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Boron evaporation in thermally-driven seawater desalination: Effect of temperature and operating conditions

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ABSTRACT

The volatilization of boron in thermal desalination processes, namely multi-stage flash (MSF) and air-gap membrane distillation (AGMD) was investigated for the first time. This phenomenon was observed at feed temperatures above 55 °C in both studied processes. In simulated MSF process with two feeds, model boric acid and Red Sea water, boron concentration in distillate increased with feed temperature increase from 55 °C to 104 °C because of the increase in boric acid vapor pressure. Salinity and pH were the main factors controlling boron evaporation. The achieved boron concentrations in simulated MSF process were consistent with those measured in distillate samples collected from commercial MSF plants. The AGMD process also revealed a strong influence of operating temperature on boron removal. However, unlike MSF process, the boron concentration in AGMD permeate decreased with the feed temperature increase from 55 °C to 80 °C due probably to increase in vapor production and corresponding permeate dilution. When AGMD was operated in concentrating mode at a constant feed temperature of 80 °C, permeate boron concentration increased with process time due to concentration polarization and membrane fouling. A 10% flux decline observed after 21 h was attributed to $CaCO_3$ scaling on the membrane surface.

1. Introduction and background

Boron is a transitional element between the metals and non-metals, and at concentrations below 22 mg/L, the predominant boron forms are boric acid [H_3BO_3] (predominates in acidic conditions) and borate ion [$B(OH)_4^-$] (predominates in alkaline conditions) [1]. The increase in temperature and salinity shifts the reaction equilibrium of boric acid – borate ion system towards formation of borate ions [2–4].

Boric acid is volatile at elevated temperatures according to the following equation [5]:

$$H_3BO_3(s) = H_3BO_3(g) \quad (1)$$

where (s) and (g) denote solid and gaseous phases of boric acid, respectively.

Brandani et al. [6] observed increase in vapor pressure over boric acid solutions with temperature increase concluding that evaporation of boron from boric acid solutions followed Henry's law. In a later study, Dickson et al. [3] investigated the combined effect of temperature and salinity on the boric acid – borate ion equilibrium and reported that at any given temperature, the values of equilibrium constants increased with salinity increase.

The variability of permissible boron concentrations in treated waters is based on health and environmental implications, boron occurrence and distribution in drinking water supplies, agricultural activities, and cost-efficiency of treatment technologies [7]. In general, countries which rely on freshwater as a major drinking water supply (*e.g.*, USA, Canada), have more flexible boron regulations as comparing to those which use seawater desalination for drinking and irrigation purposes (*e.g.*, Saudi Arabia) (Table 1).

Although the optimal boron concentration in irrigation water is in the range of 0.3–0.5 mg/L to ensure safe plant cultivation, some plants require lower boron concentrations to alleviate possible adverse effects [8]. The situation is more complicated in the arid and semi-arid areas of Middle East and Northern Africa (MENA) where the reduced boron leaching from the soils due to low annual rainfalls would promote boron accumulation in soils and may elevate boron uptake by the plants and crops [9].

1.1. Boron removal by thermal desalination

Over the past decades, seawater desalination has become a reliable and, in many cases, solitary technology of the freshwater production in

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Table 1
Drinking water standards in different countries.

Country/ Authority	Boron concentration (mg/L)	Reference and Remarks
WHO	2.4	Recommended guideline [6]
Saudi Arabia	0.5	SASA standard for bottled water (also used as a standard in drinking water distribution system) [7]
U.S. EPA	Not regulated	–
Minnesota	1	Recommended drinking water concentration [9]
California	1	State notification level [10]
Canada	5	The maximum acceptable concentration [11]
EU	1	Council Directive 98/83/EC [12]

countries which experience severe shortage of conventional water sources [10]. This encourages local authorities to extend the traditional thermal-based desalination technologies like multi-stage flush (MSF) and multi-effect distillation (MED), as well as augment the water supply by seawater reverse osmosis (SWRO), or by developing methods which combine membrane separation and thermal processes, *e.g.*, membrane distillation (MD). The MD process is based on the transport of water vapor through the micro-porous hydrophobic membranes due to transmembrane temperature difference [11]. Since the water vapor is the only component which is transported through the membrane, high rejections of ions, low molecular weight organics and colloids can be achieved [12,13]. MD does not require an intensive pre-treatment and offers better product quality compared to SWRO [14–17]. Another advantage of the MD technology is its lower heating regime as opposite to thermal evaporation where top brine temperature reaches 110 °C [18–20].

