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Towards zero liquid discharge in the presence of silica: Stable 98% recovery in nanofiltration and reverse osmosis

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ABSTRACT

Silica scaling can be a limiting factor for membrane treatment at very high recoveries. In this work the feasibility of reaching very high recoveries (⩾98%) was investigated in a pilot plant consisting of cation exchange pretreatment, nanofiltration (NF) and reverse osmosis (RO), with pretreated ground water as feed water, with no aluminum detected. Experiments were carried out at total recovery (NF + RO) of 98% and 99% and with the addition of two different antiscalants at 99% recovery. 98% recovery was possible during 23 days of operation with only a minor decrease in the membrane permeability. At 99% recovery SEM–EDX analysis showed that silica and ironsilicate scaling occurred in the RO membrane, and strongly decreased the membrane permeability. The addition of antiscalants to the pilot plant did not prevent the occurrence of scaling. The laboratory beaker experiments did not prove the efficiency of the antiscalants either. The mean residence time of water in the pilot plant was estimated at 1 h. The occurrence of scaling in the presence of antiscalants can be attributed to factors such as the long residence time in the pilot plant, which is probably longer than the induction time, and the relatively high concentration of particulate iron in the feed water.

1. Introduction

Water treatment by nanofiltration (NF) and reverse osmosis (RO) can remove many pollutants from water in a single treatment step. Three main drawbacks to the current state of the art use of spiral wound NF and RO are fouling, energy consumption and the production of concentrate [1–4]. When bivalent cations are absent (for example after removal by cation exchange), silica is one of the main limiting factors when trying to reach high recovery in reverse osmosis [5,6]. Silica has a solubility of about 100–150 mg/L, but the solubility decreases in the presence of other compounds such as aluminum or iron. For example, if the water contains trace amounts of Al^{3+}, aluminosilicate scaling will occur before silica scaling becomes a problem [7,8]. In previous research in a high recovery system consisting of ion exchange, nanofiltration and reverse osmosis, we showed that a total recovery higher than 94% resulted in severe scaling of the RO membrane. The scaling was composed of silica, Fe and Al. The scaling was thought to be due mainly to the presence of particulate Al-containing compounds, which act as a seed for silica scaling [7,8]. In the absence of such a particulate Al-containing compound, silica might remain in solution and permit higher total system recoveries.

Strategies to control or prevent the occurrence of silica scaling are either the removal of silica from solution [9–12] or the addition of dedicated silica antiscalants [13–15]. Precipitation with Al^{3+} is a very efficient method to remove dissolved silica, but residual aluminum must be as low as possible when membranes are used subsequently, to prevent the possible occurrence of aluminosilicate scaling. Several researchers have investigated the effectiveness of antiscalants against silica scaling. Antiscalants can work as inhibitors, preventing crystals to form or modifying the crystal structure, or as dispersants, preventing scale particles to aggregate and grow [16]. Three methods to test antiscalants are: laboratory beaker experiments [16], laboratory scale membrane flat sheet tests [17] or directly in a pilot plant with spiral wound membranes [13]. While the third method is the most reliable, the other two are faster and cheaper, and they are usually performed prior to pilot plant operations to try to discern between potential antiscalants. In the

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case of silica, which typically crystallizes slowly at low supersaturation [18], all three methods do not necessarily represent conditions of full scale plants. Translation of the obtained results at small scale to full scale is far from straightforward, and the results should be critically analyzed. When using the pilot test method, for instance, it is important to take into account the desired configuration of the system, which can be either (i) single pass or (ii) recirculation. The residence time distribution (RTD) differs substantially for the two configurations, and it is an important parameter to consider when dosing antiscalants. While a single pass system configuration typically has a mean residence time in the order of a few seconds [19–21], recirculation systems can have considerably larger residence times.

In this paper we present different experiments with a pilot plant at high recovery, 98% and 99%, using tap water with high silica content and no Al detected. Two of the experiments were performed with the addition of two commercial general silica antiscalants, BD25 and OSM96. Laboratory beaker tests of the two antiscalants were performed as well, previous to the pilot testing. Data were statistically analyzed and compared with model simulations to determine the mean residence time of silica in the RO membrane. With the results obtained we can determine if 98% and/or 99% recovery is possible, which method is better to test antiscalants, and if the antiscalants are suitable to increase the recovery in such a system.

