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Autopsy of RO desalination membranes
Part 1. Microbial characterization of foulants

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ABSTRACT

Comprehensive autopsies of RO membrane elements from a seawater desalination plant were performed before and after chemical cleaning. The RO membrane elements (FILMTEC, SW30HR LE-400 8″) selected for the autopsy studies have been in service for nearly 2 years and were located in front position of a pressure vessel from the first pass of one of the RO units. Process performances have been quite stable for the whole period of operation. Before and after chemical cleaning both membrane elements showed a visible deposit on the membrane surfaces with wet matter of 27 g/m^2 (before) and 11 g/m^2 (after) cleaning. By ICP-OES analyses before cleaning, a high content of iron and manganese was found in the deposit. After chemical cleaning, most of the parameters remained stable except the manganese content which was not detected any more. The autopsies underlined the presence of a biofilm even if no obvious loss of membrane performances was observed. The high content of manganese and iron in combination with the microscopic image of the layer indicated the presence of manganese and iron-oxidising bacteria together with their metabolites. Chemical cleaning seems to have a limited impact on this type of biofouling despite the improvement observed on pressure drops.

Keywords: Desalination; Membrane fouling; Iron-oxidising bacteria; Manganese-oxidising bacteria

1. Objectives

Membrane autopsies have been performed for many years and different types of fouling phenomena have been identified such as biofouling, scaling, inorganic fouling, and silica fouling. Nevertheless, the real layers often reveal heterogeneous compositions originated from different types of fouling phenomena. It is often hard to differentiate which of the fouling components is the one or are the ones contributing the most to the decrease in performance parameters.

Several detailed module autopsies have been performed within the European research project MEDINA by using already established methods but also by developing new or modifying existing methods. The aim of all the autopsies is to evaluate the methodological tools for their applicability to seawater and their significance. The methods shall be able to help identify causes which are responsible for different types of fouling. Performing a detailed membrane autopsy and quantifying and understanding fouling phenomena will help to understand fouling mechanisms. This work will lead to conclusions about the most efficient methodology for performing autopsies as well as understanding fouling issues for desalination membranes. On the basis of the results obtained through membrane autopsies it will be possible to find explanations for fouling mechanisms on seawater (SWRO) and brackish water (BWRO) reverse osmosis membranes.

The significant and appropriate methods will be described in a public document called "Handbook for

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basic analytical methods for membrane autopsies". It will be established by the end of 2008 and visible on the internet site of MEDINA (http://medina.unical.it/).

2. Background

A statistical review of 150 membrane autopsies carried out by PermaCare and summarized by Darton and Fazel stated that all membranes have a biofilm on their surfaces which may cause problems (biofouling). According to their experience, other significant fouling problems are caused by iron and silt deposition.

Iron deposition or iron precipitates can have a biotic or an abiotic cause. The biotic iron deposits are metabolites either from "aerobic iron oxidation" or "iron oxidation by anoxygenic" bacteria. Using specific staining and microscopy, the biotic iron deposits can be visualized and identified because of their characteristic structures. Iron-oxidising bacteria are known to be able to use very low concentrations of iron. Such phenomena are very well known from wells where iron as well as manganese-oxidising bacteria have a natural habitat (blocking/clogging). Iron-oxidising bacteria have been isolated from estuary where salt concentration especially sodium chloride concentration exceeded 3%. In addition to ferrous iron, the chemically related metal manganese is also oxidised by few bacterial strains. The metabolites form typical structures as well. If these bacteria are associated with the anaerobically living iron- and manganese-reducers, a substrate cycle is established.

The elemental composition of components may be visualized with light microscopy and special staining reactions as well as using scanning electron microscopy (SEM) in combination with element dispersive X-ray (EDX) for quantitative element analysis.

3. Materials and methods

3.1. Samples

The two RO membrane elements (FILMTEC, SW30HR LE-400 8") selected for the autopsy studies had been in service for nearly 2 years and were located in front position of a pressure vessel from the first pass of one of the RO units. The pre-treatment is of conventional type: coagulation followed by a single stage dual media filtration. Process performances have been quite stable for the whole period of operation even if small differential pressure increases were noticed. Since the beginning, only two chemical cleanings have been performed; one of them was carried out just before the second autopsy. The cleaning was a classical cleaning sequence: caustic soda at pH 12 then SBS 1% followed by hydrochloric acid (pH 2).

After sampling of each RO module, pieces of membranes were disseminated to research partners for detailed autopsies according to the shipping conditions defined by each partner.