Due to variable boron drinking water standards across the world, it is important to ensure stringent freshwater quality. Depending on operating parameters, concentration of total dissolved solids (TDS) in the distillate from the thermal evaporation plants vary in the range of 5–50 mg/L [21], with Saudi Arabia setting a maximum TDS of 25 mg/L [22]. Khawaji et al. [18] emphasized that MSF plants could face constrains when brine droplets from flashing chambers are carried over with the vapor stream due to problems with the demister design, performance or its location within the evaporator, or inappropriate selection of anti-foaming agents. Moreover, due to extensive evaporation, the brine TDS is progressively increasing as brine is passing through flashing chambers which number could reach as high as 30 units [23]. As such, brine droplets, enriched with different seawater constituents, may enter condensing trays and reduce distillate quality. The existing research pertaining seawater desalination by conventional thermal evaporation reveals that neither boron volatility nor its distribution in distillate across the MSF stages as well as its overall removal efficiency and mechanisms remain a major research gap which has not been yet addressed.

Several studies investigated boron removal by the direct contact membrane distillation (DCMD), an MD process in which condensed vapor is continuously diluted into large volume of coolant solution [19,20,24,25]. Therefore, the concentration of boron in permeate is expected to be low due to the dilution effect. Hou et al. [24] reported high boron rejections (> 99.8%) from model solutions with the boron concentrations up to 1500 mg/L. In a follow up study [19], the authors found that concentration of boron in permeates was below 10 μg/L at low concentration factors (CF), but started increasing with further CF increase. Similarly to these studies, Boubakri et al. [20] observed the boron rejection was above 90% at 200 mg/L of feed boron concentration. When seawater was used as a feed, boron concentration in permeate reached 0.47 mg/L after 18 h of operation. Wen et al. [25] investigated the effect of inorganic salts addition on boron removal from radioactive water spiked with up to 5000 mg/L of boron. The authors reported that at 300 mg/L of $NaNO_3$, permeate boron concentration was less than 2 mg/L. However, the real boron removal values of all these studies are questionable due to consecutive dilution of the coolant water by condensed water vapor in DCMD where permeate is mixed with coolant. As such, the actual amounts of boron transferred through the membrane in DCMD process can be higher than the reported ones. Moreover, due to different operating parameters and lower corresponding fluxes, the boron removal patterns by other MD configurations can be quite different from those reported for DCMD.

In recent years, air gap MD (AGMD) configuration is being rapidly developed. In this process the vapor condensation is achieved within the air gap created between a condensation surface and the membrane while the coolant stream flows on the other side of the condensation surface [26]. The collected AGMD permeate is then a condensed pure water vapor. Furthermore, the low thermal conductivity of air promotes decrease in the heat conduction from the membrane feed side to condensation side [27]. The elimination of the dilution factor allows not only for accurate estimation of the amount of boron transferred to the permeate site from the feed solution, but also for elucidation of the boron removal mechanisms with respect to water matrices and operating conditions. To the best of our knowledge, no research has been reported up to date with respect to boron evaporation (removal) in AGMD and MSF. In the literature, boron removal efficiency has been studied by other technologies only, such as reverse osmosis, ion exchange and electrocoagulation [28].

The aims of this study were to fill the existing research gaps with respect to boron volatility in thermal-based desalination processes, namely MSF and AGMD, and to conduct a comprehensive study on evaluating the efficiency of boron removal by these processes under different operating conditions and water matrices and elucidating corresponding boron removal mechanisms.

To simulate MSF evaporation process, seawater was boiled at temperatures corresponding to different vapor pressures in a range of 55 °C–104 °C. The effect of pH on process efficiency was studied by conducting evaporation experiments in a pH range of 8.1–12.0 with boric acid solution at boron concentration corresponding to that of the Red Sea water. The quality of the distillate samples was than compared to that of distillate samples collected at different stages of commercial MSF plants located in the Red Sea and Gulf coasts.

We further determined the feasibility of boron removal by the AGMD process and investigated effect of operating conditions and solution chemistry on process performance and boron rejections. Firstly, we evaluated the effect of feed temperature in the range of 55 °C–80 °C on boron transport and water vapor flux. This was followed by estimating the effect of process time and feed concentration on boron removal and membrane fouling in a continuous AGMD process at a feed temperature of 80 °C. To investigate the effect of salinity on process performance, the water vapor flux and quality data from real seawater AGMD were compared with those obtained during AGMD process with boric acid solution under the same conditions.

The results of this study are expected to extend the existing knowledge with respect to removal of environmentally-relevant boron contaminant during water treatment and desalination, and aid in development of safe drinking water technologies.

2. Materials and methods

2.1. Waters

The MSF feed and distillate samples were supplied from three MSF facilities in Saudi Arabia (Plants 1 and 2 located on the Red Sea coast and Plant 3 located on the Arabian Gulf coast). The physico-chemical characteristics of these waters are shown in Table 2. Boric acid (H_3BO_3) solution with boron concentration of 5.55 mg/L was prepared by dissolving the appropriate amount of H_3BO_3 powder in Milli-Q water. The pH of solution was adjusted to 8.1 with 0.2 M NaOH by using the