Design of a Process for Supercritical Water Desalination

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ABSTRACT

The continual research and development of desalination processes have resulted in a variety of commercial desalination methods (Multi-Stage Flash (MSF), Reverse Osmosis, etc.) over the years. These conventional desalination methods have a major drawback, the production of a liquid waste stream. The treatment of this waste stream has always presented technical, economic and environmental challenges. The Supercritical Water Desalination (SCWD) process meets these challenges as it allows for the treatment of salt water streams without the production of an aqueous waste stream (Zero Liquid Discharge concept).

Proof of principle of SCWD as well as the phases present at supercritical conditions for sodium chloride (Type I salt [8]) solution has been studied in quartz capillaries. Two distinct regions, Vapour – Liquid and Vapour – Solid, and a transition Vapour – Liquid – Solid point were observed under supercritical conditions. An experimental set-up has been designed and built to separate these phases, measure the solubility of sodium chloride in these regions and determine the transition temperatures at pressures of 250 and 300 bar.

A conceptual SCWD process with a two stage (V – L and V – S at 300 bar and 1 bar respectively) separation step has been designed and simulations with water have been carried out at 250 and 300 bar pressure in Unisim Design®. Operating the SCWD process at 300 bar has been found to offer a better heat integration potential as well as a substantial reduction in energy consumption compared to operating at 250 bar. Preliminary modelling and experimental results show that the SCWD process operated at 460 ^{o}C and 300 bar will produces drinking water (750 ppm TDS[1]) and salt with an estimated stand-alone energy consumption of 460 MJ/m^3 product (MSF needs 300 MJ) for a 3.5wt% NaCl feed stream. The energy consumption can be further reduced by improving the level of heat integration. Also, the combination of the SCWD with other conventional processes as a pre-/post-treatment step should be further explored.

INTRODUCTION

Water is the basic substance of life on earth, and drinking water is becoming increasingly scarce. Every sign suggests that it's getting worse and will continue to do so. Water shortages affect 88 developing countries that are home to half of the world's population. In these places, 80-90% of all diseases and 30% of all deaths result from poor water quality [1]. In the coming years, water shortages is expected to increase. This increase is a direct result of human population growth, demands of industrialization and demographic changes amongst others.

Although water is the most widely occurring substance on earth, only 2.5% is fresh water while the remainder is salt water (brackish and sea water). Some two-thirds of this fresh water is locked up in glaciers and permanent snow covers [2]. Therefore, there is a very urgent need

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[1] Total Dissolved Solids

to obtain fresh water from these salt water streams. This can and has been achieved via desalination over the decades. The continual research and development of desalination processes have resulted in a variety of commercial desalination methods over the years. These processes can be classified into major and minor desalting processes with respect to their installed capacities and commercial successes. The major desalination processes include Multi-Stage Flash Distillation (MFD), Multiple Effect Distillation (MED), Vapour Compression (VC) and Reverse Osmosis (RO), while the minor processes include freezing, solar humidification, and electro dialysis [3]. MSF and RO are the most widely used desalination methods to obtain fresh water from salt water (sea water and brackish water) streams.

MSF units are widely used in the Middle East (particularly in Saudi-Arabia, the United Arab Emirates, and Kuwait) and they account for over 40% of the world's desalination capacity [1]. Although this desalination method produces water of very good quality (approximately 50 ppm of TDS), it has some major drawbacks such as low fresh water to feed water ratio (about 50%) and a waste brine stream (70 000 ppm TDS for sea water installations) which has to be dealt with.

Reverse Osmosis (RO) is a very appealing process for saline water desalination, and is becoming a leading method in the commercial desalination industry [3]. An important factor that has influenced the advances of the reverse osmosis process is its lower energy consumption (30 MJ/m^3 drinking water) compared to MSF plants (300 MJ/m^3 drinking water). Feed concentration affects the performance of RO plants. For example, while a yield (defined as ratio of fresh water to feed water) of 90 – 95% can be obtained for brackish water installations, only a value of 35 – 50% is achieved for sea water installations due to the high osmotic pressure [4]. Drawbacks of the RO process are the high amount of TDS in the product stream (100 – 600 ppm) [5], and the production of a waste brine stream (60 000 ppm for sea water installation).