3.2. Optical and electron microscopy

Investigations have been performed using light-, epifluorescence and scanning electron microscopy.

3.3. Element analysis

Inductively coupled plasma optical emission spectrometry (ICP-OES) has been used for quantitative analysis of the elemental composition of the layer.

3.4. Water content and loss of ignition

The layer from defined areas from the membrane surface was removed carefully with a rubber scrapper. The water content was determined at 105°C, ignition loss at 550°C.

3.5. Total and active cell number

The procedure used for enumerating total bacteria follows in this case the ASTM Standard Test Method Designation F 1095-8. The enumeration was carried out on homogenised and diluted biofilm samples using the dye 4´,6-diamidino-2-phenylindole (DAPI). The dye 5-cyano-2,3-ditolyl tetrazolium chloride (CTC) was used to determine the number of active bacteria. CTC compound is actually used to indicate intracellular redox metabolism, e.g. actively respiring cells. The CTC positive particles can be easily visualized and counted via epifluorescence microscopy using green light excitation.

3.6. Manganese-oxidising bacteria

Enumeration of manganese-oxidising bacteria have been performed by using PYM-medium. Additionally, obviously biological originated structures in the deposit on the RO membranes have been investigated by SEM coupled with element analysis in order to determine the element composition.

3.7. Iron-oxidising bacteria

Iron-oxidising bacteria have been determined qualitatively by using potassium hexacyano ferrate(II) which is reacting with iron III-substances forming blue stained components (Berlin blue). Furthermore, SEM coupled with elemental analysis was in order to determine the

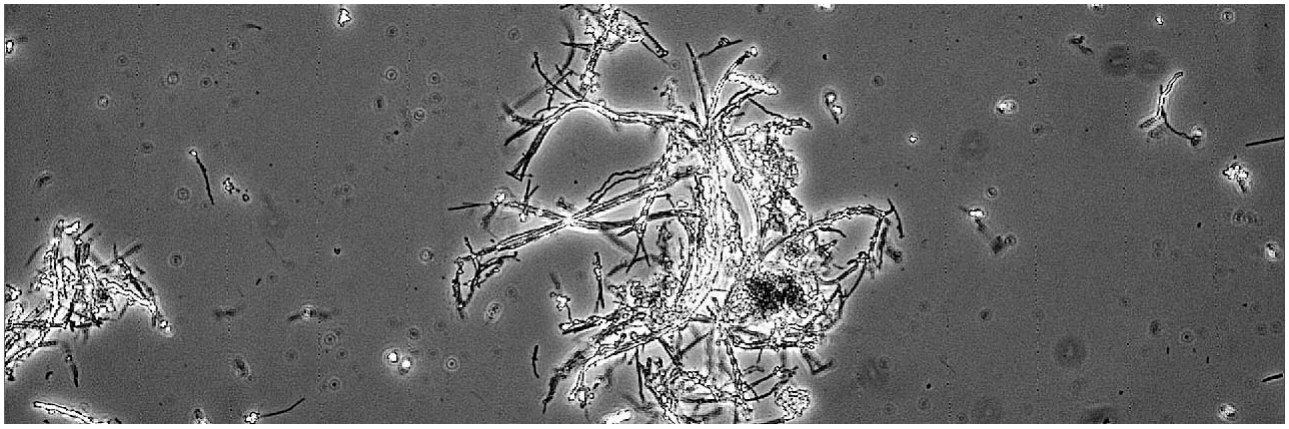

Fig. 1. Light microscopic image of a microbial aggregate showing typical structures of iron and/or manganese-oxidising bacteria and their metabolites as well as iron deposits.

elemental composition of special structures known as metabolites from iron-oxidising bacteria. Quantitatively enumeration was performed with a three-tube MPN assay using media according to Kamimura et al.[1]

4. Results and discussion

Both membrane elements investigated showed a visible deposit at the membrane surfaces which was slightly unevenly distributed. There was no layer or precipitates on the spacer. The brownish deposit layer could be easily mechanically scrapped from the membrane surface (Fig. 2). After cleaning the layer was thinner and the colour less intensive (Fig. 2b).

Before chemical cleaning, the wet matter was 27 g/m^2, water content 94% and loss of ignition at 550 °C (organic part of dry matter) 65%. After cleaning, wet deposit was 11 g/m^2, water content 94% and loss of ignition 60%. Analysis of the deposit by ICP-OES revealed a high concentration of iron and manganese (Table 1).

