



Cleaning clay from fouled membranes

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Received 26 September 2008; Accepted in revised form 20 August 2009

ABSTRACT

Within the lifetime of most reverse osmosis (RO) systems some fouling will adversely affect membrane performance. The major constituents of foulants found on the first position during six years of membrane autopsy at the Genesys Membrane laboratory are clay minerals chemically known as aluminosilicates. Clay is a naturally occurring material found in all RO feed waters composed primarily of different fine-grained minerals, which exhibit a degree of plasticity (deformation under pressure) depending on the amount of water held by polar attraction in the mineral crystalline structure. Clay deposits are difficult to remove with traditional specialty and commodity cleaning chemicals. This is due to the characteristic of plasticity, the presence of different structural cations and also the impermeability of clay to water. Clay deposits fouling the membrane rapidly reduce flux rates. In order to maintain product water output operators invariably increase feed pressure which compacts the deposit making it less porous and harder to penetrate with traditional cleaning chemicals. Ineffective deposit removal leads to more frequent cleaning and enhanced potential for membrane damage. Clay mineral fouling of membranes therefore requires immediate removal through effective cleaning. This paper explores the chemistry of clay and the mechanisms involved in membrane fouling. The process of developing and testing a new cleaning product Genesol 703 which removes clay deposits from RO/NF/UF systems is described. Comparative results with conventional cleaning products and commodity chemicals are presented. Product efficacy was determined by comparison of membrane flux rates before and after cleaning. The results demonstrate that Genesol 703 is a technically and economically viable cleaning chemical product for the removal of clay deposits from membranes.

Keywords: Reverse osmosis; Membranes; Cleaning; Clay; Fouling; Aluminosilicates; Genesol 703

1. Introduction

Membrane autopsy procedures at the Genesys laboratories in Madrid proved that over a 5 year period the most frequent foulants in the lead element of an RO plant were aluminosilicates or clays (as shown in Fig. 1). Clays naturally occur in most waters, rivers, sea, reservoirs, estuaries, aquifers and tertiary effluent treatment plant

and can therefore be present in any RO feed water. Pre-treatment to remove clay from the feed system is rarely a 100% efficient process. The following sections explain the chemistry and processes involved in clay fouling of membranes and the development of a new cleaning product. Results from the laboratory are presented with an explanation of the unique mechanisms that make this product effective.

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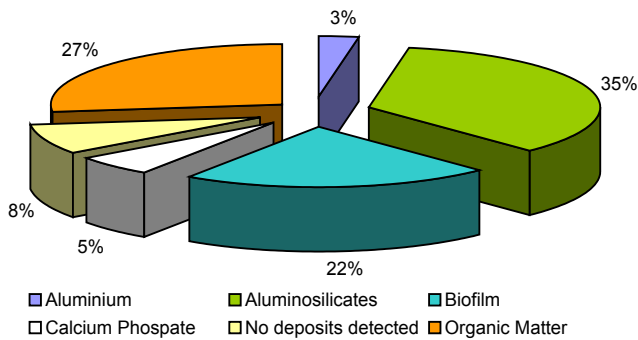


Fig. 1. The main types of foulant identified on membrane elements from the first position during autopsy (2001–2007). Source: GMP laboratories statistics.

2. Background — clay minerals

The term “Clay” is used in three different ways: as a particle-size term, as a rock or sediment term and also for designating a diverse group of fine-grained minerals. Clay minerals are typically formed over long periods by the gradual chemical weathering of silicate bearing rocks by carbonic acid and other dilute acidic solvents which migrate through the weathering rock. Clay deposits may be formed in place as residual deposits, but usually thicker deposits are formed as the result of a secondary sedimentary deposition process after they have been eroded and transported from their original location of formation by water. The transported clay minerals are deposited in surface water aquatic environments and from here can directly enter reverse osmosis feed water. The naturally occurring transportation of these minerals from the surface source makes clay minerals potentially problematic in all membrane feed waters.

