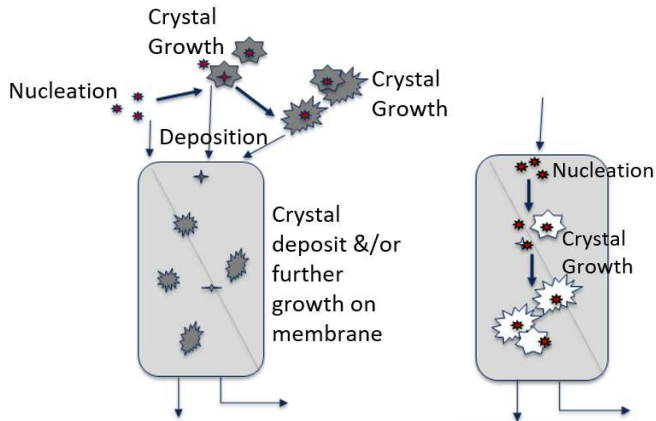


CONTRISOL: Concentrates from drinking water treatment - solutions for overcoming the technical, legal and economic obstacles when using NF/RO processes in drinking water treatment



Mechanism of homogeneous (left) and heterogeneous (right) crystallisation in membrane processes

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Introduction

Drinking water treatment using nanofiltration (NF) and reverse osmosis (RO) is primarily carried out to remove hardness, other inorganic components and trace organics. NF/RO produce different quantities of retentate stream with a higher concentration of the separated substances. Antiscalants, predominantly phosphonates and carboxylates, are dosed to avoid precipitation of salt. In recent years, the competent licensing authorities have viewed the discharge of concentrates into a water body increasingly critically, especially when concentrates contain high concentrations of anthropogenic substances, including those added during the treatment process (antiscalants). Since the refusal of a discharge permit for the concentrates is usually synonymous with withdrawal from the NF/RO process, solutions are required, which secure the use of this technology.

Research Goals

The aim of this project is to develop reliable tests to assess the efficacy of antiscalants (AS) and their ingredients, depending on the respective conditions of the membrane treatment process. This should serve to identify effective antiscalant products or mixtures, along with their suitable concentrations. Additionally, insights into the working mechanism of antiscalants against different scalants are obtained.

Approach

Laboratory tests on the effectiveness of antiscalants against sulfate and carbonate salts have been conducted. A batch test for the evaluation of homogeneous scaling in the water phase has been carried out using a static stirred-beaker setup. Induction time (nucleation time) based on turbidity increase is the key parameter evaluated during the experiments. In addition to the stirred beaker setup, commercial RO membranes have been operated in a lab-scale RO test with the similar dosage of the antiscalant, to verify the antiscalant effectiveness from the batch test. The lab-scale RO test with cross-flow filtration conditions provides results closer to real application.

Recent Results

After CaSO_4 scaling (see results in report 2022), CaCO_3 scaling was investigated along with the effect of commercial RO antiscalants (PAA, PAA+DTPMP, DTPMP, PBTC, ATMP) widely employed in drinking water treatment plants in Germany. The stirred beaker set-up was used with supersaturated carbonate solution (33 mM NaHCO_3 und CaCl_2) and 0.5 mg/L antiscalant based on total solids (TS), stirred continuously with a magnetic stirrer. The turbidity was continuously monitored. The induction time of the experiments was defined as the time in which the turbidity increased by 1 NTU since the beginning of the experiment and reflects the time needed for the development of first scaling crystal nuclei after supersaturation [Benecke et al. 2018].

The induction time determined using the batch setup for 33 mM carbonate solution with 0.5 mg/L of different AS, showed that AS based on PBTC und ATMP have the highest induction times. Thus, these AS are suitable to prevent formation of carbonate nuclei. The AS based on DTPMP has the shortest induction time (19 minutes), not much higher than the blank without AS (11 minutes). A short induction time theoretically translates to an unsuitable antiscalant for the investigated type of scaling.