The brine streams from MSF and RO processes are usually discharged in the ocean if the desalination plant is located close to the coast, otherwise, an extra treatment step is required if the plant is located inland. Discarding the concentrated brine in the ocean leads to increased salinity and turbidity which could lead to the destruction of marine lives, and with stricter regulations regarding dilution in ocean, a new desalination method which avoids the production of concentrated brine stream has to be explored. In this paper, we propose a process called supercritical water desalination (SCWD). This process allows for the treatment of salt water streams without the production of an aqueous waste stream (Zero Liquid Discharge concept), and offers an increased water yield (~ 93% for sea water feed).

DEVELOPMENT OF THE SCWD PROCESS

A conceptual design for the SCWD process is shown in *Figure 1*. Key challenges that have been identified are (i) the controlled crystallisation and removal of solid salts at these supercritical conditions, (ii) the high level of heat integration in order for the process to be economically viable, and (iii) selection of materials of construction that can withstand the extreme conditions of temperature, pressure and chemical corrosion.

In order to design a SCWD unit, it is essential to know the phases that are present at supercritical conditions and understand the effect of system parameters (Pressure and temperature) on separation efficiency. The phases present at supercritical conditions will be investigated in a small scale quartz capillary tube.
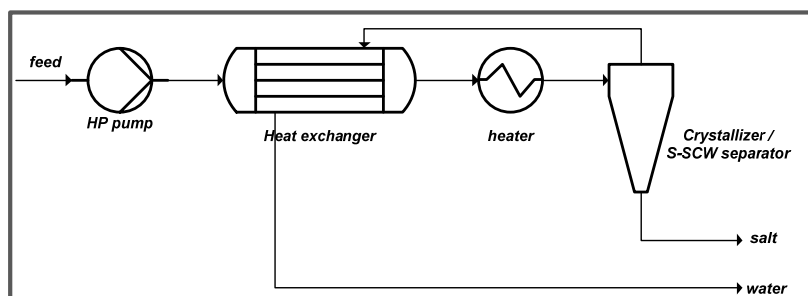
Figure 1: Conceptual design of the SCWD Process.

Experiments and Procedures

The experiments are divided into two parts; visualisation experiments to determine the phases present under supercritical (SC) conditions, and solubility measurements under SC conditions at two pressures (250 and 300 bar) and different temperatures (380 – 500 ^{o}C). The focus is on sodium chloride (NaCl) as the main constituent of sea water.

Visualisation Experiments

To determine the phases present at SC conditions, visualisation experiments were performed with sodium chloride solution in quartz capillaries. In the experiments, a sodium chloride solution (3.5 wt.%, roughly the same amount present in sea water) was injected into a quartz capillary $(id = 2\ mm, Length = 170\ mm, liquid\ level = 20\ mm)$. The capillary is then sealed and put into an oven with a sight glass at the front. A thermocouple is attached to the outer wall of the capillary to measure the temperature. This wall temperature is taken as the temperature in the capillary. A video camera is positioned in front of the oven for recording. Because the system is closed (isochoric), the temperature and pressure inside the quartz capillary are dependent on each other. However, the maximum pressure the system can attain for a desired temperature can be controlled by the amount of liquid that is injected in the quartz capillary. The quartz capillary can be operated up to 300 bar and 500 ^{o}C.

