

Method for evaluating antiscalants, as applied to the treatment of water from the River Oise

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Abstract Nanofiltration, used in the Méry-sur-Oise water treatment plant (90 MGD) provides a softened water with a low organic matter content from which micropollutants and microorganisms have been removed. The experience acquired on the site since 1992 has revealed that the use of a crystal formation inhibitor is essential to slow down the clogging of the nanofiltration membranes, essentially on the third stage. Given the complexity of the action of the antiscalants (threshold effect, metal ion sequestration capacity, particle dispersion capacity), it is difficult to theoretically define the type of product to be used and its optimal dosing level. In addition to laboratories or modelling studies, pilot experiments are needed to assess antiscalants and optimise their doses. Nanofiltration cycles being long (1–2 months), it is nevertheless difficult to compare results of cycles, and the objective of the project was to develop a methodology for sequestering agent testing.

To carry out strictly comparative studies of commercially available products as well as studies using the same product but at several different dosage levels, a pilot unit comprising three parallel nanofiltration trains was built. The pilot unit is fed with 2nd stage concentrate, produced without sequestering agent, and each train has its own separate antiscalant injection point. The first cycle aimed to provide answers to the following: (i) choice of the antiscalant best adapted to the treatment of water from the river Oise, (ii) identification of the clogging agents, (iii) the efficiency of the chemical regeneration procedure.

A production cycle using the same antiscalant at three different doses (0, 1 and 3 g.m⁻³) demonstrated that this product acted through a threshold effect. Analysing the cleaning waters provided further information on the type of clogging agents deposited on the membrane. Although for all the cycles the overall nature of the clogging is identical, essentially composed of organic matter and mineral elements (calcium, phosphorus, aluminium, etc.). The similarity of the water permeability and salt rejection at the beginning of two consecutive cycles tends to demonstrate that the chemical regeneration procedure (caustic soda/citric acid) is efficient.

Keywords Cleaning; nanofiltration; scaling; sequestering agent

Introduction

Nanofiltration was chosen as the final polishing step for the new Mery-sur-Oise Surface Water treatment plant (Cote *et al.*, 1993). The main objective of this treatment is to remove natural organic matter and pesticides. The new plant was started in the fall of 1999, raising the total capacity of the Mery-sur-Oise plant to 70 MGD. Prior to nanofiltration, the treatment includes (Ventresque *et al.*, 2000): ballasted flocculation and lamellar settling, ozonation, PACL addition, rapid dual-media filtration, and microfiltration.

Membrane fouling is one of the main problems encountered in membrane technology and nanofiltration. This is caused by material deposits in the water becoming attached to the membrane and settling in the pores, thereby reducing system performance (a reduction in production, an increased pressure drop or a modified salt retention). Those deposits most frequently responsible for fouling can be divided into four categories (Amjad *et al.*, 1990) and include the precipitates of mineral salts (CaCO₃, BaSO₄, SrSO₄, CaSO₄, ...), colloidal particles (SiO₂, Fe(OH)₃, Al(OH)₃, FeSiO₃, ...), organic matter and biological development.

The means to overcome deposit formation very much depend on the nature of the deposit. Pre-treatment resulting in water with a low fouling coefficient (number of particles of a size exceeding 1.5 μm less than 200/mL, Silt Density Index lower than 3) and a low organic matter content (TOC) content less than 2.7 mgC/L considerably reduces inorganic colloidal deposits and organic matter (Democrate *et al.*, 2000). Acidification and the addition of a sequestering agent lead to reduced salt precipitation. All these preventative actions reduce the frequency of chemical regeneration on the nanofiltration membranes. Obviously, the products used depend on the nature of the deposit. Hence, base products are far more efficient against inorganic colloids whereas certain salts and acid products are far more efficient against mineral precipitates. A disinfecting phase (formaldehyde, hydrogen peroxide, peracetic acid) is essential to overcome any biological development. However, the efficiency of products dealing with organic deposits, is very limited.

The Oise River water is medium-hard (350 mgCaCO₃.L⁻¹), and the addition of an antiscalant proved necessary. The problem, which then occurred, was selecting the best product available on the market, or optimizing the dose for a given product. Several methodologies were tested to fulfil this need, giving poor results. This paper describes the material and results obtained with a pilot unit designed to allow antiscalant testing.

