



Implementation research of new phosphorus free antiscalant at an aerobic ground water RO plant

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ABSTRACT

Antiscalants are used to prevent scaling in the membrane filtration processes NF and reverse osmosis (RO). Current generation antiscalants are stable in the process equipment and slowly biodegradable in the receiving surface water. These types of antiscalants are optimized with respect to biological inertness in process equipment and biodegradable in a limited time frame in the receiving surface water. However, the phosphorus from these antiscalants can cause undesirable eutrophication in the receiving surface water and this will result in restrictions for concentrate disposal. A solution to this problem is the use of stable antiscalants without phosphorus groups. 4 Aqua BD25 is a phosphorous free carboxy methyl inulin based antiscalant that is first applied at a drinking water RO in Dinxperlo, the Netherlands. Before the application in practice, biofouling tests with membrane fouling simulator's had shown that biofouling was not aggravated by BD25. After those preliminary tests BD25 was dosed to one of the four stacks of the RO treatment and meanwhile the mass transfer coefficient (MTC) in the stack was checked with a Scale Guard on the concentrate. Beside that the MTC and normalized pressure difference of each stage of the stack was monitored and checked. The stable MTC shows that no scaling has occurred. After a half year of tests is decided to apply 4 Aqua BD25 at all stacks of the RO plant. 4 Aqua BD 25 is drinking water approved by Kiwa assessment on toxicological aspects and NSF standard 60. Right now a phosphorus and assimilable organic carbon free antiscalant is available for application.

Keyword: Antiscalant phosphorus-free CMI

1. Introduction

Antiscalants are used in drinking water production and the process industry to prevent scaling, usually in

membrane processes such as reverse osmosis (RO) and nanofiltration. Occurring when the solubility limit of sparingly soluble salts is reached, scaling causes precipitation to settle on the membrane surface. Antiscalants delay this process and allow higher

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concentrations of salts, resulting in greater water recovery. However, the underlying mechanism of scale control is poorly understood [1].

Antiscalants are stable in process equipment and slowly biodegradable in the receiving surface water [2]. On one hand, these antiscalants are optimized to biological inertness in process equipment, so they do not contribute to biofouling [3]. On the other hand, antiscalants are optimized to be biodegradable for a limited time in the receiving surface water. However, when broken down, the phosphorus component of most of these antiscalants can cause eutrophication in the receiving surface water. Increased awareness of this environmental impact is prompting more stringent concentrate disposal restrictions for phosphorus and nitrogen, resulting in Dutch and European legislation [4]. In some cases, phosphorus by-products in these antiscalants can contribute to biofouling, an effect known as P-limitation [5].

2. Carboxy methyl inulin (CMI) specifics

A possible solution to these problems is to develop stable and inherently biodegradable antiscalants without phosphorus groups. This article describes developing and testing a new phosphorus-free antiscalant based on CMI, which is shown in Fig. 1.

The properties of CMI as a threshold antiscalant for calcium (Ca), magnesium (Mg), barium (Ba), and strontium (Sr) have been known for more than a decade [6]. Aquacare Europe and Royal Dutch Cosun

joined forces in 2005 to develop the new antiscalant 4 Aqua BD25. Using CMI's known antiscalant properties as a starting point, experiments investigated the effects of different molecular weights, degrees of substitution, cross-linking, and incorporation of different active groups. Subsequently, the properties of resulting products were investigated.

Biodegradability tests in freshwater and seawater, Organisation for Economic Cooperation and Development (OECD) 302A and 306, indicated that the new product was inherently biodegradable for both environments. Testing also revealed that the product was not mutagenic. In addition, the OECD 117 test showed no bioaccumulation, and aquatic toxicity tests in freshwater and seawater indicated low toxicity as follows:

Freshwater

- Bacteria EC10 > 10,000 mg/L
- Daphnia EC 0: 2,000 mg/L
- Daphnia EC50: 5,500 mg/L
- Fish LC 0 > 10,000 mg/L

Seawater

- ISO 14669: Bacteria NOEC > 1,000 mg/L
- ISO 10253: Algae NOEC: 1,084 mg/L
- OECD 203: Fish NOEC > 1,000 mg/L

Also, because inuline is derived from the chicory root, the product's main source is renewable.