Phase Equilibrium Measurements

The visualisation experiments gave some insight as to the phases present at supercritical conditions for sodium chloride solution. There is a presence of a vapour–liquid phase at some temperatures well above the supercritical temperature of pure water. In order to determine the composition of these phases, an experimental set-up that can be used to measure the solubility of salt in the vapour (supercritical) phase and liquid phase was designed (see *Figure 2*). The experimental set up is a modification of the one used by Leusbrock [6]. Pressure up to 400 bar is provided to the unit with a HPLC pump (0.1 – 20 mL/min) and controlled with a back pressure regulator. Electrical heating is provided in the pre-heater and oven. The pre-heater is used to raise the temperature of the pressurised feed from room temperature to about 250 ^{o}C. Due to the very corrosive nature of chloride containing feeds at subcritical temperatures [7], Titanium grade 1 is used for the tubing between the pre-heater and the oven. Inside the oven, a cylindrical vessel (separator) is installed, in which the phase separation occurs. The separator is made of Incoloy 825 with an internal diameter of 10 mm and a length of 85 mm. Thermocouples are installed in the pre-heater and oven to measure and control the temperatures therein. Thermocouples are also attached to the inlet, middle and outlet of the separator to measure the temperatures at those points, and the average of these three temperatures is taken as the temperature in the separator. The temperatures recorded by the three thermocouples differ from one another by ± 2 ^{o}C.
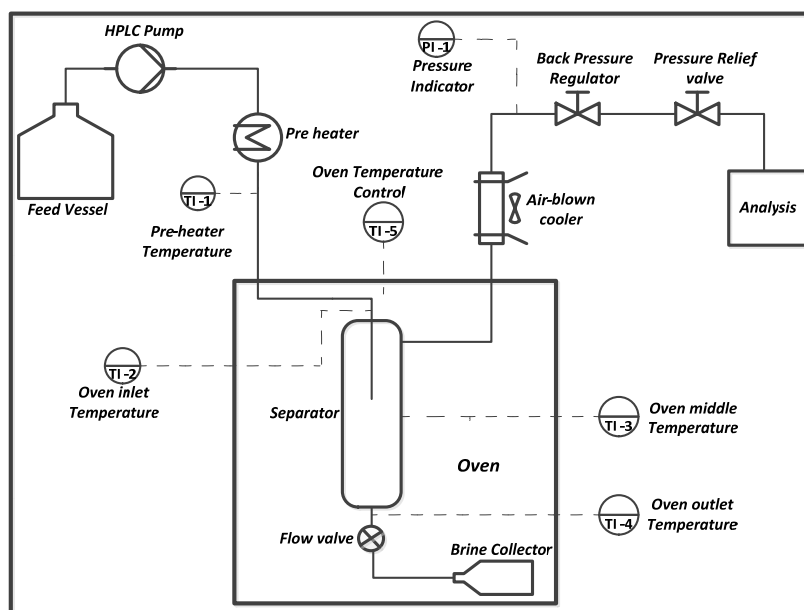
Figure 2: Schematic of Experimental Set-up for Phase Equilibrium Measurement.

The saline feed (3.5 wt.% NaCl) is prepared using demineralised water and pure sodium chloride (> 99.5 % purity) from Sigma-Aldrich. The temperatures in the pre-heater and oven as well as the pressure are then set to the desired values. Saline feed is supplied to the unit at a flow rate of 0.2 mL/min. The feed is pre-heated to a temperature of 250 ^{o}C, and further heating to the desired temperature is done in the oven. Inside the separator in the oven, phase separation takes place with the supercritical phase (product water stream) leaving from the top while the liquid phase stays in the separator. The outgoing supercritical phase is cooled (with a fan), depressurised to room conditions, and collected for analysis. The resulting liquid phase (brine) is collected, under experimental conditions (pressure and temperature), into a liquid collector (0.5 mL) using a flow valve (see *Figure 2*). The salt concentration of the collected samples (product water stream and brine collector content, after dilution) are determined via conductivity measurement. Mass in and out of the experimental set-up were measured to ascertain if the mass balance is closed. Mass balance error was calculated to be less than 2%.

Results

The visualisation experiments gives an insight into what actually happens in the separator of our experimental set-up (see *Figure 2*) when the pressurised saline solution is heated. As the solution in the quartz capillary is heated, its temperature as well as the pressure in the system rises (the system is isochoric). At temperatures above the critical temperature of pure water (374 ^{o}C), three distinct regions exist. At about 380 ^{o}C (pressure equivalent of about 220 bar), a vapour – liquid (V – L) region is formed in the system. And as the temperature increases, the liquid level in the capillary decreases, resulting in an increasing salt concentration in the liquid phase. At around 450 ^{o}C (app. 250 bar), a transition vapour – liquid – solid (V – L – S) region appears, and the system enters a vapour – solid (V – S) region. This observation is consistent with the behaviour of a Type I salt-water system [8].

These observations are more evident in the solubility measurements as presented in *Figure 3*. *Figure 3* shows the solubility of sodium chloride in the vapour phase and liquid phase at pressures of 250 and 300 bar and supercritical temperatures (380 – 500 ^{o}C). An important feature of the phase diagrams at these two pressures is the existence of a vapour – liquid phase

region at temperatures above the supercritical temperature of pure water (374 ^{o}C). The measurements presented in this study are in agreement with the results of Armellini [8]. Thus, by controlling the temperature in the separator (see *Figure 2* and *Figure 3*), solids formation, which can lead to equipment blockage, can be avoided.

This principle will be applied in the final design by having a two stage separation. First, a V – L separator to remove the supercritical product water from the liquid phase at 250-300 bar followed by a V – S separator to obtain the solid salt by flashing the liquid phase (a highly concentrated salt solution) to atmospheric pressure.

