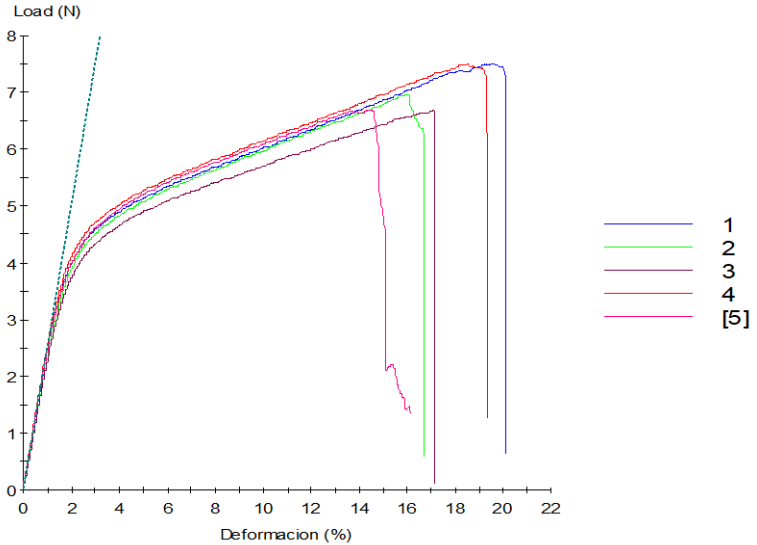
	Before CIP	After CIP	%
Normalized permeate Flow, m^3/h	794	893	+12,5
dp, bar	1,51	0,96	-36,4
Feed pressure, bar	67,0	63,0	

Electricity consumption -6,0% per m^3 of permeate produced

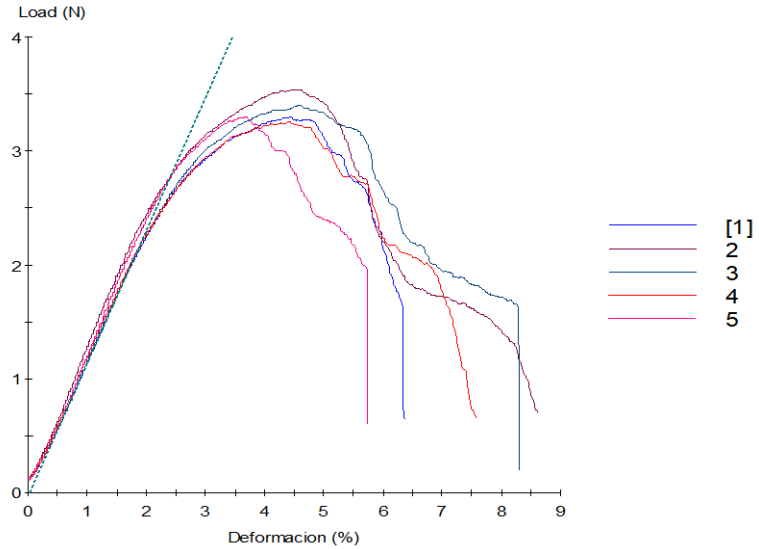
Chemical damage – Aggressive chemicals

- ⇨ Always use **membrane compatible chemicals**
- ⇨ Check manufacturer's cleaning guidelines (pH, Temp.,…)

Tensile test curves of RO membrane reference



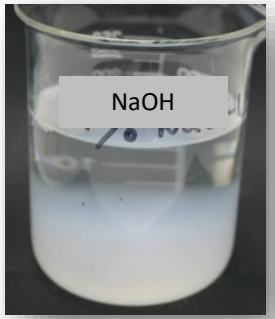
Tensile test curves of RO membrane after NaOH cleaning (aggressive conditions)

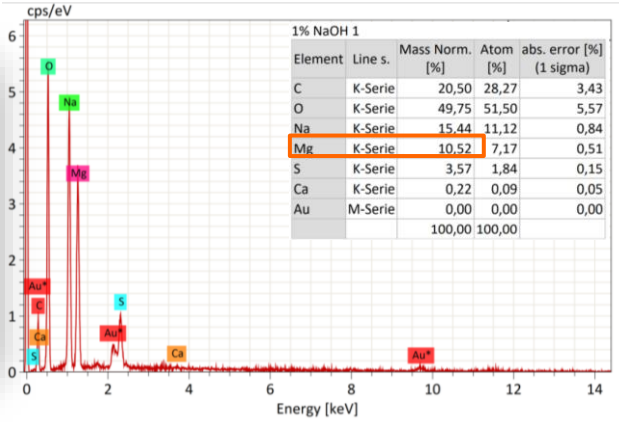


Chemical issues

⇨ Increases in pH may produce secondary problems that are atenuated when buffered products are used.

