Supercritical water for the treatment of hypersaline brine waste

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1. Introduction

As freshwater becomes a strategic resource, there is a worldwide drive to develop and diversify the existing freshwater supply system. Therefore, water desalination has become a promising technology to convert seawater to freshwater in the past 20 years[1]. As the leading technology for water desalination, the Reverse Osmosis (RO) technology is widely used due to its high efficiency and low energy consumption[2]. However, RO generates a considerable volume of brine waste—roughly a gallon of waste per gallon of clean water produced. Brine waste is challenging to treat[3]. Moreover, since most desalination facilities are usually installed and operated near the ocean for economic reasons, the locally elevated salinity from concentrated brine waste discharged during plant operation creates significant environmental impacts and threatens the marine ecosystem. The current RO brine waste treatment methods include direct discharge into surface water, deep-well injection, and evaporation ponds[3]. All those methods establish a real threat to the local ecosystem. The supercritical water desalination concept (SWD) is emerging as a promising technology that could be used to treat hypersaline brine waste with zero liquid discharge potential. SWD utilizes the unique thermodynamic properties of water. Above critical temperature and pressure (T>374°C, P>221bar), the intermolecular hydrogen bonds between water molecules break, resulting in a decrease in dielectric constant—the dielectric constant is a measure of the polarity of compounds. This change results in decreased solubility of inorganic components, such as salt. Thus, SWD could be used to treat brine waste and completely separate salt and water. Moreover, in SWD, the product water quality is independent of feed water concentration, and the energy consumption improves as salinity increases due to the high heat capacity of salt. However, the SWD technology is still at the early stage of development[4,5]. Thus, it requires an improved understanding and further development before it can be practically adopted.

2. Materials and Methods

A detailed process flow diagram of the SWD system—designed, built, and commissioned by our team—is shown in Figure.1: (a) piping and instrumentation diagram (P&ID), (b) picture of the physical model, and (c) 3D model. The system is continuous and has a capacity of ~0.15 gal/h. It takes seawater or brine waste discharge from traditional desalination plants and converts it into solid salt crystals and clean water without any liquid waste. The design can be divided into six main sections: I. Feed pumping; II. Preheating; III. Salt separation; IV. Condensation; V. Pressure regulation and protective gas system, and VI. Freshwater collection.

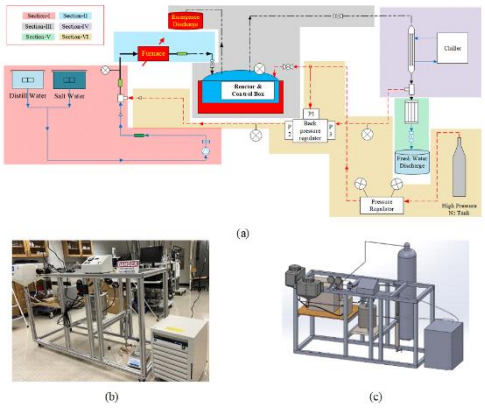

Figure 1. Supercritical water desalination system (a) piping and instrumentation diagram (P&ID), (b) physical model, and (c) 3D model.

3. Results and discussion

Table.1 summarizes some preliminary experimental results for two selected concentrations: 3.45wt% (a typical Seawater concentration) and 7.5wt% (a typical RO brine waste discharge concentration). The steady-state continuous operational time for 3.45wt% condition is 720min, and experiments were conducted at five temperature and pressure combinations (Exp. No. 1–5). The 7.5wt% waste experiments were performed at four conditions (Exp. No. 6-9) for 700min. The salt removal efficiency and the corresponding dielectric constant are shown in the last two columns for each condition. These preliminary results show that (1) the system performance (the salt removal efficiency) increases with temperature at constant pressure and concentration (Exp. No. 2&3) and (2) efficiency improves with a decrease in pressure at constant temperature and concentration (Exp. No. 4&5 and Exp. No. 6&7). These could be due to the

dramatic decrease in the water dielectric constant, decreasing salt solubility. Figure.2 shows a plot of the dielectric constant in the range of our pressure and temperature and superimposed with the experimental results of salt removal efficiency (the curves are plotted using the NIST database). The results show that salt removal efficiency is high regardless of the feed concentration when the dielectric constant is low. The dielectric constant is a measure of the polarity of compounds. When pressure and temperature exceed the critical condition, the dielectric constant of water drops below 4. This low dielectric constant causes the water to become strongly nonpolar, making the salts insoluble.