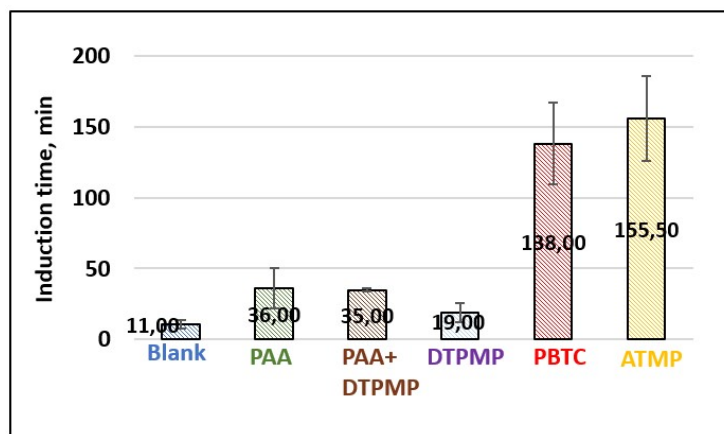


Figure 1: Induction time at 1 NTU for 5 commercial antiscalants with 33 mM NaHCO_3 und CaCl_2 + 0.5 mg TS/L AS in stirred beaker setup at $T \approx 11^\circ\text{C}$ (n=2)

The lab-scale high-pressure plant was operated with a 140 cm^2 cell with flatsheet CR100 RO membrane (DuPont) under recirculation mode (without feed spacer) at constant transmembrane pressure (TMP) 25 bar, with 22 mM NaHCO_3 und CaCl_2 as feed and cross-flow velocity of 0.1 ms^{-1} . Antiscalant dosage of 0.5 mg/L based on total solid (TS) content was used to compare effectiveness of the active ingredients of the AS. All experiments were carried out at a temperature of 11°C .

As seen in Figure 2, the permeate flux decreases rapidly in the test without AS. In the test with AS based on ATMP or PBTC the permeate flux is stable, indicating good performance of the antiscalant in accordance with the stirred-beaker setup. The tests with PAA- and PAA+DTPMP-based AS also show a stable permeate flux (after 600 min). This is unexpected because of the short induction time in the stirred beaker setup. Microscopic analysis (scanning electron microscope) of the scaled membrane surface from the tests shows dispersed carbonate crystals. These AS act via dispersion. The carbonate nuclei are quickly formed (short induction time), but the small crystals formed stay in suspension in the solution and do not form layers on the membrane surface that cause permeate flux decline.

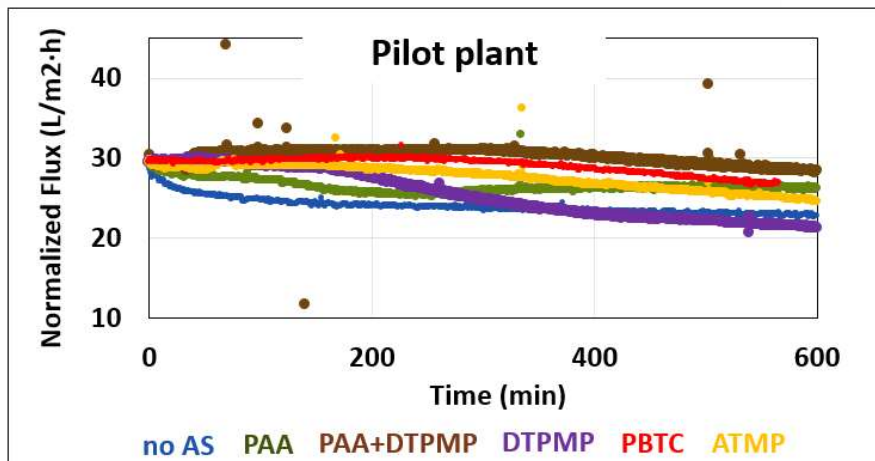


Figure 2: Flux behaviour in the pilot plant for 5 commercial antiscalants with 6 L of 22 mM NaHCO₃ und CaCl₂ + 0.5 mg TS/L AS as feed, constant TMP =25 bar, recirculation mode, cross-flow velocity=0.1 ms⁻¹, T ≈ 11 °C

Conclusion and Outlook

The presented work in the project KonTriSol aims to develop a suitable test to easily assess the effectiveness of scale inhibiting substances. It also helps to understand how antiscalants interact with different scalants at different dosages and subsequently inhibit scaling. The stirred beaker tests are sometimes associated with a high standard deviation since they are extremely sensitive to changes in hydrodynamic conditions. Further, the test is limited by its ability to adequately replicate NF/RO filtration conditions, but could nonetheless, potentially be useful as pre-determination step for antiscalant selection.

Project Partners

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