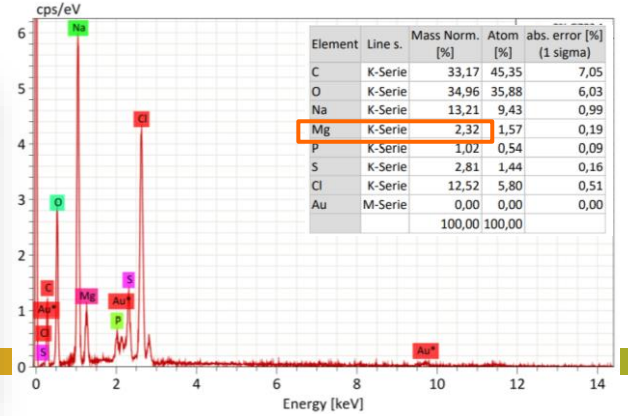
NaOH 0,5% + 500 ppm Mg



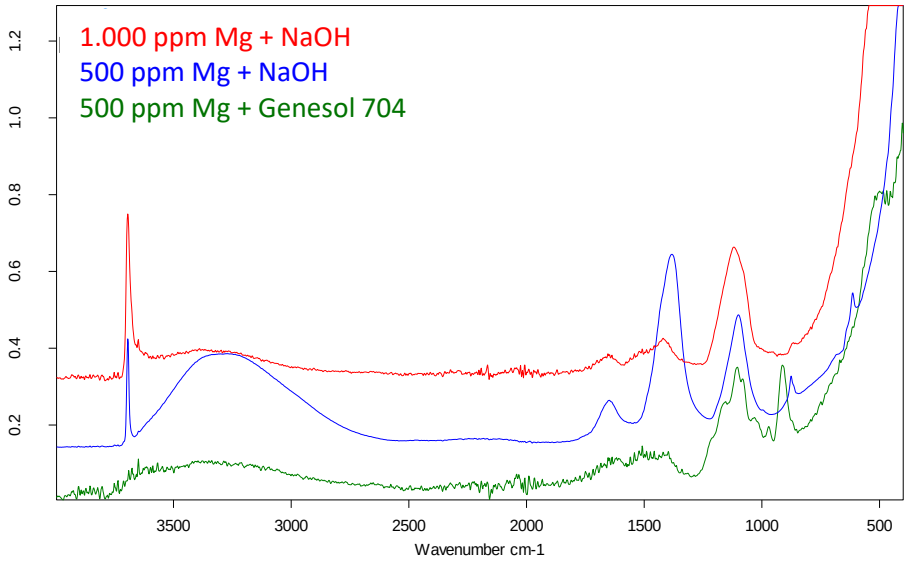


Element	Line s.	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)
C	K-Serie	20,50	28,27	3,43
O	K-Serie	49,75	51,50	5,57
Na	K-Serie	15,44	11,12	0,84
Mg	K-Serie	10,52	7,17	0,51
S	K-Serie	3,57	1,84	0,15
Ca	K-Serie	0,22	0,09	0,05
Au	M-Serie	0,00	0,00	0,00
		100,00	100,00	

Formulated 1% + 500 ppm Mg

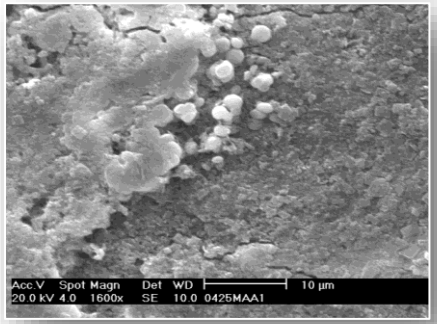


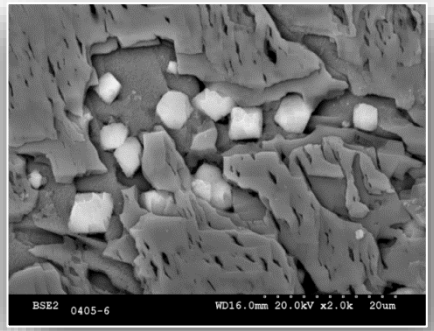
Element	Line s.	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)
C	K-Serie	33,17	45,35	7,05
O	K-Serie	34,96	35,88	6,03
Na	K-Serie	13,21	9,43	0,99
Mg	K-Serie	2,32	1,57	0,19
P	K-Serie	1,02	0,54	0,09
S	K-Serie	2,81	1,44	0,16
Cl	K-Serie	12,52	5,80	0,51
Au	M-Serie	0,00	0,00	0,00
		100,00	100,00	

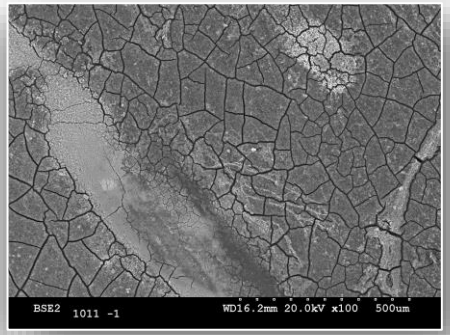


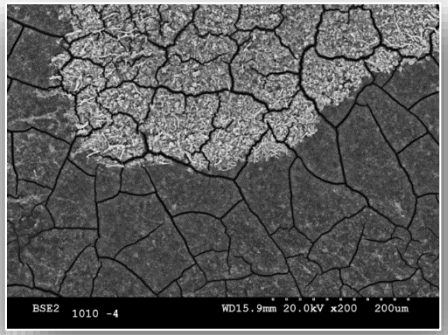
Foulants composition is commonly composite

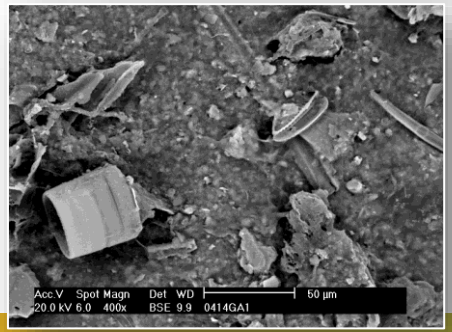
It is almost impossible to find pure foulant on membranes surface.
The 38% of the membranes show a significant presence of a **secondary foulant**