This green profile provided a good starting point for investigating the effects and possible side effects of the product as an antiscalant for membrane installations.

3. Tests and results

Because the relation of assimilable organic carbon (AOC) to biofouling in membrane installations is well-known [3], the first concern was the product's behavior. The first AOC tests KWR Watercycle Research Institute ranked the product low in contributing to biofouling.

Next, the product was ready for longer term biofouling testing by Westus Center of Excellence on a membrane fouling simulator (MFS), as shown in Fig. 2 [7]. The product passed the test, confirming the testing and certification facility's results. Next, the product was tested at the Netherlands drinking water company Vitens NV.

4. Bench-scale test

The first test on groundwater was carried out with one 4-in. bench-scale element at Vitens drinking water treatment plant Dinxperlo. This pilot was equipped

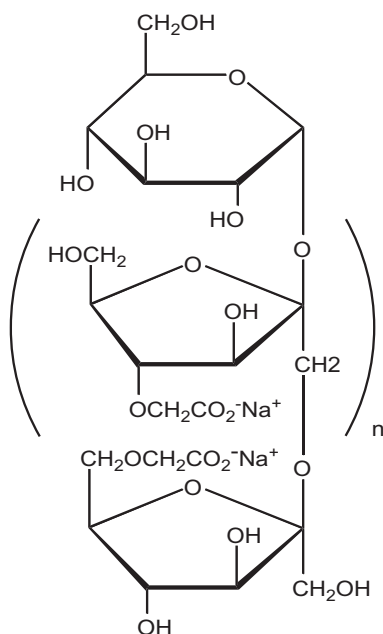


Fig. 1. Molecule of CMI.

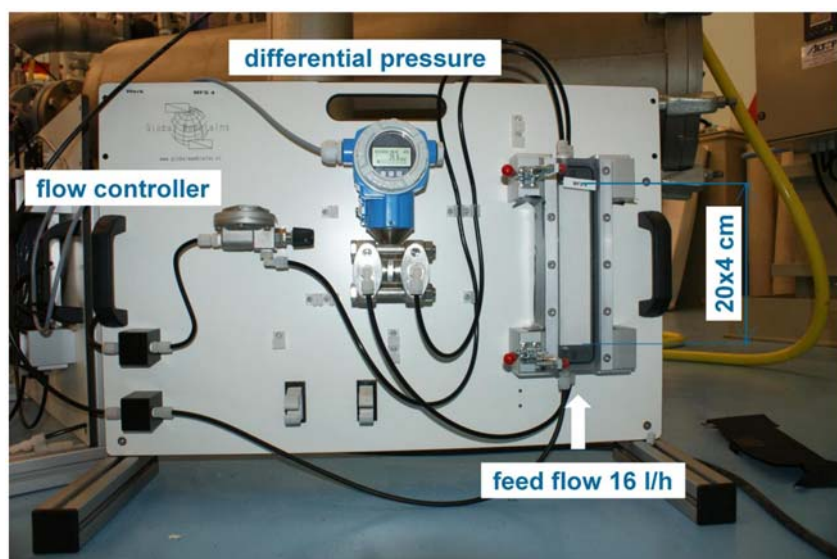


Fig. 2. MFS in operation.

with a recirculation mode and operated at 80% recovery. The dosage of the new antiscalant was 5.0 ppm. During the tests, the operation of pilot was stable and no scaling occurred. The threshold capacity was promising. This pre-commercial version of BD25 showed some biofouling, more recent versions of BD25 did not show this problem anymore, as explained in this paper.

5. MFS test

After the bench-scale test four MFSs were installed, before and after the cartridge filters, after dosing 2.5 mg/L of the new antiscalant BD25, and after dosing the reference P-free antiscalant, that was in use in Dinxperlo at that moment. The MFSs confirmed the efficiency of the cartridge filters and the results of the normalized pressure difference (NPD) readings before cartridge filter, indicating general fouling.

The graph of water without antiscalant and the BD25 line are to satisfaction flat. The pressure drop in the reference graph raised because of biofouling.

Work then began to procure assessment on toxicological aspects (ATA) approval of the new antiscalant for use in drinking water installations. The product subsequently received ATA and National Science Foundation ANSI standard 60 approval.

