1.7 SafeRO: safe and legally compliant application of antiscalants in drinking water treatment using reverse osmosis and nanofiltration

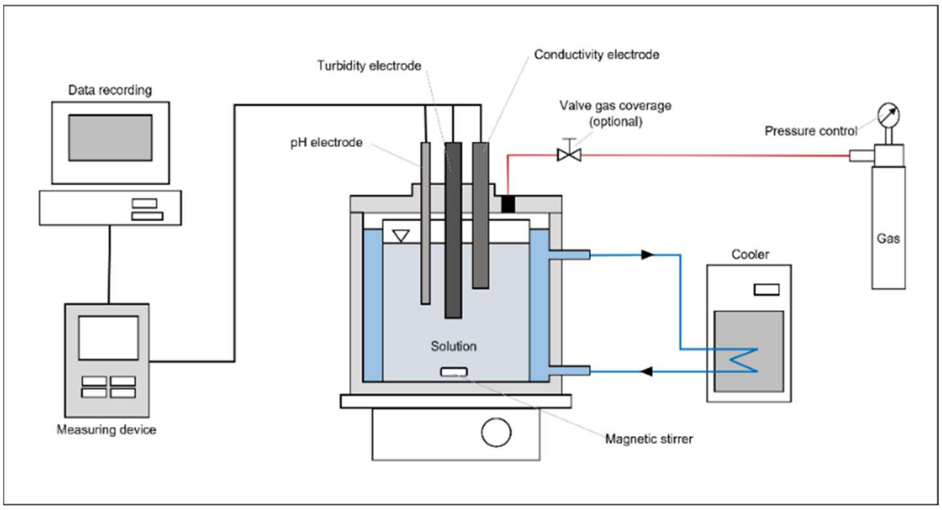

Figure 1: Lab scale set-up for investigating homogeneous scaling

Project Duration

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DVGW-Project No.:

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Introduction

Drinking water treatment by nanofiltration (NF), low-pressure reverse osmosis (LPRO) and reverse osmosis (RO) is widely used to remove hardness as well as other inorganic and trace organic compounds. In Germany approx. 90 facilities utilize NF/RO membrane processes while usually dosing antiscalants (AS) into the Seed stream to prevent salt precipitation and inorganic membrane fouling. Commonly used AS formulations are based on phosphonic acids (e.g. ATMP, DTPMP, PBTC), with a growing shift toward phosphorus-free products containing polyacrylic acids (PAA) as well as mixed formulations. More recently, so-called “green” AS derived from plant-based polymers, such as sodium carboxymethyl inulin (CMI), have entered the European market.

However, recent research has shown that the use of antiscalants in drinking water treatment is associated with several challenges. Residual concentrations of all AS types currently authorized under the § 20 list of the German Drinking Water Ordinance (P & PAA) have been detected in permeates or drinking water from associated systems. These residuals may be transformed into potentially harmful by-products in downstream treatment steps, such as disinfection. As part of the process concentrate, there are further potential environmental risks such as the eutrophication of natural waters in the case of phosphorous-based AS. A detailed analysis of a PAA-based formulation showed a substantial fraction of low-molecular-weight components that potentially can pass through NF/RO membranes more easily. Laboratory studies suggest that these low-molecular-weight fractions do not effectively inhibit salt precipitation and thus do not contribute significantly to scale control.

Research Goals

SafeRO aims to close existing knowledge gaps regarding the use of antiscalants, with a emphasis on regulatory aspects relevant to real-world applications. For the project partner DVGW-TUHH, the research focuses on three key aspects:

- Effectiveness: Evaluation of the AS efficacy in preventing scale.
- Passage: Assessment of the extent to which AS pass through membranes.
- Bioavailability: Determination of the bioavailability of the AS.

The research concentrates on phosphorus-free antiscalants, specifically polyacrylic acids (PAAs) of various chain lengths, as well as the plant-based “green” antiscalant CMI. The overall objective of the project is to develop recommendations for adapting DVGW regulations on RO/NF membrane filtration. These adjustments will be aligned with the Drinking Water Ordinance (§ 20 list) and relevant EU regulations in close cooperation with the UBA.

Approach

Laboratory experiments are conducted to evaluate the effectiveness of antiscalants in preventing the formation of sulphate and carbonate scale. A batch test is performed using a static, stirred-beaker setup to assess the potential for homogeneous scaling within the aqueous phase. Here the so-called induction time indicated by an initial increase in turbidity, serves as the key evaluation parameter. With the laboratory setup an isolated assessment of the antiscalants' effectiveness against homogenous scaling is possible. To further investigate and validate the results, experiments with RO, LPRO and NF membranes are conducted in a lab-scale RO pilot plant thereby including additional factors such as heterogenous scaling on the membrane. This approach provides verification under practical filtration conditions and also offers insight into the passage of antiscalants through the membranes.