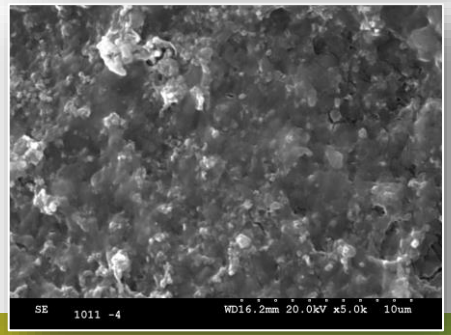












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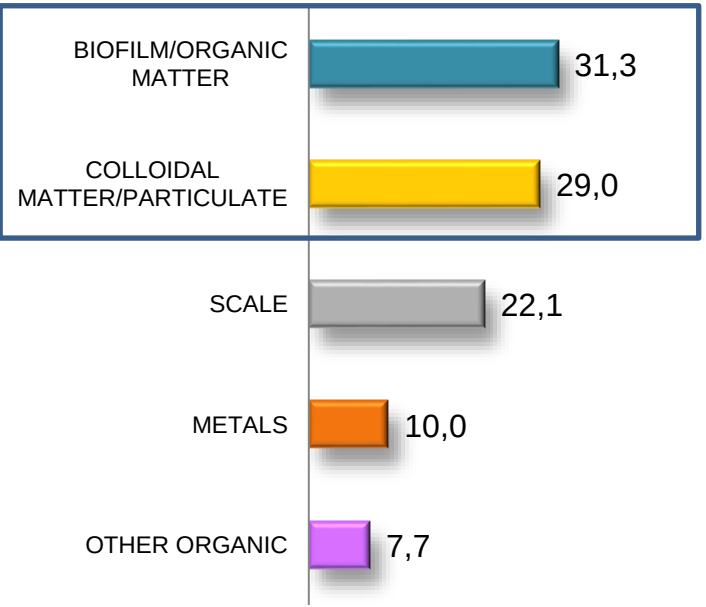
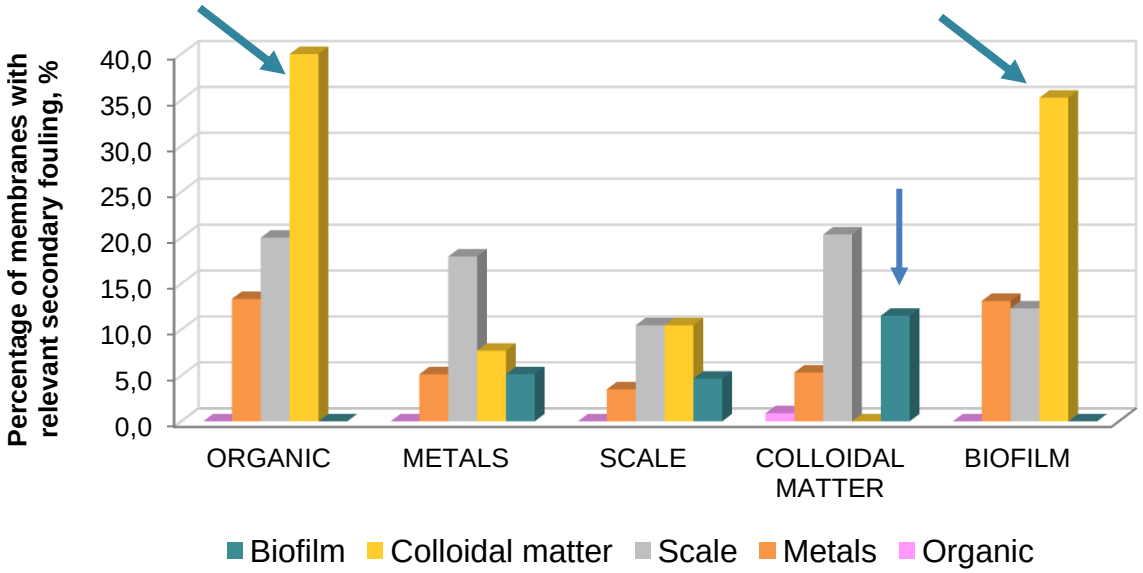
Foulants composition – RO membranes