Clay minerals are part of the Phyllosilicate (sheet structures) subclass of minerals. Structurally they are composed of tetrahedron rings linked by shared oxygen atoms to other rings in a two dimensional plane forming a sheet-like structure. These sheets are connected to each other by weakly bonded layers of cations which often have water and other neutral atoms or molecules trapped between the sheets giving clay their soft compressible nature. The resultant crystal structure is flat and plate like. According to Swaddle [1] we refer to them as aluminosilicates when some of the Si^{4+} ions in the silicates structure are replaced by Al^{3+} ions. For each Si^{4+} ion replaced by an Al^{3+} , the charge must be balanced by having other positive ion such as iron, magnesium, alkali metals, alkaline earths and other cations.

Principally these minerals are naturally resilient to breakdown by chemical attack and also high temperatures and pressures. In nature they are often the last minerals to be broken down by erosion and weathering processes. This is an important factor in the resistance of clays to “normal” cleaning products. The weakly bonded

Table 1
3 main types of clay minerals and their properties

Clay type	Structure and property
Kaolinite	The most common clay composed of silicate sheets bonded to aluminium oxide/hydroxide layers
Illite	Structure contains a wide range of cations including Al, Mg, Fe and potassium
Montmorillonite/smectite	Structure includes Ca, Na, Al, Mg and is notable for its ability to take up and lose water

layers of cations in some clay are easily exchangeable with others and clays also have the ability to take up or lose water according to the surrounding temperature and amount of water present.

Mineralogically, clays are divided into 3 principal groups, with more than 30 different minerals within these groups. Table 1 shows the main types of clays which exhibit the different characteristics affecting membrane performance and their ease of removal through cleaning.

There are 2 main properties exhibited by clays which make them harder to remove from membranes:

2.1. Water impermeability

The kaolinite clay structure consists of 2 sheets (silica/oxygen and aluminum/oxygen) with hydroxyl functional groups present on the outer surface providing a hydrogen bond which in the aggregate holds the crystal sheets together and protects the internal structure from water and cations in solution entering the internal layers. This structural strength means that only the outside surface is available for attack by the cleaning solution.

Cations such as iron and magnesium are able to substitute for aluminium and silicon in the lattice structure — isomorphous substitution creates a net negative charge on the crystal surface attracting cations to the surface, further protecting the outer surface of the deposit from attack.

2.2. Plasticity

Plasticity can be described as “the deformation of a material undergoing a non-reversible change of shape in response to applied forces”. This characteristic allows the shape of the deposit to change and deform under applied pressure causing the deposit to form and block the pores at the membrane surface. In the montmorillonite group the crystal layers are not tightly fixed with hydrogen bonds so water molecules can enter the interlayer which increases the interlayer spacing resulting in significant swelling of the clay on hydration, this reduces porosity of the deposit preventing entry of cleaning solutions to the internal structure. This swelling effect also increases flux reduction at the membrane surface.

3. Effects of clay fouling in membrane operating performance

Pretreatment processes such as coagulation, flocculation and low pressure membrane filtration (microfiltration and ultrafiltration) have been used in front of RO processes to remove particles and large colloids, but fouling by small colloidal matter ($<2 \mu\text{m}$) and fine suspended particles is still a problem [2]. The principal consequence of membrane fouling by clay minerals is an increase in hydraulic resistance resulting in a greater energy requirement to operate the process. The formation of highly impermeable deposits by clay minerals on the membrane surface will result in significant problems in maintaining permeate flux with frequent cleaning eventually being required to maintain system operation.

The primary effects of fouling by colloidal particles in a membrane system will be seen mainly in the elements in the first positions. However if this problem remains untreated fouling will gradually effect all membrane elements. The effects will include a reduction in membrane flux (reduction in product flow rate), an increase in salt passage and also an increase in ΔP . Membrane damage through abrasion processes have also been identified during membrane autopsies performed on systems fouled with clay mineral deposits due to the compression of the crystalline structure against the membrane surface by increased operating pressures.