6. Full-scale test

During the last experiments at Vitens NV, one of four RO stacks (Fig. 3) at DWTP Dinxperlo was



Fig. 3. Scale Guard with RO stack 3 at Dinxperlo.

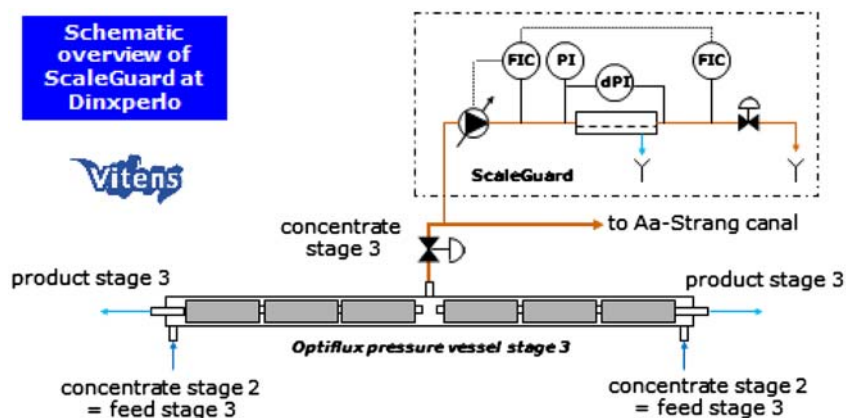


Fig. 4. Principle of Scale Guard.

treated with the new antiscalant; the remaining three stacks were treated with 2.5 ppm of another phosphorus-free antiscalant that is also in the development stage, here called reference. Each stack has a $87.5 \text{ m}^3/\text{h}$ feed flow of pretreated aerobic groundwater and operates at 80% recovery. The rough concentrate composition is: 590 mg/L Ca, 560 mg/L SO_4 , 0.5 mg/L Ba, 0.4 mg/L Fl, 65 mg/L SiO_2 .

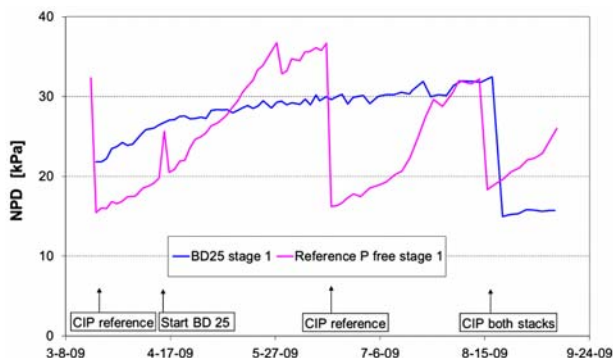


Fig. 5. Pressure drop in stage 1 of BD25 stack and in reference stack.

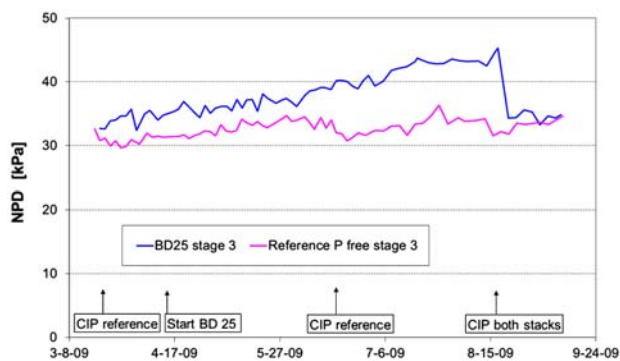


Fig. 6. Pressure drop in stage 3 of BD25 stack and in reference stack.

Besides, monitoring the NPD and mass transfer coefficient (MTC) at each stage of all stacks, the stack treated with the new antiscalant was equipped with the scale signal device Scale Guard [8] to check on scaling tendencies of the concentrate (Fig. 4). This unit generates a sensitive, early signal if scaling occurs in the element of the device.

During the next 6 months, the test showed a small increase in NPD, indicating a CIP frequency requirement of two to three times less than the alternative product (8 months instead of 3 months), as shown in Figs. 5 and 6.