For comparison, the results obtained by another partner are presented in Figure 3. They are in the same order of magnitude. The dry matter content and the proportion of organic/inorganic remained stable despite the cleaning. After chemical cleaning, manganese was not detected any more but iron showed a high concentration as before cleaning (Fig. 3).

4.1. Number of microorganisms and microscopy

Scanning electron microscopy revealed that the elements were not homogenously distributed but mostly

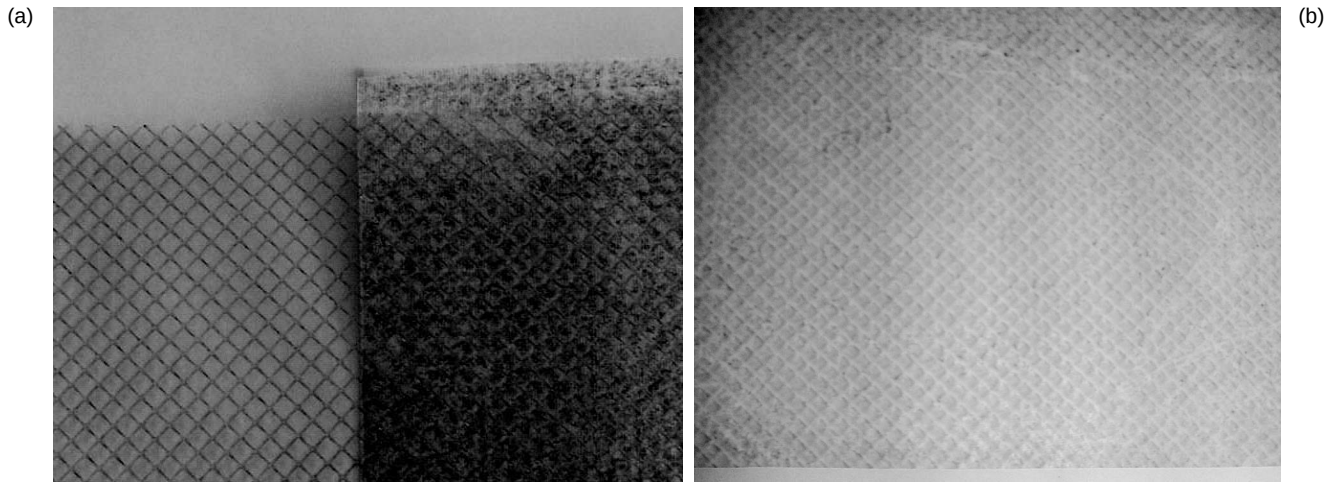

Fig. 2. Optical view of the membrane surface and the spacer before cleaning (a) and after cleaning (b).

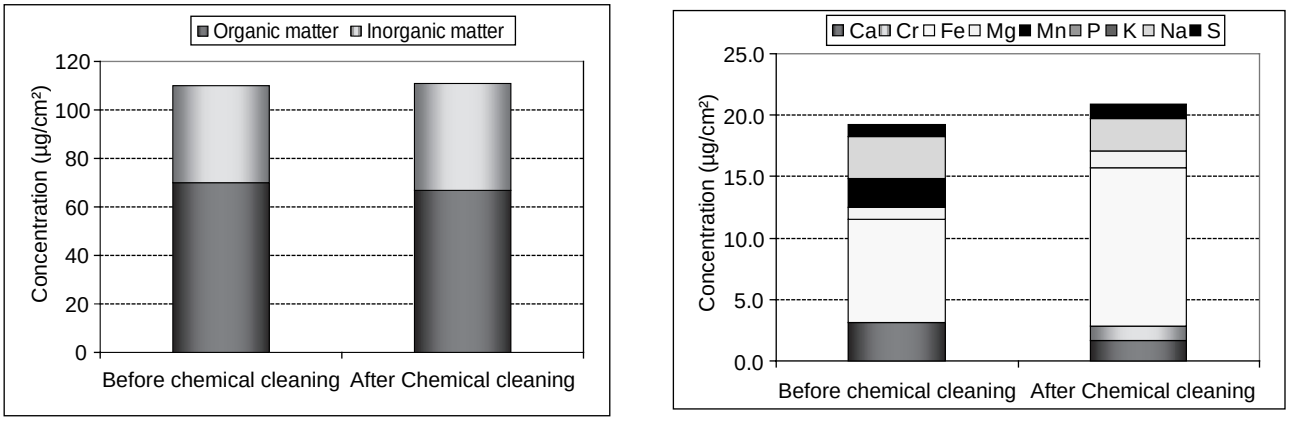

Fig. 3. Organic and inorganic content of the deposit scrapped on the membranes before and after cleaning (partner 2).