Main foulant components

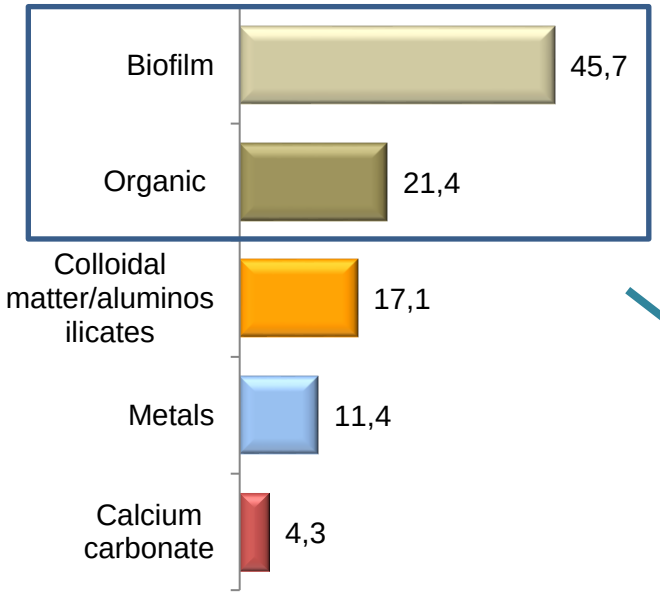


Secondary foulant components

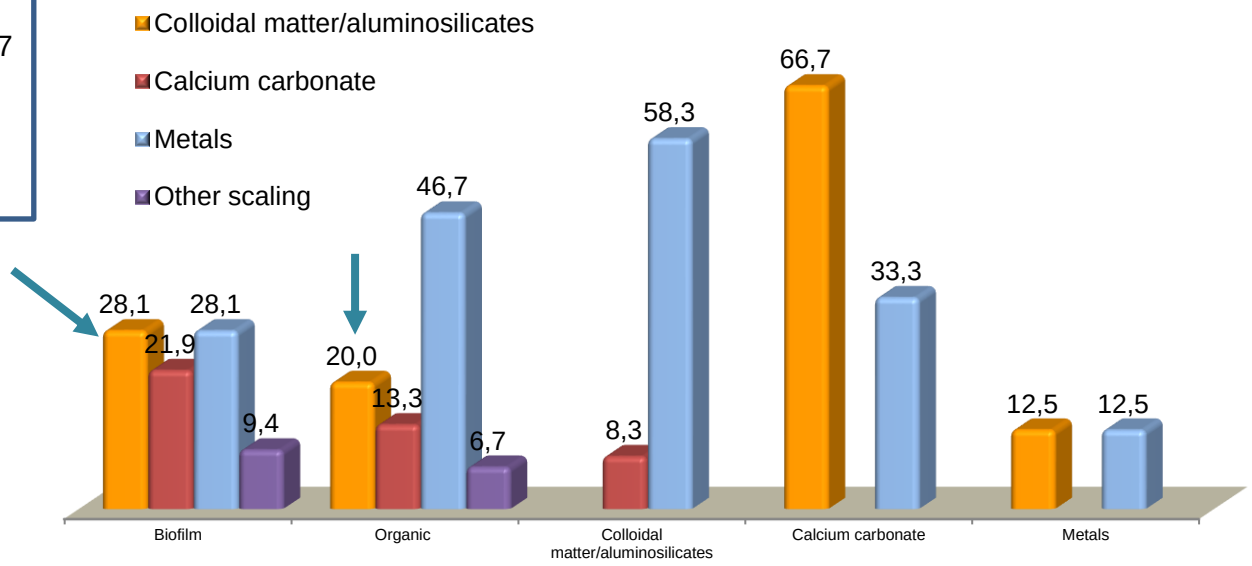


Foulants composition – UF membranes

Main foulant components

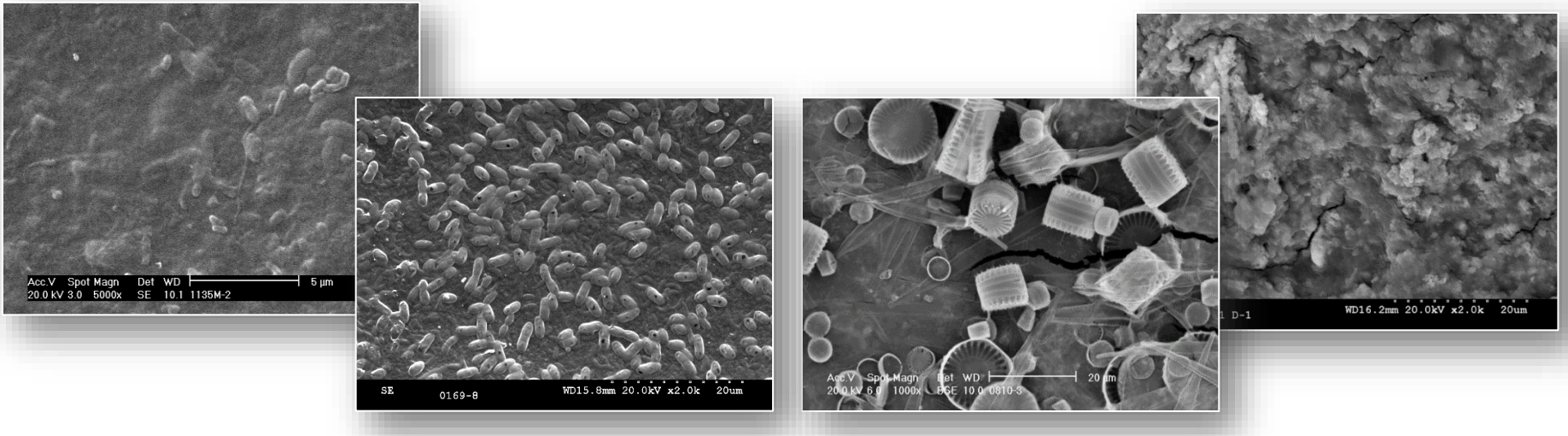


Secondary foulant components



Commodities are broadly used both during CEB and CIP

RO Foulants composition: Most common is biofilm/organic matter + clays-colloidal matter



This kind of foulant is particularly difficult to clean, specially when it is not removed in time, since it ages and get compressed by the effect of pressure

Main commodity cleaners used for membranes:

- ✓ Detergents: Phosphate based STPP, Na-DDBS, Na-DDS
- ✓ Surfactants: SDS, SLS
- ✓ Complexing agents/chelants: Na-EDTA
- ✓ Alkaline agents: NaOH
- ✓ Acid agents: Hydrochloric, citric, phosphoric, sulfamic acid
- ✓ Reducer agents: SBS
- ✓ Disinfectant agents: NaOCl, H_2O_2

Table 1.- Cleaning recommendations of some of the leading membrane manufacturers

Membrane manufacturer		Biofilm / Organic matter	Colloidal matter / Aluminosilicates
Dow Filmtec	OI	0.1% (W) NaOH and 0.025% (W) Na-DSS, pH 12, 35°C max. (Preferred) 0.1% (W) NaOH and 1.0% (W) Na_4EDTA, pH 12, 35°C max. (Alternative)	0.1% (W) NaOH and 0.025% (W) Na-DSS, pH 12, 35°C max.
	UF -CIP	0.2% HCl, 2% citric acid or oxalic	0.1% NaOH + 0.2% NaOCl
Hydranautics	OI	pH = 11.5 of 0.1% (w) de NaOH and 0.03% (w) SDS (sodium dodecylsulfate).	pH of 10.0 2.0% (w) STPP (sodium tripoliphosphate) ($Na_5P_3O_{10}$) and 0.8% (w) Na-EDTA 2.0% (w) citric acid ($C_6H_8O_7$)
	UF – CIP	NaOH, HCl, H_2SO_4, or citric acid	
Toray	OI	Sodium dodecyl sulfate (DSS, sodium lauryl sulfate), 0.03 - 0.2% with alkaline solution or Na polyoxyethylene lauryl sulfate (PSLS), 0.1 – 0.5% with alkaline solution	1 – 2 % citric acid adjusted with ammonia
LG – NanoH_2O	OI	NaOH, EDTA / permeate RO NaOH: until 0.1% weight EDTA: until 1.0% weight Citric acid / RO permeate until 2.0% weight	
Pentair	UF - CIP	NaOCl (active chlorine) 500 ppm max. H2O 1000 ppm max. NaOH pH ≤ 11 Nitric acid pH ≥ 1 Phosphoric acid pH ≥ 1 EDTA pH ≤ 11 Citric acid Enzyme compounds	
Inge / BASF	UF - CIP	NaClO H_2O_2 NaOH Acid pH	