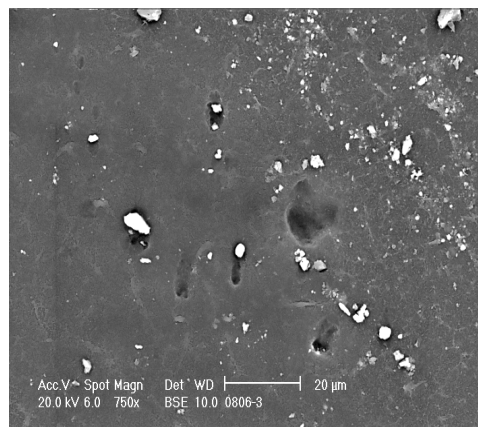
If we accept that due to inadequate chemical and physical pre-treatment systems clay particles will continue to enter the membrane system then it is important to reduce the frequency of required cleaning. In order to reduce cleaning frequency and minimise membrane damage the operator can achieve optimum deposit removal by cleaning with a technically correct product.

4. Mechanisms of clay fouling

The physiochemical mechanisms of fouling compo-

nents attaching to the membrane surface are complex and poorly understood. Physical adsorption, electro-static charge and bridge-formation are fouling mechanisms frequently reported in literature [3]. These effects are primarily governed by concentration polarization and particle accumulation in the cake layer on the membrane surface. The velocity and turbulence of the water flow along the membrane surface in cross flow RO and NF systems prevents some particles from being deposited. Particles which are deposited result in a mechanism of particulate fouling — cake formation. Particle accumulation in the cake layer process is controlled by system hydrodynamics, physiochemical operating conditions and solution chemistry [4]. The porosity of the deposit cake, and hence the effect on membrane flux, depends on the size of the particles being deposited and also the interactions between those particles. In general terms - the smaller the particle size then the lower the porosity of the deposit and the larger the reduction in membrane flux. We also have to take into account the action of chemical pre-treatment flocculants and coagulants which will effectively increase the size of the clay particles (over naturally occurring clay particles) and change their porosity and potential resistance to effective cleaning.

After chemical pre-treatment we would expect clay flocs which have passed through physical filters in to the feed water to be larger in size and therefore should be more porous, we would therefore expect removal through cleaning to be comparatively straight forward. However cake compression also has an effect on porosity of the deposit — at higher transmembrane pressure (TMP) the cake is compressed reducing the porosity of the deposit to cleaning solutions. The shape of wet clay is altered due to the rearrangement of the particles, in the case of a membrane environment due to an increase in pressure which compresses the cake particles and reduces the porosity of the deposit.



Figs. 2 and 3. SEM micrographs. Aluminosilicates and iron oxides on RO membrane surface. Abrasion process related.

5. Genesol 703 – new cleaning approach

Cleaning agents can affect fouling materials present on a membrane surface in three ways: (i) foulants may be removed, (ii) morphology of foulants may be changed (swelling, compaction) and/or (iii) surface chemistry of the deposit may be altered, such that the hydrophobicity or charge is modified [5]. Reported foulant-cleaning agent reactions are hydrolysis, peptization, saponification, solubilisation, dispersion (suspension) and chelation.

If an inappropriate cleaning agent is chosen negative effects can appear and membrane performance can be adversely affected. Membrane manufacturers [6] clearly state the consequences of applying inefficient cleaning techniques: “If foulant is not successfully removed, the membrane system performance will decline faster as it is easier for the foulant to deposit on the membrane surface area. The time between cleanings will become shorter, resulting in shorter membrane element life and higher operating and maintenance costs. Most effective cleaning allows longer system operating time between cleanings and results in the lowest operating costs”.

In order to provide an effective cleaning compound for the removal of clay deposits a specific cleaning chemical was developed and tested in the Genesys laboratory. Genesol 703 is a 100% active chemical powder based on a combination of high pH phosphate cleaners, a blend of chelants, surfactants and other active compounds. The product is approved under NSF/ANSI 60 guidelines.

This combination of products has a detergent and surfactant effect on the colloidal foulant and in addition creates high ionic strength at the membrane surface.

