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A novel approach for SWRO desalination plants operation, comprising single pass boron removal and reuse of CO_2 in the post treatment step

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ABSTRACT

A different approach is presented for the operation of seawater RO desalination plants in which the boron concentration in the product water should not exceed 0.3 mgB/l. The approach is based on strong acid (either H_2SO_4 or HCl) dosage to the feed water to attain pH ~ 4.3, followed by CO_2 stripping and subsequently strong base addition to pH 9.00–9.25. At this high pH range, a high B removal efficiency is attained, and since the water is practically devoid of carbonate species, no $CaCO_{3(s)}$ scaling takes place, and pH elevation is limited by $Mg(OH)_{2(s)}$ precipitation, expected only at pH > 9.45. The approach enables operation in the absence of antiscalants. Furthermore, CO_2 stripping is effected in stripping towers in two steps: the high $CO_{2(aq)}$ concentration is first stripped by vacuum-operated stripping towers and the CO_2-rich air is used for dissolution of calcite in the post treatment stage. The remaining CO_2 mass is stripped to the atmosphere using blower-assisted stripping towers. This paper aims at introducing the new concept and providing "proof of concept". The paper addresses experimental and theoretical aspects of the proposed process, as well as engineering and economic evaluation. The proposed approach is shown to be both technically feasible and cost effective, as compared with conventional boron removal alternatives.

1. Introduction

Removal of boron species (B) from desalinated water is a significant component in the process design of many seawater reverse osmosis (SWRO) desalination plants. At concentrations above ~1.0 mg B/l, boric acid is known to damage various agricultural crops and plant species used in municipal gardening. For example, crops such as avocado and most citrus types are sensitive to B at the concentration range 0.5–0.75 mgB/l [1]. Therefore, although the world health organization (WHO) had recently updated up the guidelines for B concentration in drinking water from 0.5 to 2.4 mg/l [2] (due to strictly human health reasons), it is most likely (and also apparent from the results of recent international bids) that the demand for low B concentration (0.3–0.8 mgB/l) in desalinated waters will remain unchanged. Boron exists in natural fresh water as a weak acid with a thermodynamic pK value of 9.23. At pH values lower than the pK, the protonated, neutral, boric acid species ($B(OH)_3$) dominates, while above it the negatively charged borate ion ($B(OH)_4^-$) prevails. In seawater, which usually contains ~5 mg B/l, the apparent pK value is ~8.6 due to seawater's ionic composition [1]. The boric acid species, which dominates in natural seawater pH of ~8.2, is poorly rejected by the commonly available RO membranes. While the rejection of charged ions, such as Na^+ and Cl^-, is higher than 99%, practical B rejection using standard SWRO membranes is only ~65–80%, corresponding to ~0.9–1.8 mg/l B in the permeate [3]. Thus, either ion-exchange-based post treatment (PT) or the operation of a second (brackish) RO pass is typically implemented in order to meet the sometimes strict B regulations [1]. Application of a BWRO second pass includes dosage of a strong base to the first SWRO pass permeate, in order to elevate pH to 9.5–10.5, prior to its introduction into the membrane. The pH elevation diverts the boric acid species towards the borate ion, whose rejection by RO membranes is much more efficient. Ion exchange (IX) technology utilizes a resin with a high affinity towards B, which adsorbs $B(OH)_4^-$ at basic to neutral conditions. Strong acid is required for the regeneration of the resin and a strong base is required for neutralization thereafter [1]. Several process configurations were developed that make use of these technologies, including combinations of the two [1,3,4]. New boron removal approaches have also been recently suggested [5,6]. Cost approximations for B removal from RO permeates at the post-treatment stage [4,7,8], resulted in a roughly similar cost range, i.e. between 0.04$/m^3 and 0.1$/m^3 for either the IX- or BWRO-based methods. While energy consumption is the major cost factor for the operation of BWRO B removal, consumption of chemicals is the most significant cost item associated with the IX approach. Cost evaluations

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for B removal sometime disregard permeate loss associated with the removal process. Such losses are responsible for a substantial increase in the product water cost, as shown in the cost assessment section at the end of this paper. The recovery value of the second pass is limited by brucite ($Mg(OH)_2$) and calcite/aragonite ($CaCO_3$) scaling, which is strongly pH dependent. However, pH elevation is necessary for effective B removal. Thus, an increase in the second pass recovery or B removal beyond the scaling limits requires additional dosage of costly antiscalants. Desalination of the 2nd pass brine carried out in order to increase the recovery value, as performed, for example, in the Ashkelon desalination plant in Israel, results in higher energy investment and larger footprint.