Formulated-multifunctional cleaners :

- ✓ Multifunctional product in a single container:
  - Detergents Surfactants
  - Chelating agents Buffer pH
  - Increase in osmotic pressure
- ✓ 100% active. Lower concentrations of use.
- ✓ Effective in cleaning composite foulants.
- ✓ Shipping savings
- ✓ Savings in the stock area

Best cleaner selection:

- ✓ Accurate identification of foulant
- ✓ Cleaning tests

MEMBRANE AUTOPSIES

Performance of commodities and formulated cleaners during autopsies

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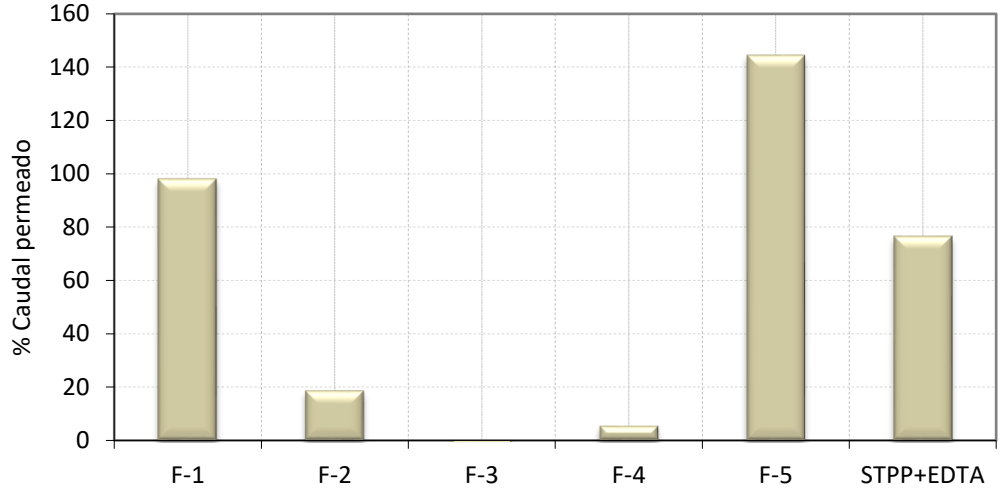
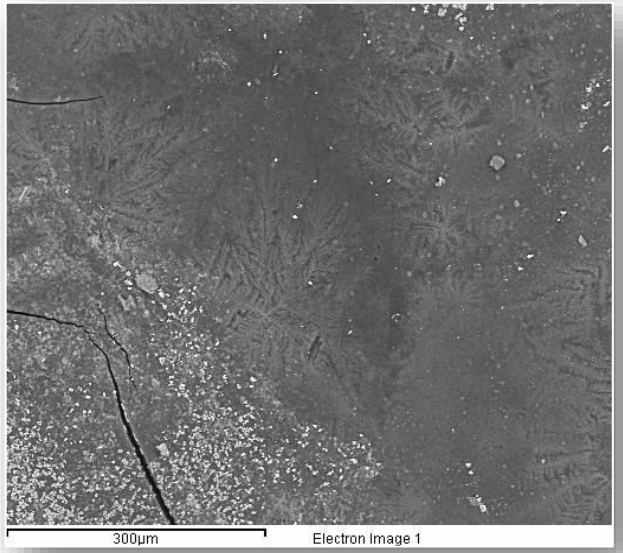
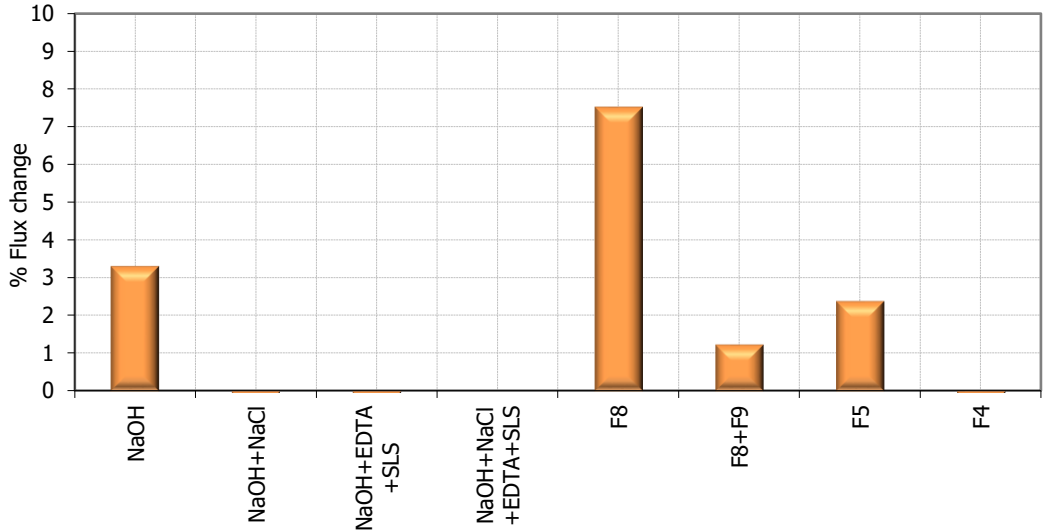
RO: Biofilm / colloidal matter removal