2. Materials and methods

2.1. Pilot plant

A pilot plant was constructed at KWR Watercycle Research Institute to carry out silica scaling research at high-recovery RO (see Fig. 1), consisting of cation exchange (CIEX), NF, and RO (with the RO implemented on the NF concentrate to increase feed water recovery). This pilot was installed at water treatment plant *Linschoten*, The Netherlands. The CIEX column was filled with approximately 50 L of a strongly acidic, gel-type CIEX resin in the sodium form with a capacity of 2 eq./L (Lewatit Monoplus S100, supplied by Caldic, Belgium). The membrane used for NF was NF-2540 (DOW-Filmtec) and the RO membrane was TW30-2514 (DOW-Filmtec). Both membranes had an active thin-film layer of polyamide layer on top of polysulfone as a porous support layer and were used in spiral wound configuration. More details of the pilot plant can be found elsewhere [7]. A 40 L tank and a dosing pump (Smart Digital DDA, Grundfos Nederland B.V.) were added to the installation to dose the antiscalants.

The recovery of the pilot as discussed here is the total water recovery of the two membrane stages: this does not include losses due to the needed water for regeneration of the CIEX resin (typically 1%).

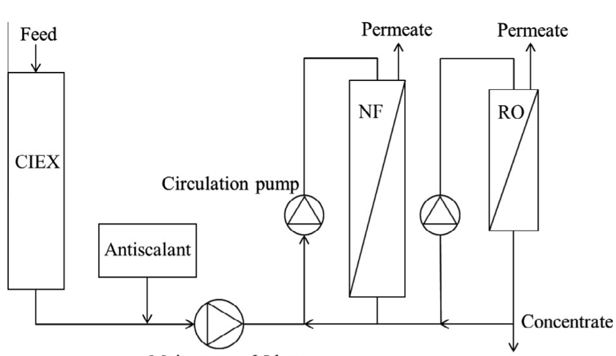

Fig. 1. Scheme of the pilot plant used in this research.

The membrane permeability, normalized pressure drop (NPD) (feed-concentrate) and salt passage, based on electrical conductivity measurements, (EC) were monitored for both membranes to investigate the beginning of scaling and other types of fouling. These process parameters were normalized for a proper control of the pilot plant and to be able to compare results from different experiments with [22]. The experiments were conducted between 13 and 23 days. In this time significant scaling formation was observed.

2.2. Residence time distribution analysis of the RO loop

In order to determine the average time silica particles reside in the pilot plant, a residence time distribution analysis was performed. The RO membrane is the most critical part of the system, because possible scaling species are concentrated substantially at the RO membrane. Therefore, the analysis is specifically aimed to determine the residence time distribution (RTD) in the RO loop. To determine the RTD, a data set was collected as follows: the RO concentrate valve was opened in order to introduce a step response in the conductivity measurements of the RO permeate.

Three methods were employed to obtain the mean residence time:

(a) Calculating statistical moments directly from data.
(b) Fitting the axial dispersion model to the response data.
(c) Fitting the exponentially modified Gaussian to the response data.

For the full derivation of the fits and used formulas, see Appendix A.

2.3. Water analysis

The pilot plant was installed at a location with high SiO_2 content (17 mg/L) but negligible amount of Al^{3+}. The feed water of the installation was tap water, which was produced from groundwater at water treatment plant *Linschoten* (Water Supply Company Vitens) by aeration and rapid sand filtration without post-chlorination. The quality of the feed water is given in Table 1. The water had an average temperature of 15 °C and pH 7.7. This water was selected due to its high silica concentration (17 mg/L SiO_2), which is in the range of typical surface and ground water. After CIEX pretreatment most surface and groundwater would have similar composition and would be ready for consumption.

The different water streams (feed water, CIEX treated (feed) water, the NF feed, NF permeate, NF concentrate, RO feed, RO permeate, and RO concentrate) (Fig. 1) were analyzed to determine the concentration of inorganic compounds including scaling salts and the rejection behavior of the membranes. With these analyses

Table 1
Feed water average quality and standard deviation.

	mg/L	STDEV
Ca^{2+}	17	2.14
Na^{+}	44	1.82
Mg^{2+}	1.31	0.17
Al^{3+}	0.00	0.00
K^{+}	0.62	0.13
Fe^{3+}	<0.01	0.00
Cl^{-}	9.76	1.82
HCO_3^{-}	172	3.42
SO_4^{2-}	0.44	0.20
PO_4^{3-}	0.06	0.02
SiO_2	17	0.75
DOC	1.58	0.04