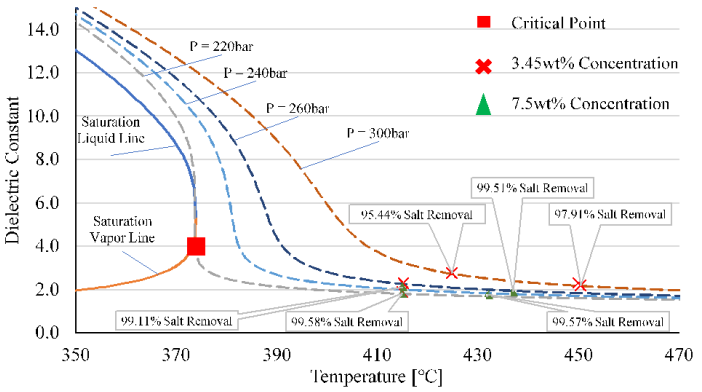

Figure 2. Dielectric Constant vs. Temperature at four selected pressure conditions superimposed with the experimental results

Also, in the SWD system, these preliminary results show that it is relatively easier to remove salts from the hard-to-treat brine waste than from seawater even when they have a similar dielectric constant (Exp. No. 2 & 6 and Exp. No. 5 & 8). This phenomenon could be explained using the classical theory of nucleation—that the rate of nucleation is higher at higher concentrations. We believe this hypothesis also governs nucleation in supercritical fluids environment. Thus, the SWD system can be integrated and used as a complementary add-on to an existing desalination system for better economic and environmental performance. While data are not yet conclusive, based on the preliminary experimental results and NaCl-H_2O model developed by Drisener[6], the results show a noticeable trend. And the trend is that the produced water quality improves in near-critical pressure conditions. However, we know that the heat capacity of water is very high in the near-critical region; thus, operating the system in this region might not be economically desirable. Therefore, we will systematically further investigate the effects of process parameters on the performance and efficiency of the SWD system.

4. Conclusions

Reverse Osmosis (RO) dominates the current desalination market (~68.7%) due to its low energy consumption. However, RO generates a considerable volume of brine waste (~50%), which is challenging to treat, creates significant environmental impacts, and threatens the marine ecosystem. This work investigates a promising advance that uses supercritical water desalination (SWD) to produce solid salt and freshwater without briny waste. The study tested a novel continuous SWD system designed and built by our team. In addition, an experimental and theoretical modeling study has been done to understand the SWD process using external protective gas (Nitrogen), which can help create sustainable and efficient operating conditions for SWD technology. The early results show that the system can operate stably close to the critical pressure condition (~22.3Mpa) and has a salt removal and water recovery efficiency up to 98% and 90%, respectively, under various feed water salinity (3.5 to 14wt%).

Table.1 Brief experiment summary for two different feed water concentration conditions

Experimental No.	Feed Water Concentration [%wt]	Operating Pressure [bar]	Operating Temperature [?]	Salt Removal Efficiency [%]	Pure Water Dielectric Constant
1	3.45 (Typical Seawater Concentration)	311	450	97.54	2.299
2		301	450	97.91	2.192
3		301	425	95.44	2.753
4		261	415	98.45	2.288
5		227	415	99.20	1.873
6	7.5 (Typical Reverse Osmosis Discharge Concentration)	251	415	99.11	2.141
7		224	415	99.58	1.845
8		253	437	99.51	1.898
9		233	432	99.57	1.784

References

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