The Genesol 703 mode of action can be described as follows: the first stage of attack occurs at the water/surface inter-phase of the clay deposit and is due to the synergistic mode of operation of the combined speciality chemicals. This process works by reducing the surface tension of the deposit allowing the surfactant to become more effective in overcoming the impermeability of the material; this allows the cleaning solution to penetrate to the inter-layer space of the clay structure. The clay then becomes more porous increasing the permeability to water and consequently increasing the surface area of the deposit allowing more active chemical to penetrate and disrupt the “body” of the deposit. Genesol 703 provides a secondary physical action which increases cleaning efficiency at the membrane surface allowing a “double edged” approach to deposit removal. This action removes blockages from the membrane pores caused by the swelling effect of the hydrated clay particles.

In normal operation of an RO system the pressure provided by the High Pressure Pump (HPP) overcomes the osmotic pressure of the feed water. During cleaning, the Genesol 703 solution is introduced to the system at a cleaning pressure below 4 bar. The feed water salinity will increase. It is possible that at the membrane surface

the local osmotic pressure may become higher than the Net Driving Pressure (NDP) of the feed water. If this were the case then potentially there may be some localised forward osmosis taking place. Any movement of permeate water through the membrane to the feed water may assist lifting of the clay deposits around the membrane pores. This in turn would allow greater access to the surfactant cleaning chemicals to remove deposits. The removal of deposits away from the membrane into the concentrate stream is likely to help minimise membrane abrasion. This phenomenon may go some way to explain the effectiveness of the cleaning formulation. Further work is required to try and observe what is actually happening at the membrane surface during cleaning.

In addition to the effectiveness of Genesol 703 in removing clay deposits its application also serves as a means of “shock treatment” of a reverse osmosis system to reduce the biofouling potential through lysis of microorganisms; in turn this helps to prevent further system contamination. Cell lysis occurs due to the semi permeable nature of the membrane surrounding the microorganism; the cleaning solution creates the movement of water from the cell cytoplasm resulting in the eventual removal of the membrane from the cell wall.

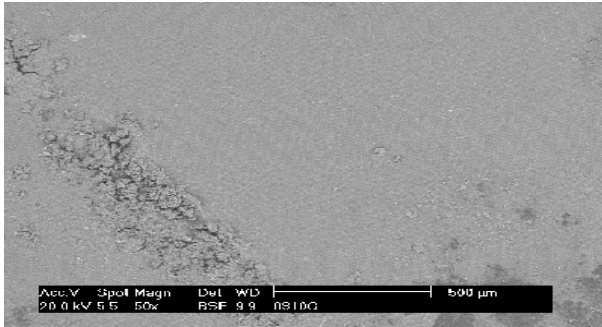
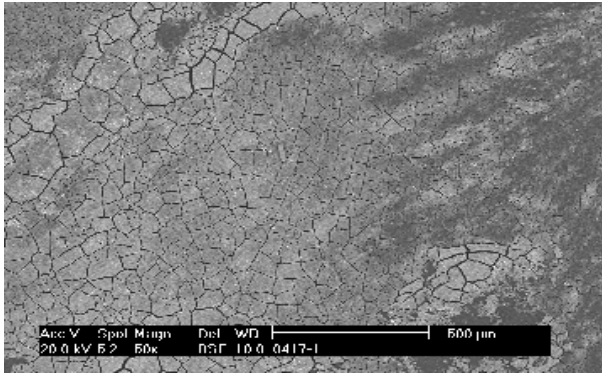
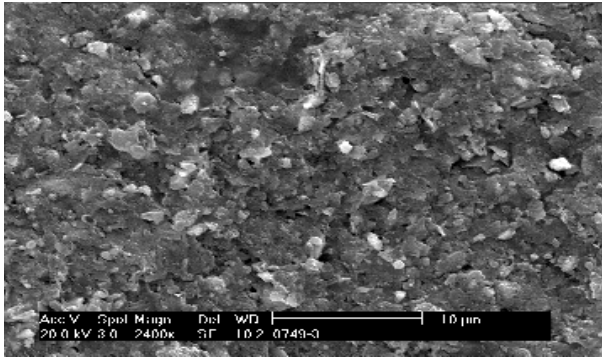
Laboratory tests (as indicated below) proved this product to be much more effective at removing clay mineral deposits than conventional acid and alkaline cleaning products.