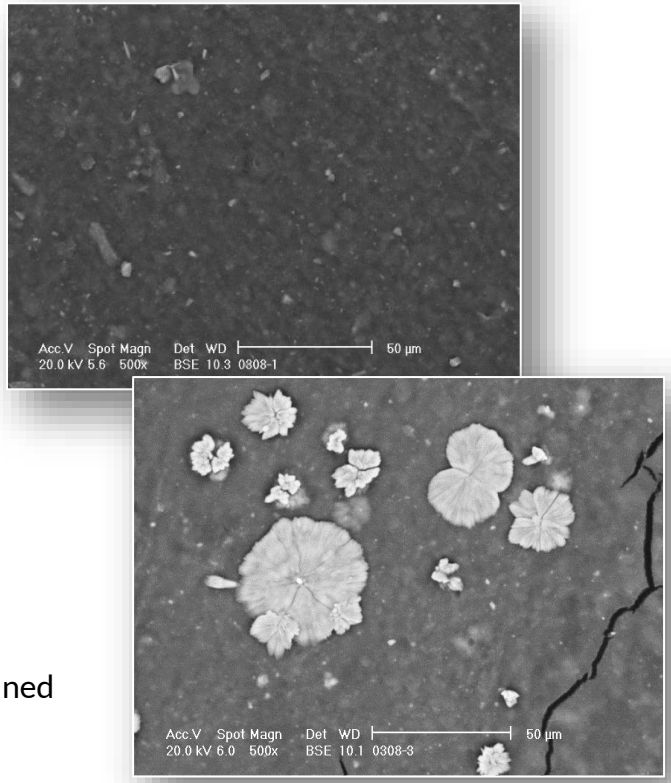




- ✓ STPP + EDTA mixture showed a good increase in permeate flux, it is smaller than the one obtained with formulated alkaline cleaners.
- ✓ It is important also to choose the best formulation to be applied for each kind of fouling, since not all the formulated cleaners improved. STPP + EDTA performance.

RO: Biofilm / colloidal matter / $CaCO_3$

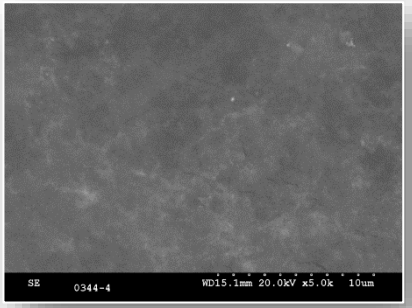


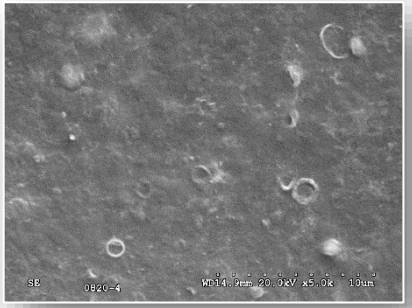


- ✓ Cleaning tests were carried out by applying sodium hydroxide alone and combined with other components.
- ✓ Permeate flux increase was only obtained when sodium hydroxide was applied alone.
- ✓ Although it achieved good results compared to other formulated cleaners, the increase in permeate flux was much higher when F8 product was applied.

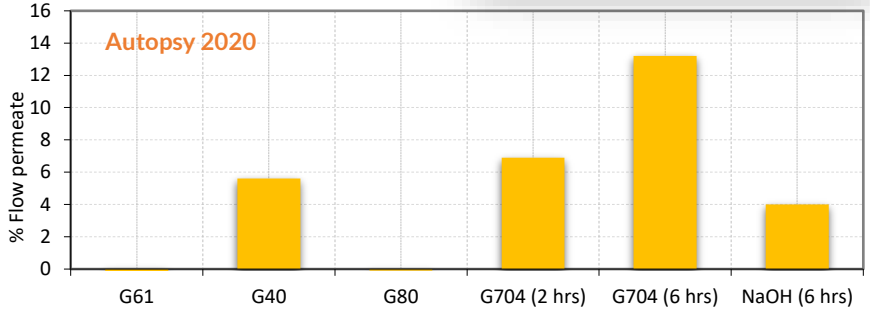
RO: Biofilm SW membranes

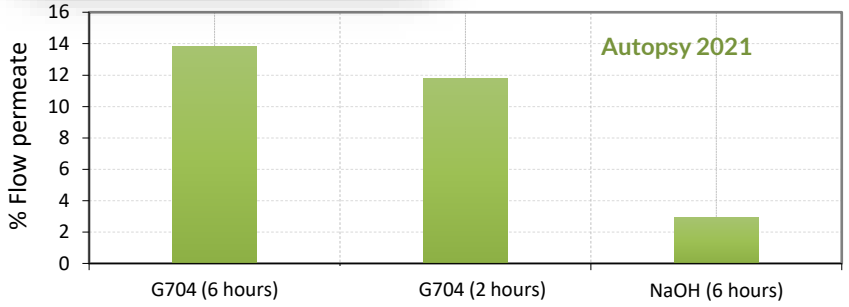
65,2% organic:
Protein derivatives
34,8% inorganic: Fe, Ca, P, S, Mg, NaCl, aluminosilicates.





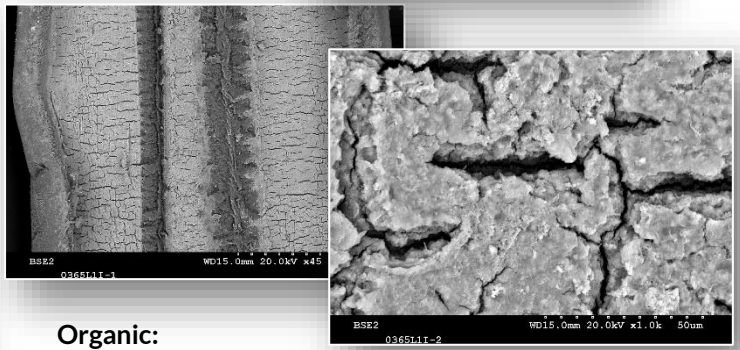
68,2% organic:
Protein derivatives
31,8% inorganic: Fe, Ca-Mg, NaCl, aluminosilicates.