Table 1
ICP results obtained by partner 1.

Parameter/ Element	Before cleaning mg/kg dry weight	After cleaning mg/kg dry weight
Al	3 890	6 220
Ca	14, 100	14 500
Cd	2.8	3.1
Co	1 040	1 210
Cr	18 000	16 400
Cu	660	510
Fe	**123 000**	**128 100**
K	2 070	< 1 720
Mg	7 940	11 300
Mn	**14 900**	**640**
Na	22 000	21 600
Ni	3 750	3 220
Pb	203	180
P	6 630	6 890
Si	6 700	9 910
Zn	172	205

localised at distinct structures. These structures were in the size of some micrometers and had the appearance of precipitates known from iron and manganese-oxidising bacteria.

Total number of bacteria was found at a high level of 3×10^7 bacterial cells/cm² before cleaning and 2×10^6 cells/cm² after cleaning (Fig. 4). These results were in the same order of magnitude for both partners. Moreover, a significant decrease of the active bacteria concentration was noticed after cleaning. But, even if a slight decrease was observed, the concentration level of total bacteria remains high after cleaning.

However, it was difficult to clearly identify the structures within the heterogeneous matrix even if the light microscope investigation showed a lot of iron deposits and typical structures known from iron and manganese-oxidising bacteria.

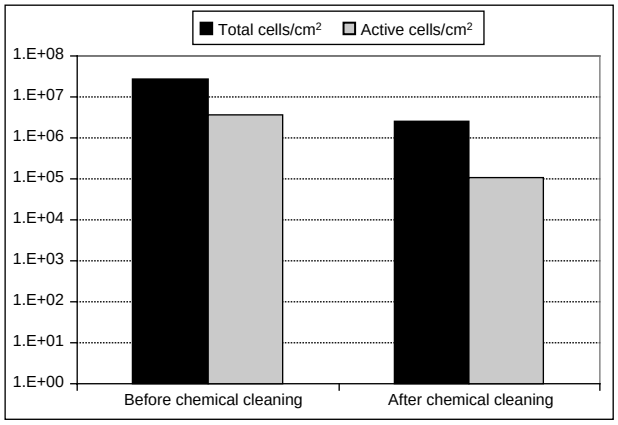

Fig. 4. Microbial content measured as total cell number of the deposit scrapped on the membranes before and after cleaning.

By scanning electron microscopy, typical structures have been identified as iron deposits by elemental analysis using electron dispersive x-ray (EDX). The microbial structures have been visible in the layer of the membrane samples "before cleaning" and "after cleaning" (Fig. 5). It was suggested that they may have played an important role in building the fouling layer. This suggestion could be positively verified by cultivation using specific agar media. Living manganese-oxidising bacteria were present up to several thousands cfu/cm² before cleaning and only a few after cleaning.

Methods for enumeration of iron-oxidising bacteria have been published for many years and it is known that enumeration of iron-oxidising bacteria may be confronted with the contamination of fungi [2]. A three tube Multiple Number Assay (MPN) based on cultivation in a liquid special media was performed with dilution levels ranging from 10^0 to 10^{-6} using the layer sample "after cleaning". The formation of a red coloured band at the water/air interface indicated the presence of iron-oxidising bacteria (Fig. 6). The results for the deposit of the sample "after