Equipment and methods

Quality of resources and reagents

For this study, the pilot plant used to test inhibitor products was supplied with the second stage concentrate produced by a small industrial plant operating in series-rejection and equipped with FILMTEC NF 200B membranes. The conversion rate for this plant varied from 67 to 75% to ensure that the concentrate produced had a level of conductivity exceeding 1,000 $\mu\text{S.cm}^{-1}$. Table 1 shows the extreme and mean drinking water variations of the pilot plant during the test.

During the study, one crystal-forming inhibitor (phosphonic acid and polycarboxylate mixture) underwent testing. The products used for the chemical regeneration of the membranes were caustic soda and citric. The calcium chloride solutions used for the membrane characterization tests were prepared from purified anhydrous calcium chloride.

Pilot unit and membrane

The pilot plant (see Figure 1) is made up of four modules, (i) low pressure pumping, (ii) pre-filtration using a filter cartridge with an absolute cut-out threshold of 25 μm , (iii) high pressure pumping, (iv) three identical nanofiltration lines arranged in parallel. These comprise two pressure tubes mounted in series, each containing a size 2,540 spiral nanofiltration module (diameter 2.5 inches and 40 inches long) and a filtering surface area of 2.1 m². Each line has its own sequestering agent injection system. The membrane used throughout these

Table 1 Quality of the water of the River Oise and the drinking water from the pilot plant (Mean (Minimum-Maximum))

Parameters	Stored water	Pilot supply
Temperature (°C)	21.9 (20.5–23.9)	22.5 (21.4–24.5)
Turbidity (NTU)	14.9 (11.4–18.1)	Nd
Particles > 1.5 μm (.mL ⁻¹)	Nd	408 (201–701)
SDI	Nd	4.3 (3.3–5.1)
TOC (mg.L ⁻¹)	3.5 (3.3–3.8)	5.4 (4.8–6.0)
pH	7.9 (7.8–8.0)	7.0 (6.8–7.1)
Conductivity ($\mu\text{S.cm}^{-1}$)	576 (554–594)	1247 (1199–1298)
Alkalinity (°F)	23.2 (22.3–24.2)	32.8 (30.9–34.4)
TH Ca (°F)	25.4 (24.2–26.5)	57.6 (51.2–64.2)

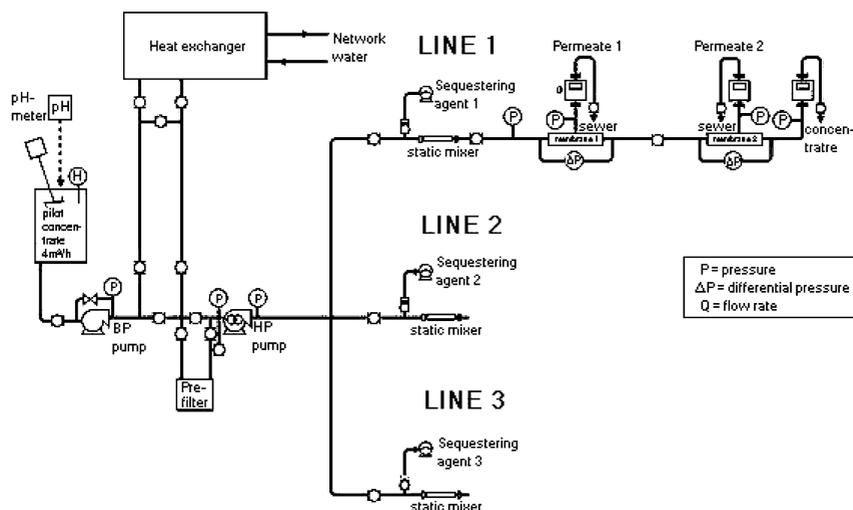


Figure 1 Pilot plant diagram

tests was the FILMTEC NF 200B, manufactured by Dow Chemicals, with the cut-off threshold estimated at 200 Daltons.