At this point in time only a few attempts for single pass B removal have been published. Field tests conducted by Redondo et al. [9] yielded B concentration of 0.79 to 0.86 mgB/l in the 1st pass permeate, using a high-rejection Dow membrane (SW30HR-380). Redondo's results conform to Koseoglu et al. [10], who investigated B rejection with different high B rejection membranes and reported 85–90% rejection at natural-pH seawater. Such approach seems impractical not only for reducing B to below 0.3 mgB/l, but even for attaining 0.75 mg/l B in the product water, because of instabilities associated with variations in temperature and seawater B concentration. Moreover, the latter authors reported a maximum of 30% recovery, while the practical higher recovery values are bound to reduce the total B rejection. Rejection of over 99% could be achieved by adjusting pH to 10.5 however, flux reduction due to chemical scaling occurred in their experiments after an operation time of merely 14 h. Dominguez-Tagle et al. [11] examined theoretically the potential for single-pass B removal for small desalination plants, by considering 14 commercial membranes. They concluded that with the most up-to-date high B rejection membranes, a high B removal ([B] < 0.5 mg/l in the product water) can be achieved at the expense of a 12% increase in energy consumption. A work done with a Doosanhydro membrane showed that by adjusting the seawater feed to pH 9.0, a total B rejection of 96% could be obtained [12]. No permeate flux reduction was observed during 45 day operation, although a laboratory experiment showed that $CaCO_3$ precipitated at this pH value even in the presence of antiscalants. SWRO operation at high pH was tested at full scale in the Larnaca SWRO desalination plant in Cyprus. The pH was elevated from 8.02 to 8.60 and 1st stage permeate B concentration was consequently reduced from 0.96 to 0.6 mgB/l. No antiscalants were added to the feed water and a thorough monitoring campaign showed that the membrane had not scaled; however, operation period lasted only five days [13]. Various configurations for seawater B removal were economically assessed as part of a work initiated by the U.S bureau of reclamation: Single-pass operation at pH 8.5 was found to be the most cost-effective alternative for arriving at a permeate concentration <1.0 mgB/l [14].

In the current work a new approach for B removal, applying a single SWRO pass, was suggested and evaluated. The process is aimed at separating boron species to attain B concentration <0.3 mgB/l in the product water, by using low-energy SWRO membranes. The idea is to elevate pH to beyond pH9, and at the same time avoid the risk of chemical fouling. Since the main solid that precipitates on the surface of SWRO membrane is $CaCO_3$ (mostly aragonite, sometimes calcite) and since the total inorganic carbon concentration (which contributes most of the seawater's alkalinity) in seawater is relatively low, the approach adopted was to almost completely divert the proton accepting species in seawater (i.e. CO_3^{2-} and HCO_3^-) to $CO_{2(aq)}$ by strong acid dosage and subsequently to separate and reuse a required portion of the CO_2 for dissolution of $CaCO_{3(s)}$ in the post treatment step. The rest of the CO_2 mass is stripped to the atmosphere. Once devoid of carbonate species, the pH of the feed water can be cheaply elevated to pH > 9, which allows attaining the required B removal percentage with no risk of $CaCO_{3(s)}$ fouling the membrane. The new approach is shown to be cost-effective compared to currently implemented post treatment alternatives. Apart from single-pass B removal the proposed approach has positive economic and technical repercussions on the post treatment stage, as detailed below. The aim of the current paper is to present the new approach and establish "proof of concept". Optimization studies are underway.

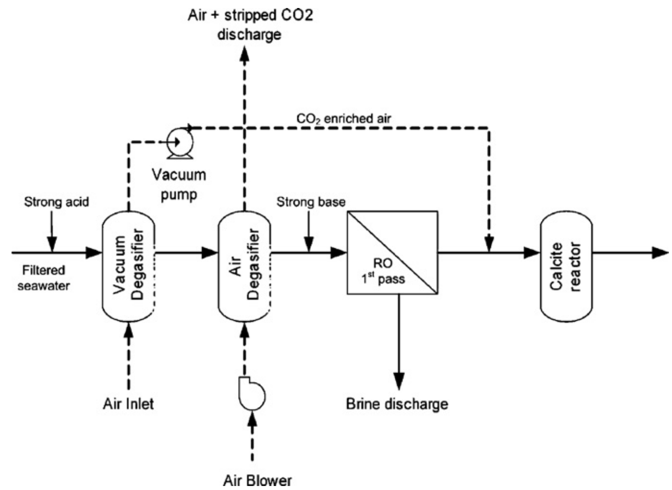

Fig. 1. Schematic of the proposed approach for single-pass B removal and CO_2 reuse in the PT step, an alternative approach to the operation of SWRO desalination plants.

1.1. Detailed process description

A schematic description of the process is shown in Fig. 1. The process begins with the acidification of the seawater feed to pH 4.3–pH 4.4, at which range the HCO_3^- concentration is reduced to below 1.0 mg/l. The acidified seawater, highly supersaturated with $CO_{2(aq)}$, is now subjected to a two-stage packed bed de-gasifying step (using conventional degassers). The first stage is aimed at removing 20–30% of the CO_2 mass by vacuum and a low air-to-water flow ratio (Q_g/Q_l,). The goal is to form an air stream rich in $CO_{2(g)}$ which will subsequently be reused for $CaCO_{3(s)}$ dissolution in the post treatment (PT) stage. The rest of the CO_2 mass is removed in the second degassing stage using an air blower and a high air-flow to water-flow ratio. The aim of this step is to reduce the inorganic carbon concentration (C_T) to below 4% of the original value in seawater (overall CO_2 removal in both stages >96%). After most of the carbonate system concentration had been removed, feed pH is raised to 9.0–9.25 by the addition of a relatively small amount of strong base, prior to entering the RO step. $CaCO_3$ scaling in the RO step is avoided due to the water's low to negligible C_T concentration, while $Mg(OH)_{2(s)}$, another potential scaling agent at this pH range, is intentionally maintained under-saturated. The permeate produced in the RO stage is mixed with the CO_2-enriched air from the vacuum (first) degassing stage, before it is transferred to the calcite dissolution reactor. That is, The CO_2-rich air is used to acidify the permeate stream, enabling calcite dissolution at a reasonable rate.

2. Materials and methods

2.1. Chemical equilibrium computer calculations

The PHREEQC software package [15] was used to simulate chemical processes in both raw seawater and desalination concentrate. Activity coefficients were calculated using SIT (Specific Interaction Theory) and Pitzer approaches (both integrated in the software's