In the last phase the dose rate was gradually decreased, to find the minimum effective dosage. MTC and NPD in Scale Guard and stack were observed closely. The MTC of the scale signal device showed no effect after 2 months of operation at lower dose rates (Fig. 7). The MTC remained stable after the dosage was finally set at 0.1 mg/L. Because the discharge line has a retention time of about 3 h and the relation between dosage and induction time proves a safe discharge, a practical dose rate of 1.25 mg/L is selected for the RO [9].

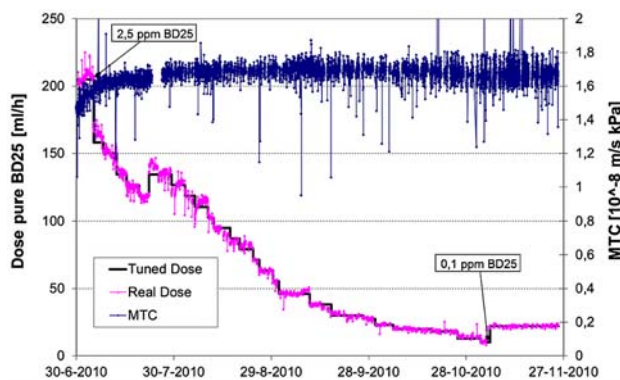


Fig. 7. Scale Guard results during reduction of dose of BD25.

During the research recovery was not increased for environmental discharge reasons.

7. Conclusions

After operating for 6 months with the RO stack, the results were satisfying. In October 2009, it was decided to apply the new antiscalant at all four stacks of the RO plant at a dosing rate of 1.25 mg/L. CIP procedures decreased from 4 times/year to once every 15 months.

With the introduction of BD25 Vitens safes annual € 40,000 on CIP and antiscalant costs for the production of 1.6 Mm³/year permeate.

The new anti scalant's induction time increases when the dose level is increased. The new antiscalant was far more effective than expected. Now a phosphorus and AOC-free antiscalant is available for application with a green profile. The effect of the new antiscalant in a seawater plant needs to be confirmed.

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References

- [1] D. Hasson, R. Semiat, D. Bramson, M. Busch, B. Limoni-Relis, Suppression of CaCO₃ scale deposition by anti-scalants, *Desalination* 118 (1998) 285–296.
- [2] S. Lattemann, T. Hopner, Environmental impact and impact assessment of seawater desalination, *Desalination* 220 (2008) 1–15.
- [3] J.S. Vrouwenvelder, S.A. Manolarakis, H.R. Veenendaal, D. Van der Kooij, Biofouling potential of chemicals used for scale control in RO and NF membranes, *Desalination* 132 (2000) 1–10.
- [4] M.M. Nederlof, J.A.M. Van Paassen, R.C.M. Jong, Nanofiltration concentrate disposal: Experiences in The Netherlands, *Desalination* 178 (2005) 303–312.
- [5] D. Van der Kooij, W.A.M. Hijnen, E.R. Cornelissen, J. Agtmaal, K.J. Baas, G. Galjaard, Elucidation of membrane biofouling processes using bioassays for assessing the microbial growth potential of feedwater, in: *Proceedings of the AWWA Membrane Technology Conference*, Tampa, FL, 2007.
- [6] D.L. Verraest, J.A. Peters, H. van Bekkum, G.M. van Rosmalen, Carboxymethyl inulin: A new inhibitor for calcium carbonate precipitation, *J. Am. Oil Chem. Soc.* 73 (1996) 55–62.
- [7] J.S. Vrouwenvelder, S.M. Bakker, M. Cauchard, R. LeGrand, M. Apacandí, M. Idrissi, S. Lagrave, L.P. Wessels, J.A.M. Van Paassen, J.C. Kruithof, M.C.M. Van Loosdrecht, The membrane fouling simulator: A suitable tool for prediction and characterisation of membrane fouling, *Water Sci. Technol.* 55(8–9) (2007) 197–205.
- [8] C.A.C. Van de Lisdonk, J.A.M. Van Paassen, J.C. Schippers, Monitoring scaling in nanofiltration and reverse osmosis membrane systems, *Desalination* 132 (2000) 101–108.
- [9] L. Boels, G.J. Witkamp, Carboxymethyl inulin biopolymers: A green alternative for phosphonate calcium carbonate growth inhibitors, *Cryst. Growth Des.* 11 (2011) 4155–4165.