Analysis and sensors

The hydraulic parameters were measured every fifteen minutes and recorded in a data acquisition system. Each line is identically fitted with a series of pressure sensors and flowmeters which are installed along the permeate circuits for modules 1 and 2 and the concentrate circuit for module 2. Differential pressure sensors measure the loss in pressure inside the nanofiltration modules. A type Pt 100 temperature sensor measures the temperature downstream of the high-pressure pump.

The physical–chemical parameters were measured once a week, apart from pH, and particles of a size exceeding 1.5 μm and conductivity were measured on a daily basis. The Silt Density Index (filtration speed ratio: 15 minutes) was measured using 0.45 μm sterile filters.

Analyses of organic matter (total organic carbon) and of the ionic balance, were carried out on various water samples (drinking water and concentrate of module 2) by an outside laboratory (Vivendi Water, Saint Maurice, France) whilst complying with current French standards. The solutions for cleaning the nanofiltration membranes have also been the subject of individual analyses carried out by the same laboratory, i.e. aluminium, barium, calcium, chlorides, fluorides, magnesium, orthophosphates, total phosphorus, potassium, silicate, total sulfur, strontium, sulfates and TOC.

Definition of the clogging products on the nanofiltration membranes took place in two phases, where characterization of the deposit along the surface was achieved by way of inductive coupling plasma atomic emission spectrometry (ICP-AES) for metering the mineral chemical elements and by way of a C-N-S analyser for metering the organic elements. The quantitative analysis of the surface distribution of the clogging product was taken at pluri-micrometric level by coupling the morphological and chemical image by way of scanning electron microscopy (SEM) with an analysis and computerized numeric processing of the images. This also entailed the use of special sample preparation techniques by including the membranes and their deposit in resins, followed by ultra-thin sections ($\pm 500\text{\AA}$) by way of ultramicrotomy in order to see the profiles across the membrane.

Control

The degree of membrane fouling was monitored using the following three parameters: water permeability resulting in fouling on the membrane skin and inside the pores, loss in longitudinal load resulting in fouling along the hydraulic path of the drinking water and finally salt rejection.

Methodology

The nanofiltration modules are new at the start of the cycle. A test is broken down into several stages, the operating conditions of which are shown in Table 2.

- A standard CaCl_2 test checks the membrane properties with regard to water and calcium flow. This is carried out on six new membranes before proceeding with the production cycle and on three washed membranes, namely modules 2 for each line, in order to appraise cleaning efficiency.
- The production cycle lasts for eight weeks. The purpose of this test was to examine the influence of the dose of one and the same sequestering agent on the rate of fouling.
- Washing of module 2 for each line is broken down into two phases – one caustic sodium cleaning phase at a pH of 10.5 followed by cleaning with citric acid at a pH of 2.5 (Dow, 1999).
- Autopsies of module 1 (not cleaned) and of module 2 (cleaned) of each line were performed by the CEREGE. The aim was to characterize the importance and type of deposit in relation to the dose of one and the same sequestering and to establish the actual efficiency of the cleaning sequence deployed.

Results and discussion

Pilot results: water permeability, pressure drop and salt retention

If we look at Figure 2a, monitoring water permeability shows more rapid fouling of line 1, running without the addition of any sequestering agent, compared with the other two lines. In all, after 63 days of filtration, the water permeability of line 1 suffered an almost 60% drop as opposed to barely 10% for lines 2 and 3. The development of water permeability for line 1 is broken down into two phases: a very slow decrease during the first twenty days of filtration followed by a more rapid drop once the fouling process had started. Against this, the water permeability of lines 2 and 3 decreased slowly and consistently. The addition of a sequestering agent delayed, by more than 40 days, the onset of a drop more quickly than the rate of permeability, which was triggered once a specific quantity of deposit was present. What is more, the fact that there was no difference in behaviour between the two doses of antiscalant tested, showed that, on the one hand, with respect to the quality of the water undergoing treatment during the summer of 1999 (Table 1), the antiscalant would have an effect by virtue of the threshold effect, and, on the other, the dose of 1 mg.L^{-1} was sufficient despite the fact that the dose recommended by the manufacturers of this product for treating the water of Méry-sur-Oise was 2.1 mg.L^{-1} .