6. Testing Genesol 703 efficiency – experimental set up and procedures

In order to establish the efficiency of Genesol 703 in removing clays from a membrane surface, various cleaning tests were carried out in the Genesys Membrane Products S.L. laboratories using three actual RO membrane elements. In order to verify that the deposits were mainly composed of aluminosilicates (clays) the membrane fouling was firstly characterized by Scanning-electron microscopy – Energy dispersive X-ray analysis (SEM-EDAX) The data for each membrane sample tested is summarized in Table 2.

Cleaning experiments were performed with a laboratory scale cross-flow membrane unit. Rectangular flat sheet membrane coupons from RO elements were housed in a stainless steel cell, with an effective membrane area of 231 cm². Feed water was circulated under the characterisation conditions (pressure and salinity) established by the membrane element manufacturer in order to establish a baseline for each membrane sample. Data achieved is normalized to 25°C conditions. Different cleaning solutions were later re-circulated at 40 psi. The cleaning chemical used on each membrane and the test conditions are described below. After re-circulating the cleaning solution the membrane is rinsed with deionised water and characterised with the same conditions as used

Table 2
Summarized data for membrane samples used in laboratory tests

Membrane tested	SEM membrane surface inspection	Foulant description
Case 1 Hydranautics ESPA1 membrane Characterization conditions: 150 psi, 1000 ml/min, 1,500 ppm NaCl		Orange coloured deposit. Deposit is mainly inorganic (>85% dry mass). Composed of aluminosilicates and iron oxides.
Case 2 DOW Filmtec BW 30-400 FR Characterization conditions: 225 psi, 1000 ml/min, 2,000 ppm NaCl		Dark brown-orange deposit. Deposit is mainly inorganic (>60% dry mass). Composed of aluminosilicates and iron oxides.
Case 3 Hydranautics LFC3 Characterization conditions: 150 psi, 1000 ml/min, 1,500 ppm NaCl		Dark brown deposit covering homogeneously membrane surface. Deposit mainly inorganic (>90% dry mass). Composed of aluminosilicates and iron oxides.

in step one. The cleaning efficiency of the product is then evaluated in terms of flux and rejection perceptual variations. Additional analysis and visual inspection can be carried out to provide further evaluation.

7. Testing Genesol 703 efficiency – results and discussion

The cleaning programs were designed according to the membrane manufactures guidelines for removing this type of foulant. Established limits of pH and temperature have also been applied. The results obtained in the different cleaning tests and the conditions of analysis are summarized in Table 3. Fig. 4 depicts a graphical sum-

mary from case studies 2 and 3 showing the percentage flux change of the membrane section after the cleaning process. Individual chemical cleaning solution relate to those shown in Table 3.

The data obtained in this experimental work demonstrates that Genesol 703 is more efficient in removing this kind of clay based foulant than the other chemical blends in term of flux improvements. With regards to the evaluation of salt rejection data the results are inconclusive - as in most cases a decrease in salt rejection was observed after chemical cleaning. A reasonable explanation to these results would be membrane abrasion which is frequently documented in membranes fouled by colloids (previously described in Figs. 1 and 2).

Table 3
Summarized data for cleaning test conditions and results

	Cleaning solution	Temp. (°C)	pH	Time (h)	Flowrate (l/m ² h 25°C)			% salt rejection	
					Before	After	%	Before	After
Case 1	C1.1 Genesol 703 (1 wt%)	35	11.5	4	64.04	67.92	+6.1	95.6	94.0
	C1.2 Na ₄ EDTA (1 wt%) + sodium tripolyphosphate STP (2 wt%)	35	11.5	4	64.14	63.54	-0.9	94.0	91.5
	C1.3 Sodium dodecyl benzene sulfonate (0.25 wt%) + Na ₄ EDTA (1 wt%)	35	11.5	4	61.26	60.43	-1.4	95.0	94.4
Case 2	C2.1 Citric acid (2 wt%)		4	2	43.22	39.26	-9.2	99.2	99.1
	C2.2 Sodium dodecyl benzene sulfonate (0.25 wt%) + Na ₄ EDTA (1 wt%)	35	11.5	4	45.63	42.95	-5.9	99.1	99.4
	C2.3 Na ₄ EDTA (1 wt%) + sodium tripolyphosphate STP (2 wt%)	35	11.5	4	44.96	44.97	0.0	98.8	99.1
	Genesol 703 (1 wt%)	35	11.5	4	43.51	45.50	+4.7	99.2	99.4
Case 3	Genesol 703 (1 wt%)	35	11.5	4	17.33	58.43	+237.2	93.8	96.5