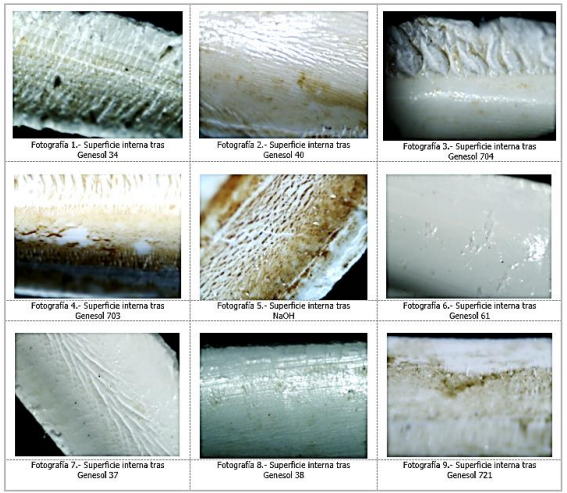
- ✓ Cleaning tests were carried out on membranes received from same plant in different periods.
- ✓ Permeate flux increase was higher for formulated cleaner even when shorter contact times were applied.

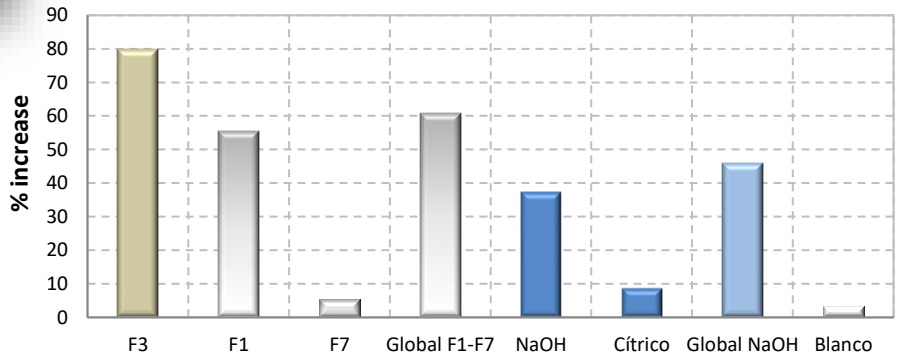
UF: Biofilm / NaCl / Fe / Zinc and other components



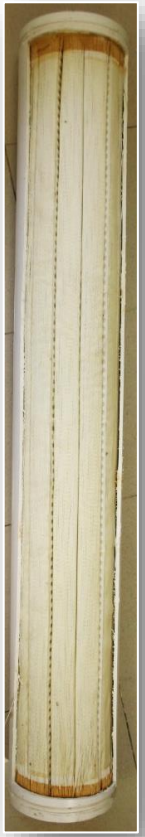
Organic:
Protein derivatives
Inorganic:
NaCl, Fe, P, Zn, Ca-Mg

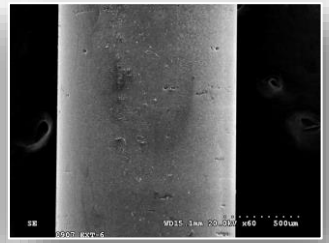
All the formulated cleaners achieved a better flux increase than the commodities commonly applied on this kind of membranes