Table 2 Operating conditions

	Standard test	Cycle 1
Drinking water	CaCl_2 (500 mg.L^{-1})	2nd stage concentrate
Temperature	25°C	$20\text{--}24^\circ\text{C}$
Feed rate	434 L.h^{-1}	200 L.h^{-1}
Conversion rate	15% (for one module)	15% (for one line)
Sequestering agent (dose)	–	Line 1: none Line 2: 1 mg.L^{-1} Line 3: 3 mg.L^{-1}

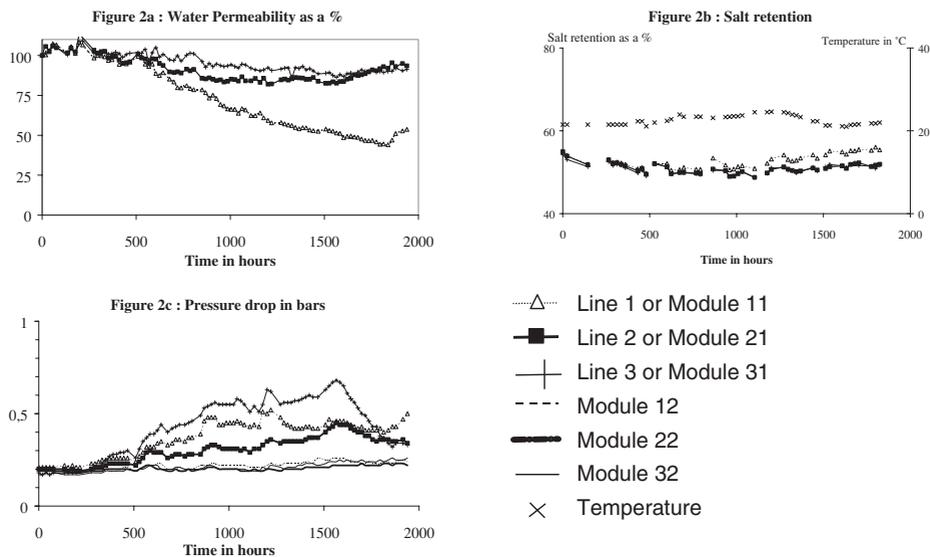


Figure 2 Permeability, loss in longitudinal load and salt retention

If we now look at Figure 2b, showing the development of salt retention, calculated on the basis of conductivity measurements, the three lines showed identical behaviour with salt retention nudging 50% during the first 40 days of filtration. Line 1 then showed a moderate increase, as this was already subject to considerable fouling. This increase in salt retention can only be seen once the loss in permeability exceeds 40%. According to Amjad *et al.* (1990), the combination of these two phenomena reduces the permeability associated with increased salt retention, and would show that fouling was mainly due to a deposit of organic matter.

Monitoring the losses in longitudinal load per module (Figure 2c) shows that, irrespective of the line being examined, the first membrane acts as a “prefilter” for the second. The four increases of the greatest amplitude recorded after 576, 864, 1176 and 1464 hours of operation, coincide with the chemical regeneration of the nanofiltration pilot plant producing the “2nd stage concentrate”. In fact, it had already been decided during these extended stoppage periods, to supply the “three-way” pilot plant with filtered sandy water, which had undergone ozonation, so as to limit the chances of a biofilm developing. The use of sodium disulfite was prohibited so as not to change the nature of the deposit prior to the autopsies. However, according to Her *et al.* (2000), supplying the nanofiltration membrane with water that had undergone ozonation, could increase the risk of fouling by organic matter. In fact, the ozone has the characteristic of transforming a good fraction of hydrophobic organic matter (negatively charged) into hydrophilic organic matter. This hydrophilic fraction, which is positively charged, can be fixed far more easily to the nanofiltration membrane, which has a negative charge.