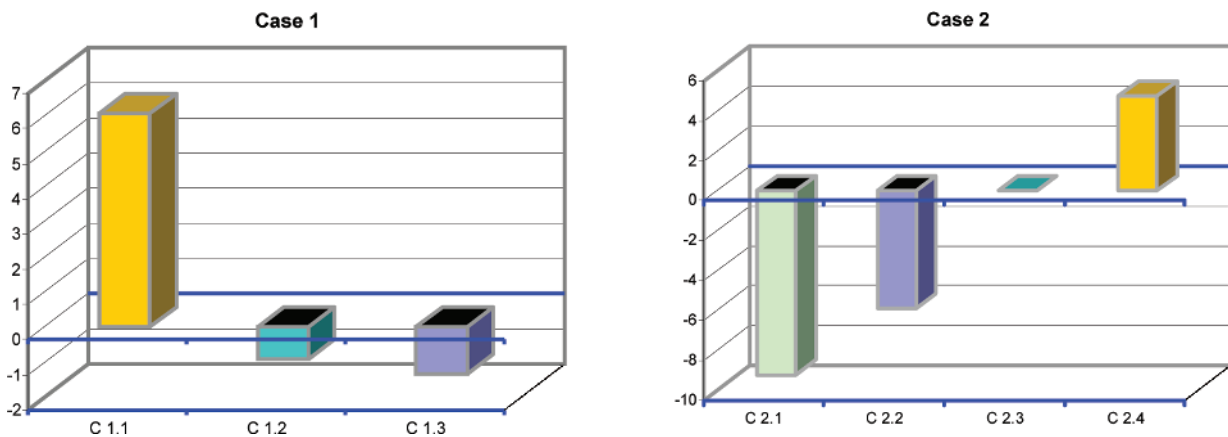


Fig. 4. Comparative data for different cleaning options in Case 1 and Case 2 (see Table 3) salt rejection and flux recovery vs. design criteria.

This product has also proved effective in cleaning membranes which are severely fouled with clay as illustrated in Case 3. In this case the initial flow rate was 57% below design specification (manufacturer technical data sheet for membrane element). After a 2 h soaking period with a 1% Genesol 703 solution the flow rate has recovered back to design values.

Alternative methods for evaluating removal of the deposit have also been taken into account. For Case 2 the section used in the cleaning tests was preserved for analysis. As shown in Fig. 4 visual inspection shows that the membrane deposit has mostly been removed. SEM-EDAX analysis confirms this removal as only traces of aluminium (Al) and silicon (Si) were identified by this method. Predominantly sulphur (S) was detected indicating that the electron beam used for analysis was able to reach the membrane polysulphone support layer.

8. Conclusions

The results of Genesys membrane autopsy laboratory data support the fact that clays are a common foulant occurring primarily on the membrane elements in the first position and they can occur in all RO feed waters.

The structural characteristics of clay minerals mean that operational increases in pressure can compress the deposit resulting in further loss of membrane flux. The test data supports the fact that clay deposits on a membrane surface can produce irreversible damage in terms of salt rejection due to abrasion processes. Improvements in pre-treatment can be considered although practical experience shows that small particulate/colloidal matter (<2 µm) cannot be completely removed from feed streams. In order to prevent membrane damage remedial action