During the phase equilibrium measurements, the system was observed to be less stable (high pressure and temperature fluctuations) at 250 bar compared to 300 bar. The phase diagram is shown to shift upwards as the pressure is increased from 250 to 300 bar. The quality (measured as TDS) of the water produced also decreased with increased pressure at the same system operating temperature (for example, at 440 ^{o}C, the concentration of NaCl at 250 bar is 400 ppm, while at 300 bar the concentration is 1000 ppm). This findings reveal that a lower pressure of 250 bar favours better quality of produced water, however, operating pressure of 300 bar favours system stability.
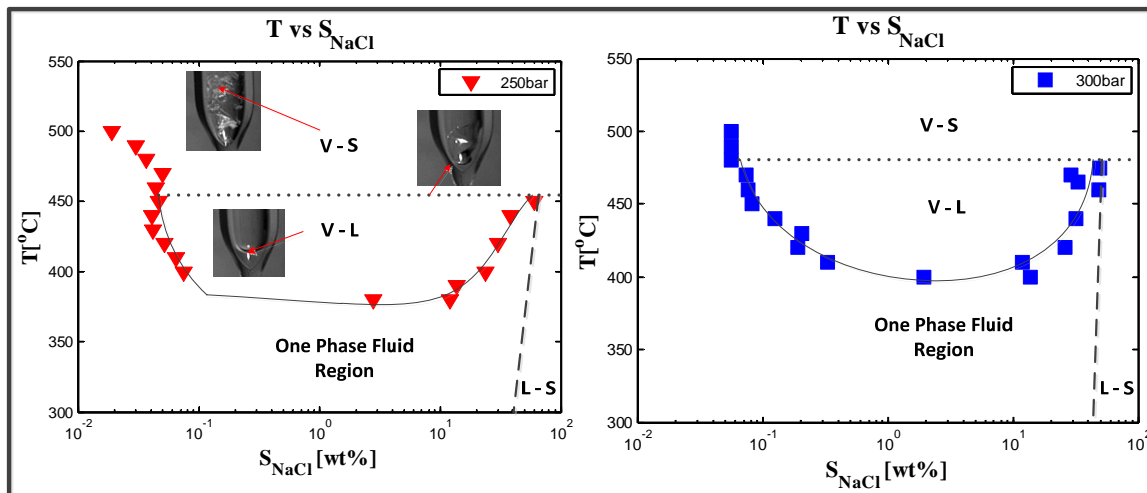

Figure 3:Phase diagram of NaCl at 250 bar (with snapshots of capillary experiment) and 300 bar, and Supercritical Temperatures, (- - -) estimated from [9].

PRELIMINARY PROCESS SIMULATION

Preliminary process simulations with water in the commercial flowsheeter, Unisim Design® were carried out at the two pressures (250 and 300 bar) to determine how the system operating pressure influences the heat exchanger efficiency and heater duty (*Figure 1*) for separation. The temperature for simulations at the two different pressures have been chosen to avoid solids formation in the real separator. The phase equilibrium measurements, *Figure 3*, guide the choice of temperature. As such, 440 ^{o}C is chosen as the operating temperature (for phase separation) at 250 bar, while 460 ^{o}C is chosen as the system temperature at 300 bar. The process flow diagram (PFD) of the conceptual design (*Figure 1*) is shown in *Figure 4*. The feed is pressurised and enters a shell and tube heat exchanger (E-100) where it is preheated with the supercritical water coming from the separator (E-101). The stream then enters the separator (E-101) where additional heating required for separation is added. The outlet stream (#3) is split (TEE-101) into 93% product (#4) and 7%, mimicking the brine (#5). Stream #4 is