Analyses of foulants

The hypotheses concerning the nature of the predominantly organic deposit, conducted on the basis of water permeability and salt retention developments, have been confirmed by analysis of the cleaning water and autopsies of the modules placed in the first position on the line, which did not undergo chemical regeneration. Figure 3 shows the quantities of products deposited on the surface of the membranes and recovered by way of complete chemical regeneration, thereby combining a base phase and acid phase. Table 3 shows the chemical composition of fouling products analysed on the modules prior to regeneration. If we consider this figure and table, it can be seen, on the one hand, that the volume of

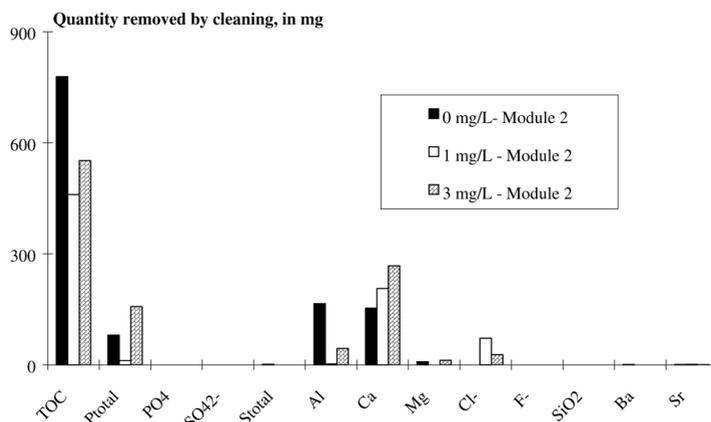


Figure 3 Analyses of foulants in the cleaning solutions used in modules 2

elements recovered is greater on the membrane of line 1, which was running without the addition of any sequestering agent, and, on the other, we see that the organic matter represents the majority of components. With respect to the cleaning solutions, it should be noted that the Total Organic Carbon (TOC) is only metered during the base phase, because acid washing is carried out with a citric acid solution, an organic compound. As for the mineral deposits, they contain essentially phosphorus, calcium and aluminium. The silicate, as seen in Table 3, is a mineral element whose presence in the deposit is quite marked (between 6 and 10 mg.m⁻²). However, it is not detected in the analyses of the cleaning water. The quantity of phosphorus deposited on the membrane surface increases with the sequestering agent dose. Thus, for line 3, the quantity of phosphorus analysed on the membrane surface was 17.35 mg.m⁻² as against 9 and 5 mg.m⁻² respectively for lines 1 and 2. This deposit could originate from the precipitation of the sequestering agent. In fact, Amjad *et al.* (1996) demonstrated that from a certain concentration of sequestering agent onwards, and given special pH, hardness and temperature conditions, the phosphonates can react stoichiometrically with the calcium ions to form calcium phosphonate salts.

The observations and analyses carried out using a scanning electron microscope meant that it was possible to measure the thicknesses of the various deposits for each line, which were 50 to 60 µm respectively for line 1 and 40 to 50 µm for lines 2 and 3, and to highlight two phenomena with respect to the chemistry of the fouling agents.

Table 3 Chemical composition (as a %) of the foulant of the three lines

Element	0 mg/L	1 mg/L	3 mg/L
Si	1.47	2.38	2.97
Al	3.50	0.44	1.47
Fe	0.60	0.29	0.17
Ca	4.13	3.72	4.29
Mg	0.23	0.28	0.78
Na	0.43	0.62	0.22
K	0.42	0.54	0.25
P	2.11	1.71	4.36
Total	12.90	9.98	14.51
Organic C	27.6	33.5	26.3
N	5.2	5.5	4.8
S	0.94	1.24	0.81
Total	33.74	40.24	31.91

The first phenomenon concerns the occurrence of mineral elements, which is all the more slowed down the higher the injected dose of sequestering agent. Hence, in the fouling agent of line 1, the mineral elements are detected right at the base of the deposit, followed mainly by aluminium, phosphorus and calcium and, to a lesser degree, by silicon and iron. Moving away from the membrane surface, other elements start to appear – magnesium in the intermediate area and chloride and sodium in the external area. Their relative frequency in relation to the layers of foulants seem to vary in relation to the volume of carbon. The mineral deposits seem to increase towards the top of the foulant. The foulant of line 2 contains significant amounts of mineral elements as detected from the end of the first layer (roughly 15 μm from the base) right to the top. Aluminium is the most abundant element, the volume of which also increases towards the top. Compared with this, phosphorus and calcium are very much in the minority. The mineral elements in the foulant of line 3, only take on a significant appearance in the external layer. Phosphorus is the most abundant mineral element, coming before aluminium and calcium, which are encountered in similar proportions.