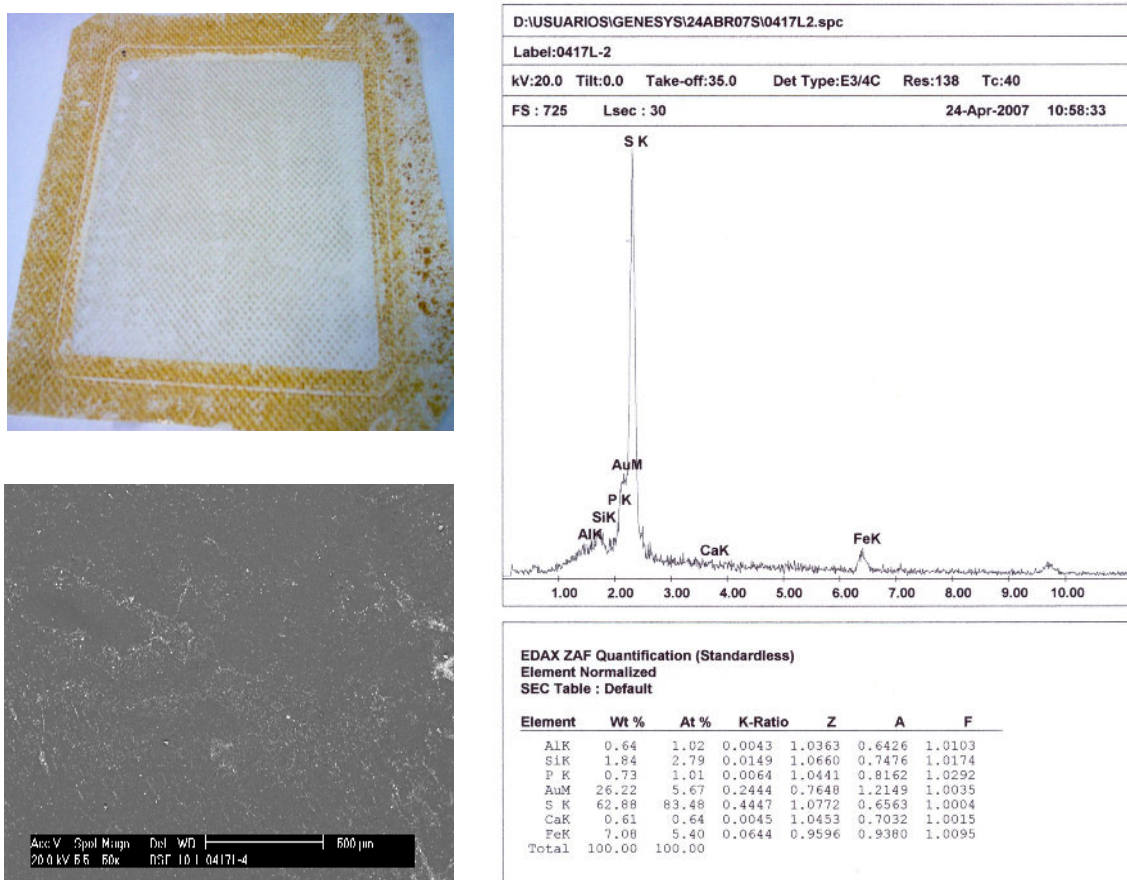


Fig. 5. Membrane coupon used in Case 2/cleaning 4. SEM-EDAX evaluation results.

should be taken immediately when the first symptoms of fouling are detected.

Laboratory studies indicate that Genesol 703 is more effective at removing clay minerals from membrane surfaces at a dosage rate of 1%. This is significantly lower than traditional cleaning chemicals. In these analyses real membrane samples have been used which have been fouled by clay deposits during their natural operation and the effectiveness of the product has been proven in terms of the results of significant increases in membrane flux.

The product has been used in over thirty operating plants with clay fouling problems with encouraging results. In real operational plants, rejection values have been reported to either improve or be maintained. In some cases, rejection has decreased after cleaning procedure. Behaviour in salt rejection values depends on the type of foulant and condition and how they affect membrane rejection properties. During autopsy procedures in all cases when rejection decreased after using G703 in clay based deposit removal, physical damage on the membrane surface was reported caused by abrasion by solid particulates and not chemical damage (using SEM-EDX in membrane coupon after cleaning - deposit removal). The

product has been tested in line with the DOW protocol and results indicate that salt rejection has not decreased.

Further studies will be conducted and the authors hope to present additional case study information in the future.

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