cooled by using it to preheat the feed. Further cooling and depressurisation are done in cooler (E-102) and relief valve (RV-100) respectively.
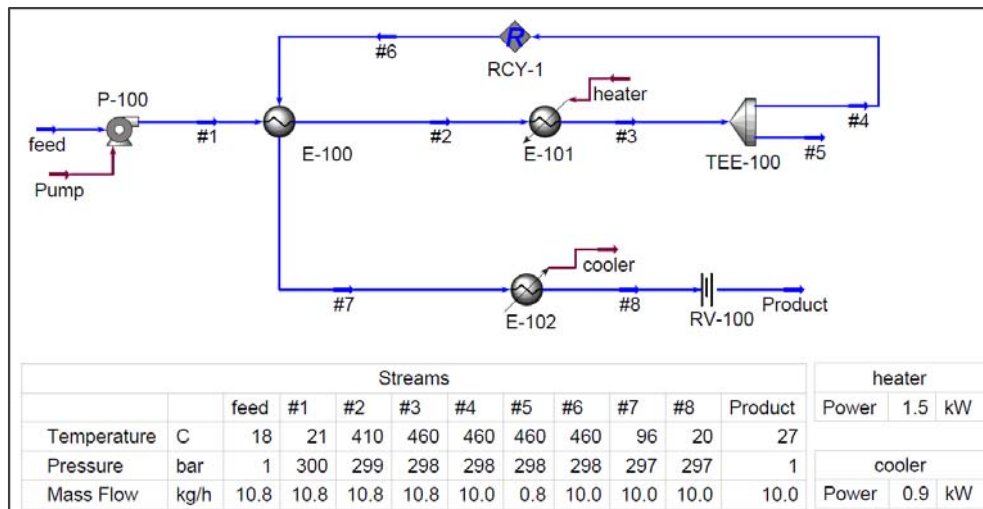

Figure 4: PFD of Unisim Design® Simulation based on water only at 300 bar.

The performance of the heat exchanger (E-100) and the duty of the heater (E-101) are of interest. And in order to make a fair comparison between the two pressures, the duty and logarithmic temperature difference of the heat exchanger (E-100) were set to the same value (see *Table 1*) for the two simulations. Important results of the simulation are shown in *Table 1*. The minimum approach temperature in the heat exchanger at a pressure of 300 bar is higher than that at 250 bar, which suggests a better heat integration potential for the process at 300 bar.

Table 1: Unisim Design® Simulation Output.

P (bar)	250	300
E-100 duty (GJ/m^3 product water)	2.5	2.5
E-100 ΔT_{min} (^{o}C)	*15*	*20*
E-100 LMTD (^{o}C)	46	46
UA (W/^{o}C)	150	150
T_#3 (^{o}C)	440	460
E-101 duty (MJ/m^3 product water)	*670*	*520*

In addition, the extra heating required to boost the temperature of the preheated stream (#2) from the heat exchanger to the desired operating temperature is lower (22% reduction) when the system is operated at 300 bar compared to operating at 250 bar.

For system stability, heat integration potential and less energy consumption, we have decided to operate the SCWD process at a pressure of 300 bar.

PROCESS DESIGN OF PILOT UNIT

A proposed process design for the SCWD process for producing 10 kg/hr of drinking water is shown in *Figure 5* with the stream properties table added. The feed stream is pressurised and heated up to a pressure of 300 bar and a final temperature of 460 ^{o}C in the separator. At this

supercritical conditions, the stream is separated into a vapour (supercritical) phase and a liquid (concentrated brine) phase. The supercritical phase has a salt concentration of about 750 ppm, while the concentrated brine phase has a concentration of about 50 wt.% NaCl. It is important not to go above this temperature in order to prevent salt crystallisation (see phase diagram, *Figure 3*) which could lead to equipment blocking and by extension equipment failure and downtime.

Heat integration is very important in order to recover most of the energy put into the process and reduce energy consumption. Therefore, the supercritical product stream is used to heat the cold feed stream in a counter-current heat exchanger. The feed stream goes through the tube, while the product stream passes through the shell. The extra heating required to boost the temperature of the heated feed stream (#3) to the desired operating temperature is provided in the heated separator.
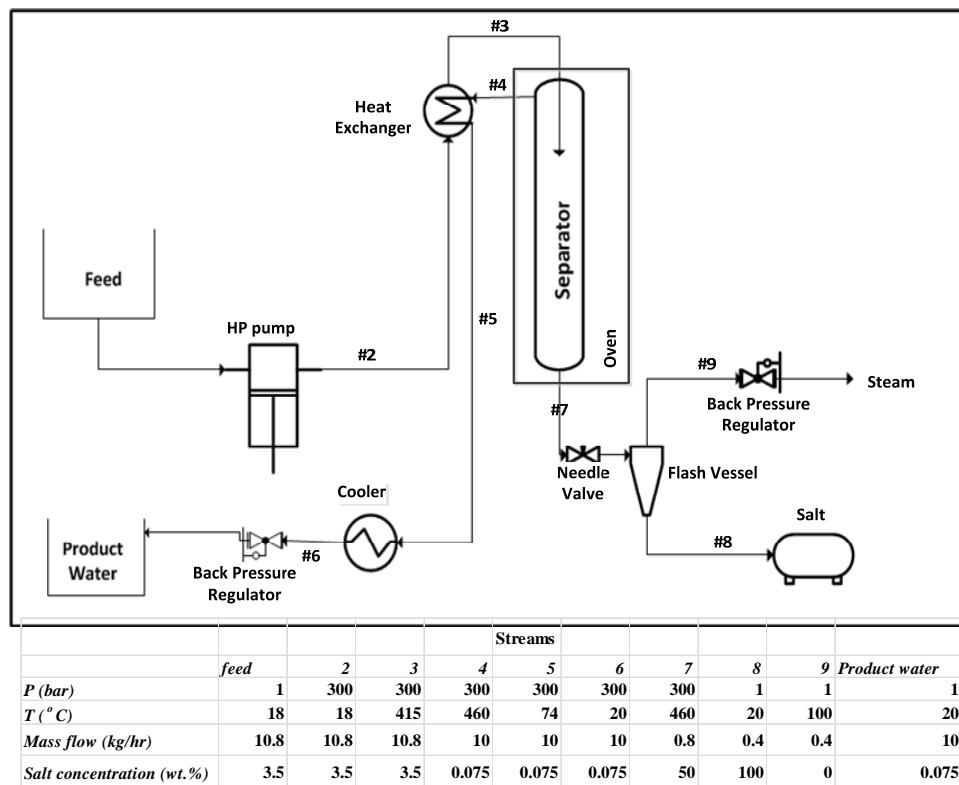