Recent Results

Results on the antiscalant efficacy of various commercial antiscalant products against homogeneous $CaCO_3$ and $CaSO_4$ scaling in the beaker setup are presented in Figure 1. As an experimental water matrix basis, continuously stirred 33 mM carbonate and 68 mM sulphate solutions are used. The corresponding saturation indices are SI = 2.06 and SI = 0.72, respectively. During the experiments, pH, electrical conductivity and turbidity are monitored. As mentioned, the key parameter for evaluating antiscalant performance is the so-called induction time. The induction time is defined as the initial increase in turbidity by 1 NTU and reflects the time required for the formation of the first scaling crystal nuclei after the start of the experiment under supersaturated conditions. A longer induction time correlates with a higher effectiveness of the investigated product.

As a first step, three commercially available antiscalant products were examined. Each of them represents one of the main chemical groups studied: an ATMP-based product as a phosphorus-containing antiscalant, and CMI- and PAA-based products as phosphorus-free antiscalants. As shown in Figure 2, all of them significantly increase the induction time for both carbonate and sulphate scaling compared to the control without any antiscalant. The ATMP-based product stands out with very high effectiveness against homogeneous calcium carbonate scaling. The phosphorus-free products do not perform as well in comparison, although they still extend the induction time by a factor greater than eleven - relative to the control. For homogeneous calcium sulphate scaling, the CMI- and PAA-based products perform notably better, achieving induction times more than twice of those of the phosphorus-containing ATMP antiscalant. In terms of pure effectiveness, the polyacrylic acid-based antiscalant outperforms the chicory root-based CMI product.

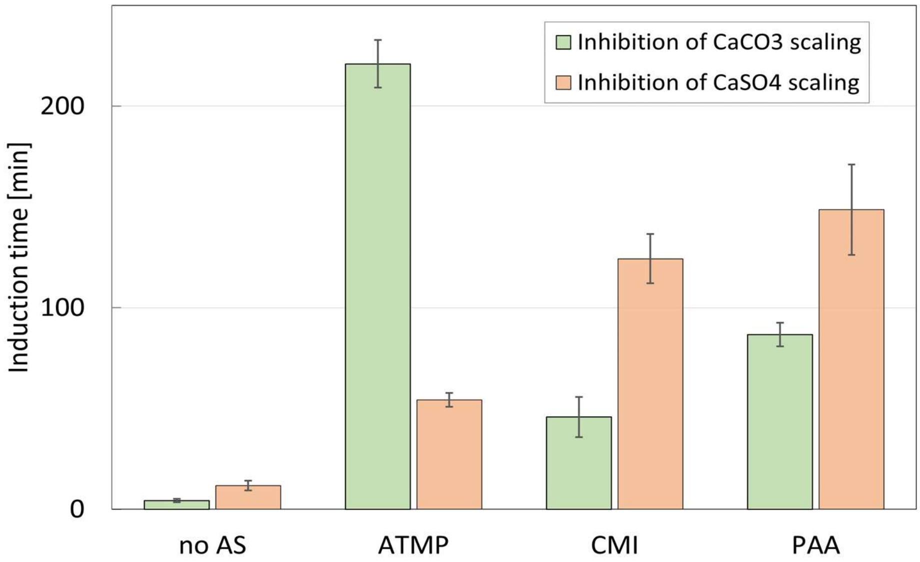

Figure 2: Induction time for various commercial AS products against a 33 mM carbonate & 68 mM sulphate solution (SI = 2.06 & 0.72; AS-Dose: 1 mg_{TS}/L, T = 11°C, n = 3)

Further investigation of the relationship between the polymer chain length of polyacrylic acids and their antiscaling performance was carried out. Seven pure CAS-listed PAA substances with different average molecular weights were examined analogue to the described method. A strong correlation between efficacy and chain length could be demonstrated, with a peak performance against $CaCO_3$ scaling in the range of approximately 2,500–5,500 Da.

Conclusion and Outlook

The present study is part of the ongoing project SafeRO aimed at investigating phosphorus-free antiscalants and providing recommendations for regulatory guidelines concerning RO/NF filtration. Although it does not serve as a comprehensive representation of real-world operating conditions, the stirred beaker setup functions as a tool for the comparison of antiscalant effectiveness against homogeneous scaling. Within the described experiments, all tested antiscalants significantly delayed $CaCO_3$ and $CaSO_4$ scaling, with ATMP showing the highest efficacy against $CaCO_3$ and PAA providing the best overall performance among the phosphorus-free products. For PAA, performance against $CaCO_3$ scaling peaked at intermediate molecular weights of approximately 2,500–5,500 Da. Further investigations on this matter including membranes and heterogeneous scaling are being conducted in an RO pilot plant.

Project Coordination

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