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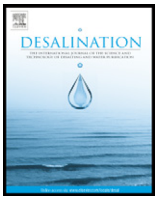

Accelerated desupersaturation of reverse osmosis concentrate by chemically-enhanced seeded precipitation

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ABSTRACT

A two-step chemically-enhanced seeded precipitation (CESP) process was demonstrated for accelerated desupersaturation of antiscalant-containing, gypsum-supersaturated model solutions, which mimicked reverse osmosis (RO) concentrate from RO desalting of agricultural drainage water of high mineral scaling propensity. In the CESP process, $CaCO_3$ precipitation is first induced via lime dosing for antiscalant scavenging, followed by subsequent $CaSO_4$ precipitation via gypsum seeding for concentrate desupersaturation. It was demonstrated that lime-precipitated $CaCO_3$ particles were able to scavenge generic and commercial polycarboxylic-acid antiscalants, thereby facilitating subsequent $CaSO_4$ precipitation to progress with minimal retardation. The study demonstrated via a series of batch CESP cycles that gypsum particle recycling can sustain $CaSO_4$ precipitation, suggesting that a continuous CESP process could be feasible. Process analysis suggests that CESP can be significantly less chemical-intensive than conventional precipitation softening and, with its integration as an intermediate RO concentrate demineralization process, can enable desalination water recovery enhancement via secondary RO desalting. For the present case of gypsum-saturated RO feed water, enhancement of overall water recovery from 63% up to 87% or higher appears to be feasible. The study suggests that there is merit for developing a continuous CESP process for high recovery RO desalting of brackish water of high gypsum scaling propensity.

1. Introduction

Advances in reverse osmosis (RO) technology over the past three decades have led to a significant reduction in the production cost of water desalination [1]. Brackish water desalination, however, is often challenging because of the high costs associated with residual RO concentrate management, especially at inland locations [1–3]. The integration of intermediate concentrate demineralization (ICD) with RO has recently been shown to be promising for concentrate minimization in a variety of brackish water desalting applications [4–9]. In this approach, a primary RO (PRO) step desalts the brackish source water up to a water recovery level just below the threshold of membrane mineral scaling. Mineral scale precursors are subsequently removed from the PRO concentrate in an ICD step, where sparingly soluble mineral salts are precipitated and are subsequently removed via solids–liquid separation (e.g., sedimentation and filtration). The ICD step lowers the mineral scaling propensity of the PRO concentrate, thereby enabling additional product water recovery from the PRO concentrate in a subsequent secondary RO (SRO) desalting step and reducing the final volume of the residual SRO concentrate waste.

Previous laboratory and pilot-scale studies have shown that chemical precipitation (e.g., precipitation softening) is an effective, but chemical-intensive ICD method [6,7]. For example, precipitation softening, which involves calcium ion removal as $CaCO_3$, can be applied for desupersaturating/undersaturating PRO concentrate with respect to calcium-bearing mineral scalants (e.g., gypsum ($CaSO_4{\cdot}2H_2O$) and calcium carbonate ($CaCO_3$)) [7]. Precipitation softening relies on the use of alkaline chemicals (e.g., $Ca(OH)_2$ (hydrated lime), NaOH, or Na_2CO_3) to generate the required PRO concentrate supersaturation for inducing and driving $CaCO_3$ precipitation. The alkaline chemicals are needed in (at least) stoichiometric amounts with respect to the desired extent of calcium removal, which in turn dictates the attainable level of overall water recovery enhancement via a subsequent SRO desalting step.

An alternative ICD method is seeded precipitation, which takes advantage of the fact that PRO concentrates are often already supersaturated with respect to the mineral scalants of concern, which may be stabilized by antiscalant carryover from the PRO desalting step. Inoculation of the supersaturated PRO concentrate with seed crystals can enable concentrate desupersaturation via precipitative seed crystal growth [5,10,11]. Because the pre-existing PRO concentrate supersaturation is utilized to drive precipitative crystal growth, coupled with the potential ability for recycling and reuse of seed crystals, seeded precipitation may potentially be a less chemical-intensive ICD method than chemical precipitation (e.g., precipitation softening via caustic,

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lime, or soda ash addition). However, antiscalant carryover from the PRO concentrate can significantly retard or inhibit crystal growth in seeded precipitation and can thus significantly lower the rate of concentrate desupersaturation [11].

The use of organic chelants, polymeric coagulants, or chemical/electrochemical oxidation for "disrupting" antiscalant action (i.e., by antiscalant scavenging or degradation) has been proposed as a pretreatment method for accelerating concentrate desupersaturation via seeded precipitation [11–15]. A potential concern in the application of these methods, however, is the carryover of residual additives and their byproducts (e.g., colloids, oxidation byproducts, microcontaminants, etc.) into downstream SRO operations and the final residual SRO concentrate. Studies have shown, for example, that coagulants and coagulation byproducts, even at trace levels, can adversely affect antiscalant treatment and cause RO membrane fouling [16–19].

The goal of the present study is to demonstrate that a sequential combination of chemical and seeded precipitation can balance chemical use with favorable precipitation kinetics in the demineralization of antiscalant-containing PRO concentrate—an approach termed hereafter as chemically-enhanced seeded precipitation (CESP). Focusing on high recovery desalting of agricultural drainage (AD) water of high gypsum scaling tendency as an illustrative test case, the present CESP approach to ICD involves an alkaline pretreatment step for antiscalant scavenging by precipitating $CaCO_3$ particles. This alkaline pretreatment step is aimed at minimizing antiscalant retardation of calcium sulfate ($CaSO_4$) precipitation in a subsequent gypsum seeded precipitation step, thereby accelerating concentrate desupersaturation. Relative to ICD via chemical precipitation (e.g., precipitation softening), CESP has the potential benefit of consuming alkaline chemicals (e.g., lime, NaOH, or Na_2CO_3) only to the minimal extent required for dissolved antiscalant removal by precipitated $CaCO_3$, without introducing chemical constituents that are foreign to typical RO concentrate solution matrices.