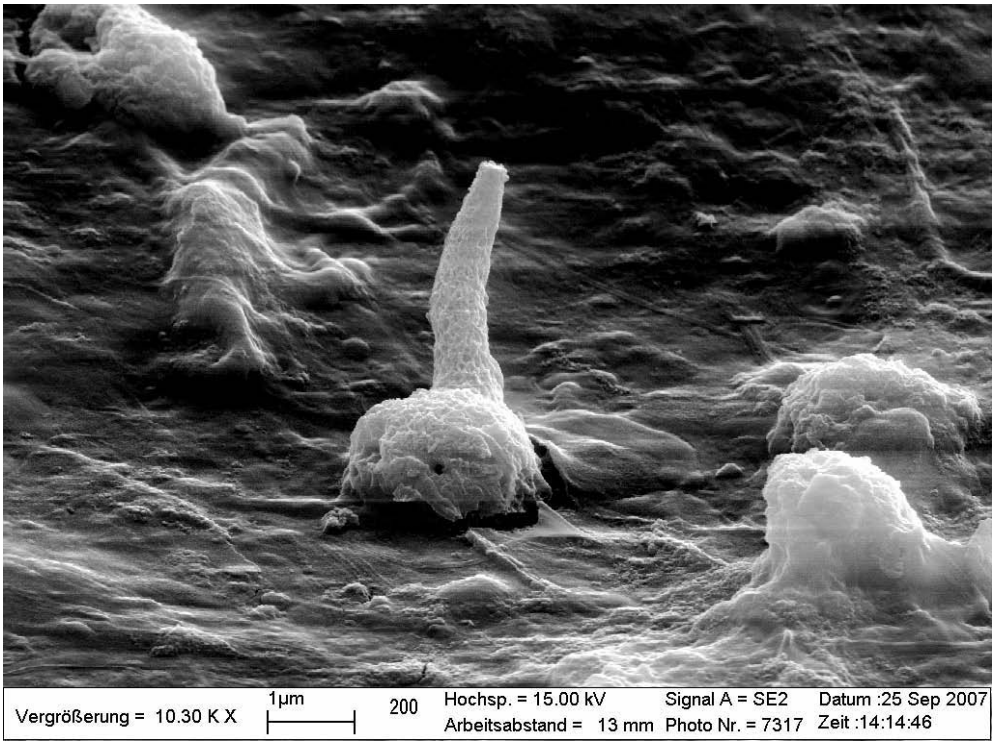

Fig. 5. Deposit on the membrane after cleaning showing the same type of structure originated from iron-oxidising bacteria but slightly "damaged" compared to the ones before cleaning; the elemental composition showed iron but no manganese-oxidising bacteria.

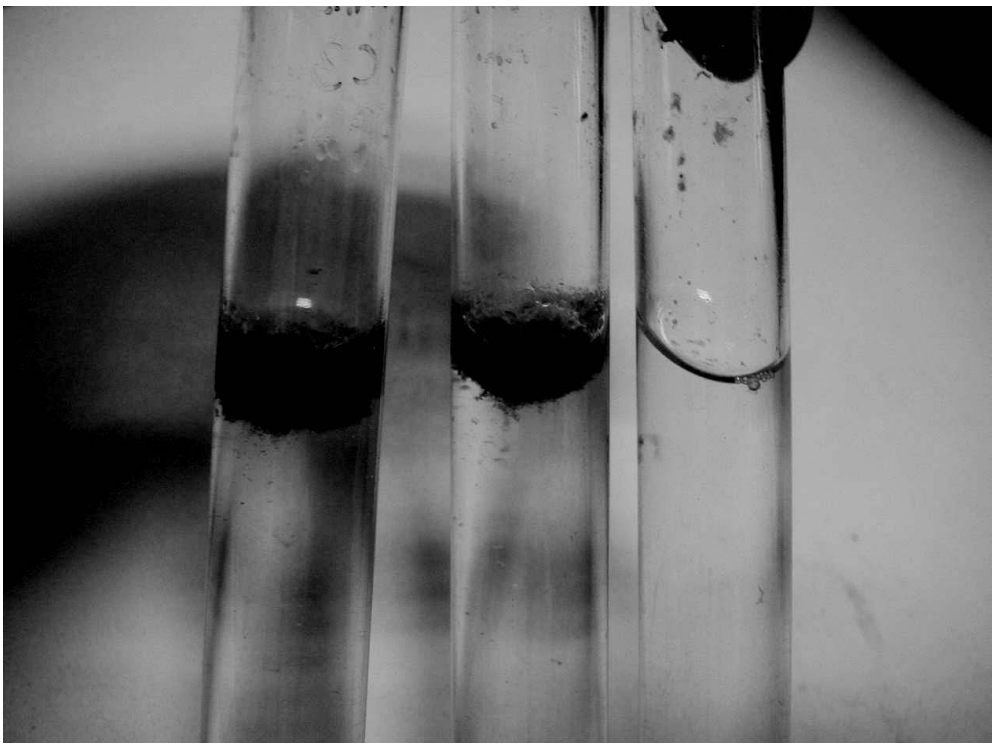

Fig. 6. Image of the water/air interface of the three MPN tubes with dilution level 0 using the media for enumeration of iron-oxidising bacteria.