					Streams					
	feed	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*Product water*
P (bar)	1	300	300	300	300	300	300	1	1	1
T (°C)	18	18	415	460	74	20	460	20	100	20
Mass flow (kg/hr)	10.8	10.8	10.8	10	10	10	0.8	0.4	0.4	10
Salt concentration (wt.%)	3.5	3.5	3.5	0.075	0.075	0.075	50	100	0	0.075

Figure 5: Proposed Process Design of Pilot unit for the SCWD Process.

Kritzer [7] and Marrone & Hong [10] have identified the region just below the critical temperature as the maximum point of corrosion especially for chloride containing streams, hence, the material of choice for this part of the process has to be one that is resistant to such a corrosive environment. The heat exchanger tube will be operating in such environment, therefore, Titanium grade 1 has been chosen as material of construction for the tube. The shell and separator are constructed from Incoloy 825.

The highly concentrated brine stream (#7) is moved into a crystalliser operated at much lower pressure (down to 1 bar) where the liquid is flashed to obtain salt and steam which can be re-used. The outlet of the heat exchanger shell is then cooled and de-pressurised to obtain drinking water of about 750 ppm TDS (safe limit for drinking water is 1000 ppm [1]).

The estimated energy consumption of this process is about 460 MJ/m^3 drinking water. This value is higher compared to the 300 MJ/m^3 drinking water for MSF [1]. The estimated energy consumption of the proposed SCWD process can still be improved. For example, by increasing the heat exchanger area by 30%, a 20% reduction in energy consumption is estimated.

CONCLUSIONS AND RECOMMENDATIONS

A design of a pilot plant unit for the supercritical desalination of salt water streams with zero liquid discharge has been introduced. Proof of principle as well as the phases present at supercritical conditions for sodium chloride solution has been studied in quartz capillaries. Under supercritical conditions, two distinct regions, V – L and V – S as well as a transition V - L - S were observed. The transition temperature from V – L to V – S was found to be about 450 ^oC at 250 bar, and 475 ^oC at 300 bar. Solubility of salt in both the vapour and liquid phase in the V – L region was found to increase with increasing temperature and decrease with increasing pressure. In addition, the phase equilibrium curve, shifts upwards and becomes narrower at the higher pressure of 300 bar. All results are in agreement with literature.

A conceptual SCWD process with a two stage (V – L and V – S at 300 bar and atmospheric pressure respectively) separation step has been designed and preliminary simulations with pure water to mimic the process have been carried out at 250 and 300 bar pressure. Operating the SCWD process at 300 bar pressure has been found to offer better heat integration potential as well as a 22% reduction in energy consumption.

A SCWD process design for the production of 10 kg/hr drinking water (~750 ppm TDS) which eliminates the production of any waste stream (ZLD) has been explored. Although the process offers two valuable products (drinking water and salt) as opposed to the conventional MSF and RO processes, its stand-alone energy consumption of 460 MJ/m^3 is higher than the 300 MJ/m^3 [1] drinking water produced by MSF, however this can be reduced by improving the level of heat integration. Its combination with other conventional processes as a pre-/post-treatment step should be further explored.

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