2. Chemically-enhanced seeded precipitation (CESP)

The present approach to chemically-enhanced seeded precipitation (CESP) applies to desalination concentrate solution that, due to the action of antiscalants (e.g., polycarboxylic acids, polyphosphonates, etc.), is initially stable at supersaturation with respect to the mineral scalant of concern. In general, the supersaturation level of RO concentrate, with respect to a mineral scalant x, is assessed in terms of a thermodynamic saturation index, $SIx = IAP/K_{sp,x}$, where IAP is the ion activity product and $K_{sp,x}$ is the solubility product for the mineral salt x (where x is either c: calcium carbonate (as calcite) or g: gypsum). As illustrated in Fig. 1 for the case of gypsum-supersaturated RO concentrate with lean bicarbonate content, concentrate desupersaturation via CESP involves two sequential steps: (1) alkaline pretreatment for antiscalant scavenging by precipitating $CaCO_3$ particles, followed by (2) gypsum seeded precipitation (GSP) for concentrate desupersaturation. In the first step of CESP, alkaline pretreatment is initiated by dosing with an alkaline chemical (i.e., lime, NaOH, or Na_2CO_3; Fig. 1) in order to elevate the RO concentrate pH and deprotonate bicarbonate ions present in the concentrate, thereby elevating the RO concentrate supersaturation with respect to calcite (SIc). The objective of this step is to induce rapid nucleation and growth (precipitative and aggregative) of $CaCO_3$ particles, leading to concomitant scavenging of antiscalants by these $CaCO_3$ particles [20–22]. The second CESP step (i.e., GSP) is initiated by inoculating the alkaline-pretreated RO concentrate with gypsum seed crystals (Fig. 1b) in order to induce $CaSO_4$ precipitation. The goal of the overall CESP process is to minimize dissolved residual antiscalant concentration to an extent that concentrate desupersaturation via $CaSO_4$ precipitation can occur with minimal retardation by antiscalants.

Antiscalant removal during active precipitation of $CaCO_3$ has been previously attributed to the entrapment of surface adsorbed antiscalant into the solid matrices of precipitating $CaCO_3$ particles, caused by epitaxial particle surface overgrowth and particle aggregation [20–22]. Surface adsorption is the first step to antiscalant scavenging with precipitating $CaCO_3$ particles. The extent of antiscalant scavenging, over a given time period, should therefore depend on the time-evolving total surface area of these $CaCO_3$ particles (i.e., total surface sites available for antiscalant adsorption), as well as the initial antiscalant concentration in solution (i.e., the initial adsorption driving force). The evolution of total surface area of $CaCO_3$ particles, in turn, depends on the rate of $CaCO_3$ particle nucleation, in addition to precipitative and aggregative growth rates, which are governed by the calcite supersaturation level in the solution (i.e., SIc) and thus the required alkaline dose (e.g., [23]). The evolution of the total surface area of precipitating $CaCO_3$ particles is also influenced by the initial antiscalant concentration in solution, given that antiscalants also retard $CaCO_3$ precipitation [21,22,24,25]. It is postulated that, for a given initial antiscalant concentration in RO concentrate, the extent of antiscalant scavenging by actively-precipitating $CaCO_3$ particles, and thus the residual dissolved antiscalant concentration remaining after alkaline pretreatment, are governed by the alkaline dose and pretreatment duration.

In the GSP step of CESP, the rate of concentrate desupersaturation will depend on the rate of $CaSO_4$ precipitation, which in turn is influenced by the gypsum supersaturation level post alkaline

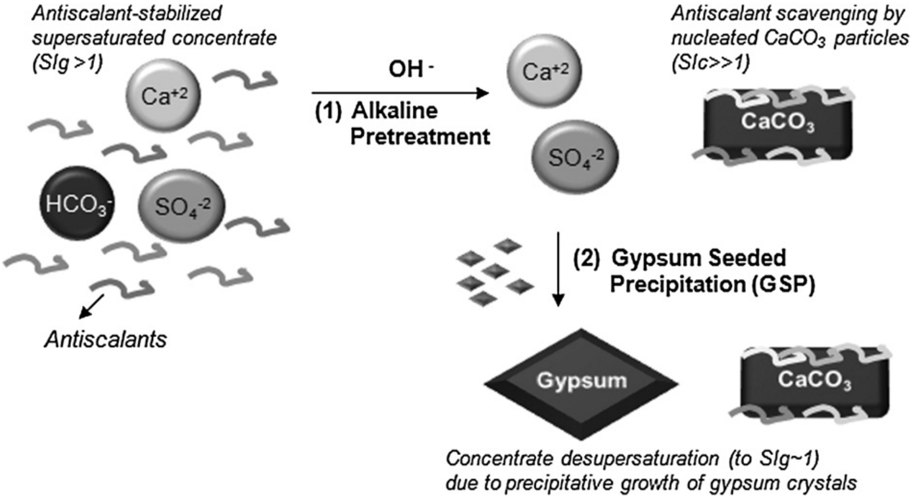

Fig. 1. Illustration of chemically-enhanced seeded precipitation (CESP) for desupersaturation of antiscalant-containing RO concentrate with high gypsum scaling potential. SIg: gypsum saturation index and SIc: calcite saturation index.