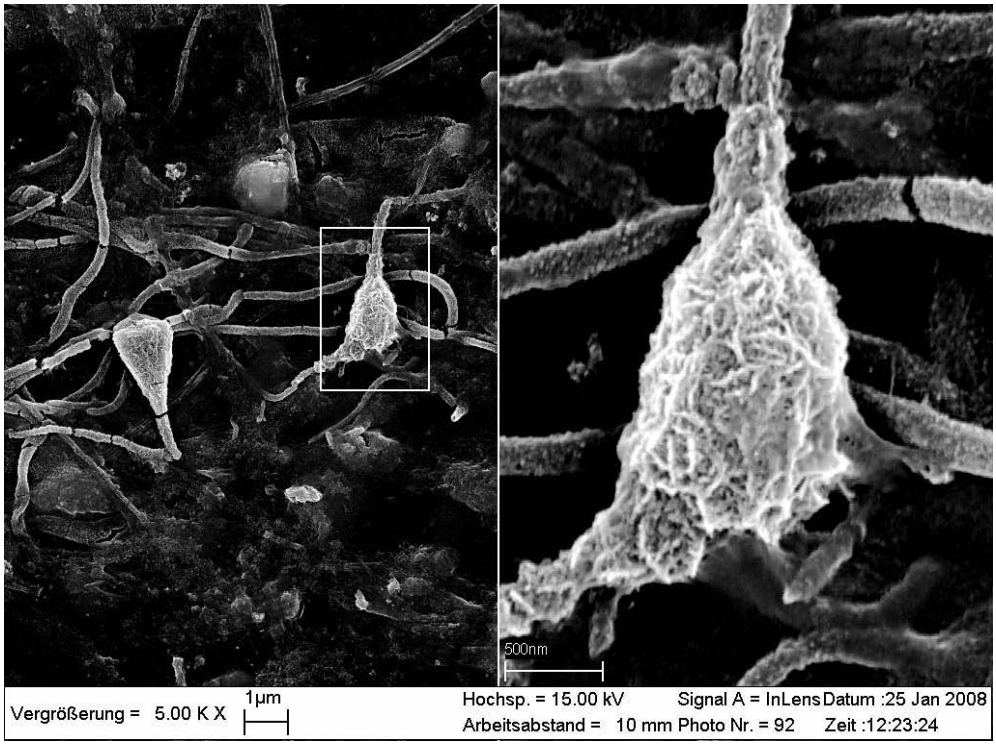

Fig. 7. SEM picture of typical structure (manganese-oxidising bacteria) on the deposit surface before cleaning.

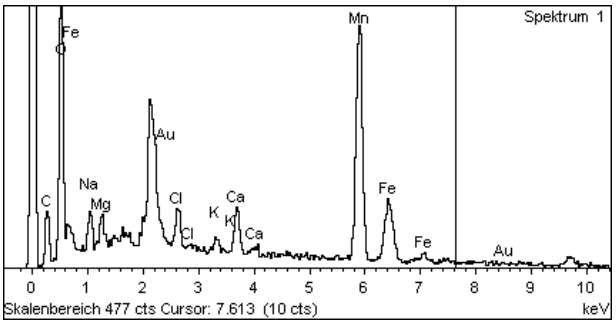

Fig. 8. Element composition of an area with typical biological structures (4 µm^2) as shown above in Figure 7.

cleaning" indicated a low level of iron-oxidising bacteria with a few hundreds per square centimetre. This is not in contrast to the microscopic observation because cultivation requires living cells. Cleaning may have killed a lot of the bacteria but not removed their metabolite products. The presence of a lot of biological originated structures as shown in the SEM pictures (Figs 7, 5) indicated a lot of iron-oxidising bacteria: Element composition of an area with typical biological structures is shown in Fig. 8.

5. Conclusions

Deposits on RO membranes may be partly originating from iron and / or manganese-oxidising bacteria. The role of manganese and iron-oxidising bacteria in membrane fouling have not been investigated intensively. The biotic deposition of iron substances play a role under specific conditions as it does in microbial consortia in environmental samples which has been proven. The use of iron containing water additives and even small amounts of iron may result in building a habitat for iron and / or manganese-oxidising bacteria.

The autopsies underlined the presence of a biofilm even if no obvious loss of membrane performances was observed. The high content of manganese and iron in combination with the microscopic image of the layer indicated the presence of manganese and iron-oxidising bacteria together with their metabolites.

Chemical cleaning was found to be efficient for removing manganese contained in the biological deposits but not for the iron ones.

Acknowledgements

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