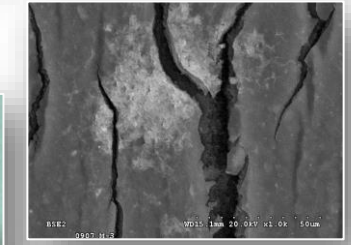


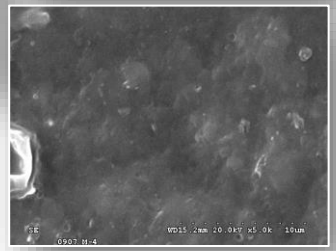


UF: Biofilm / Fe

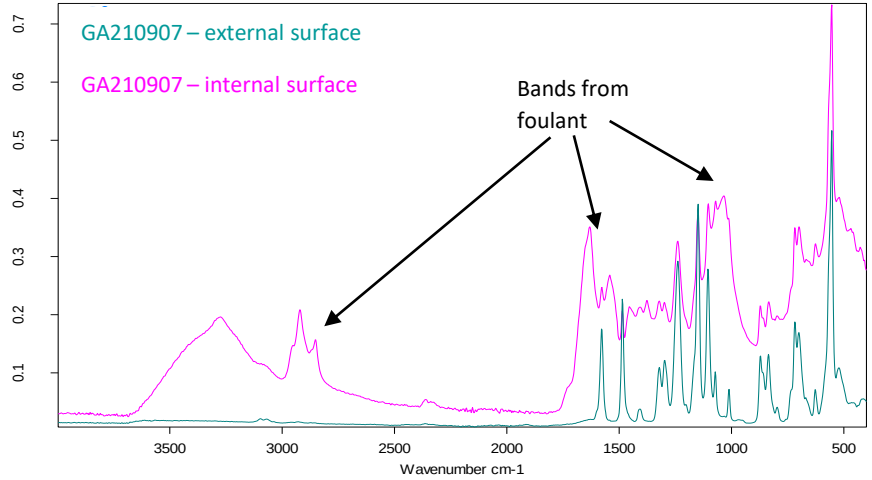


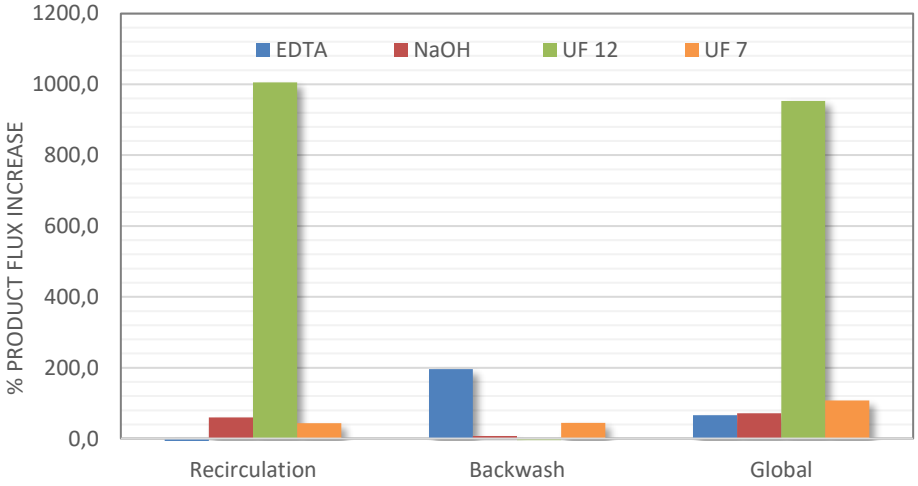




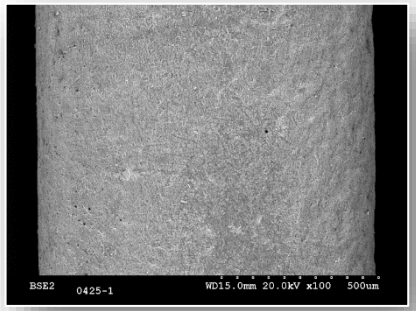


Organic:
Protein derivatives
Inorganic:
Fe,P, traces other elements.

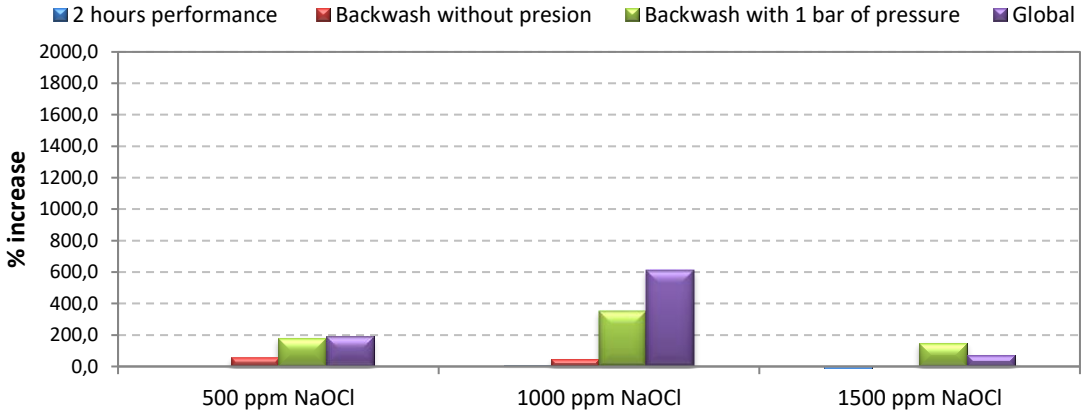


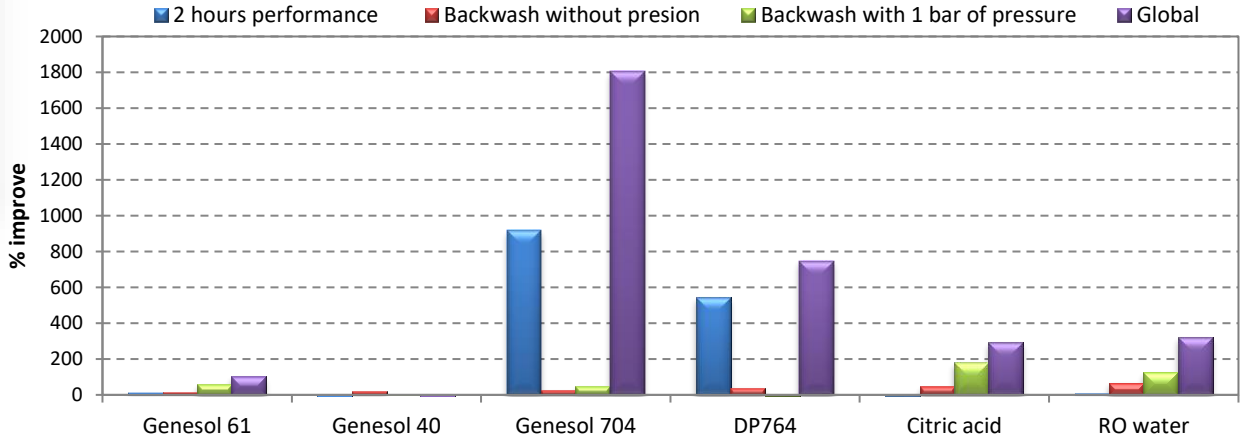


UF: Biofilm / aluminosilicates / Fe



Organic:
Protein derivatives
Inorganic:
Aluminosilicates, Fe.





CONCLUSIONS

- The results obtained during many autopsies revealed the common composite nature of fouling.
- When considering a cleaning procedure, it is very important to use in time cleaners both versatile and effective to ensure the greatest removal of fouling components from the membrane surface.
- Formulated cleaners usually contain mixtures of components which provide them the necessary multifunctionality to ensure a safe more effective elimination of fouling than when commodities are used.
- The multicomponent formulated products makes easier the use and application than mixtures of commodities.

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