The second phenomenon concerns the organic elements, carbon and sulfur; the accumulation of sulfur in relation to carbon is encouraged by the presence of the sequestering agent. Hence, in the foulant of line 1, carbon is always clearly predominant compared with sulfur over the deposit as a whole. With respect to the foulant of line 2, the carbon to sulfur ratio is more complex. Basically, the proportions seem to be equivalent; in the first 15 micrometres, the sulfur proportion is greater compared with that of carbon, only then to become negligible over the next 10 micrometres. In the outside layer, carbon is almost the exclusive organic element. In the foulant of line 3, these two elements show a clear differentiation in the deposit, broken down into two parts: in the lower section (20 μm), sulfur clearly predominates over the carbon but then gradually decreases. The carbon, on the other hand, is shown to be the exclusive organic element along the surface.

Efficiency of cleaning operations

The autopsies performed on the second modules of each line following chemical regeneration show that there is a residual deposit of a mean thickness of between 30 and 40 μm (Figure 4). It would essentially comprise organic matter, whereas in the case of aluminium, this was only present in traces.

Conclusions

A pilot plant, comprising three parallel lines, was constructed to operate under conditions that were representative of the third stage of nanofiltration. This unit was supplied with a

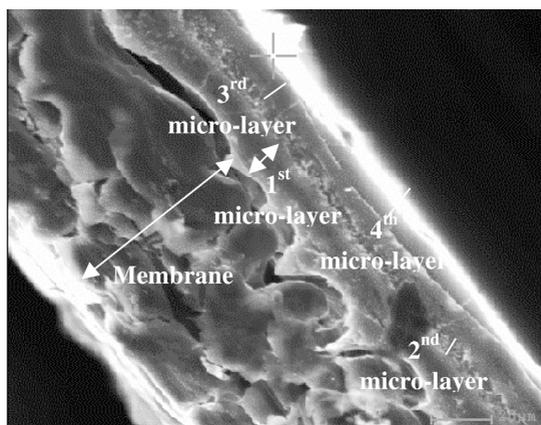


Figure 4 Section view of the cleaned membrane of line 1

2nd stage concentrate, produced by a second pilot plant running without the addition of a sequestering agent. Each of the three lines had its own sequestering agent injection station. It was therefore possible to compare the three different product types or three different doses of the same product.

The nanofiltration cycle was executed by adding the same sequestering agent in three different doses: 0, 1 and 3 g.m⁻³ respectively. The purpose of this test was to qualify the procedure and ensure the correct coincidence between the anticipated and actual results. This first test confirmed that the use of a sequestering agent in the treatment of the water of Méry-sur-Oise was essential. In fact, the water permeability of membranes operating without a sequestering agent, recorded a drop of almost 60% in two months, against a moderate drop of approximately 10% for the other two lines. The similar behaviour of the two lines injected with the sequestering agent showed that, given the quality of the water treated, the threshold effect action of active substances was predominant. However, this result would have to be confirmed by additional tests.

Combining the pilot studies and membrane autopsies to include a global analysis of the fouling and observation of the cross sections of the membranes under the scanning electron microscope, provided us with very precise information on the genesis and deposit stratification in relation to the nature or dose of sequestering agent used. It transpired that the antiscalant has very limited action on the organic matter deposit and that the composition of the mineral deposits depends on the dose of the sequestering agent being studied. This test demonstrated that the use of too high a dose of sequestering agent, containing phosphonates, could lead to calcium phosphonate salt precipitation.

Autopsies were performed on the modules following cleaning. These showed that the sequence of chemical regeneration is not completely efficient, especially with regard to organic deposits. Monitoring membrane performance after cleaning (water permeability and salt retention) would not seem adequate to assess the efficiency of cleaning.

To conclude, this study allowed us to develop a new method of evaluating the performance of sequestering agents under deposit-forming conditions very similar to those encountered in an industrial plant. Obviously the response time following testing is long (several weeks) but combining the pilot study with membrane autopsies produced very precise results on the onset of scaling along the membrane surface and on its nature, in relation to the product and/or dose tested. Transposing the results to industrial level should be feasible without great problem.

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