Supercritical Water Desalination (SCWD)

**Process Development, Design and
Pilot Plant Validation**

Samuel Obarinu Odu

SUPERCritical WATER DESALINATION (SCWD)

PROCESS DEVELOPMENT, DESIGN AND PILOT PLANT
VALIDATION

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VALIDATION

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To my beloved family

Summary

Conventional desalination technologies such as reverse osmosis (RO), multi-stage flash distillation (MSF) and electro dialysis (ED) have a major drawback; the production of a liquid waste stream with an increased salinity (compared to the feed) that has to be disposed of. The treatment of this waste stream has always presented technical, economic and environmental challenges. With stricter environmental regulations regarding brine disposal into water bodies, the treatment or disposal of this waste stream pose a huge challenge for the sustainability of desalination methods. Currently, research studies are being conducted to develop zero liquid discharge (ZLD) technologies for desalination.

Supercritical water desalination (SCWD) is a new desalination method that allows for the treatment of salt water streams with ZLD. A detailed literature overview of state-of-the-art desalination technologies, their advantages and major drawbacks, as well as motivations for a desalination process that eliminates the production of a waste brine stream are provided in **Chapter 1**.

The main objective of the work reported in this dissertation is the development, design and construction of a pilot plant scale SCWD process that produces drinking quality water and solid salt.

In order to design a SCWD process, it is essential to know the phases present under supercritical water conditions and understand how the process conditions (Pressure and Temperature) influence the separation efficiency as well as the overall energy demands of the process. In **Chapter 2**, visualization of the phase transition of model NaCl-H₂O under supercritical water conditions as a function of temperature and pressure was carried out 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 °C at 250 bar, and 475 °C at 300 bar respectively. In addition, the phase equilibrium

solubility of NaCl-H₂O was studied under isobaric conditions in a lab-scale experimental setup. The results of the visualization experiments and phase equilibrium measurements show that the SCWD process could be operated in two stages: (i) a V-L separator to remove the supercritical product water from the liquid phase at 250/300 bar, and (ii) a V-S separator to obtain the solid salt by flashing the liquid phase (a highly concentrated salt solution, 50 wt.% at 300 bar, 460 °C) to atmospheric pressure. The two-stage operation is necessary to avoid salts precipitation in the early stage of the process which could lead to equipment blockage and downtime.

Simulation of the SCWD process using water was carried out in UniSim Design at 250 and 300 bar pressure. Simulation results show that operating the SCWD process at 300 bar offers better heat integration potential as well as a 22% reduction in thermal energy consumption compared to operating at 250 bar. A conceptual design and a lab-scale (12 g/hr) demonstration of the proof-of-concept of the SCWD process using 3.5 wt.% NaCl-H₂O solution are presented in **Chapter 2**.

The SCWD process is energy intensive, therefore heat integration is essential to regain as much energy as possible from the process in order to make the process a commercial success. Understanding the heat transfer mechanism as well as knowing the heat transfer coefficient of sub- to supercritical water (SCW) flow is essential to design a heat exchanger required for the heat integration. In **Chapter 3**, 2D numerical simulations were carried out in COMSOL Multiphysics to provide essential insights into the heat transport mechanism of SCW flow at low mass fluxes. The results show that the heat transport mechanism is primarily by buoyancy-induced circulation resulting from gravitational force acting on density gradients (a direct consequence of temperature gradients) across the section of the tube. From the numerical results, a 1D Nusselt correlation for engineering design was developed and validated with experimental temperature measurements.

In **Chapter 4**, two experimental measurement methods – local and spatially averaged - to measure the heat transfer coefficient (HTC) of SCW are presented. Only the local measurement method has enough resolution and accuracy to detect the maximum in HTC near the pseudo-critical temperature. No noticeable effect of

an increase in mass flux is observed due to the dominance of natural convection as heat transport mechanism at the low mass fluxes investigated. An increase in pressure leads to a decrease in the magnitude of the measured HTC near the pseudo-critical temperature. Experimental results from the local measurement method are used to further validate the numerical results obtained in **Chapter 3**.

In **Chapter 5**, the detailed design (and challenges), selection of materials of construction, operating procedure and control, and experimental results of a first generation modular pilot plant for SCWD with a capacity of 5 kg/hr drinking water, the first of its kind, are presented. Experiments with NaCl feed (3.5 wt.%) have been carried out successfully with the plant running for several hours without operational problems and with good mass balance closure. The pilot plant produces drinking quality water (< 700 ppm salts) and solid salt crystals (2-15 μm).

The findings of the research work is summarized in **Chapter 6**. In addition, the current bottlenecks of the process are highlighted, and potential scope for further development of the SCWD process is given. For example, the flash operation needs to be optimized, and further tests with other salts and mixture of salts are proposed. SCWD is still more energy intensive compared to the conventional MSF distillation, and as such preliminary evaluation shows it is too expensive as a stand-alone water producing technology. The added value of combining SCWD with other conventional desalination techniques as end of pipe solution for ZLD applications should be explored.

Samenvatting

Conventionele ontziltingstechnologieën zoals omgekeerde osmose (RO), meertraps-flashdestillatie (MSF) en elektrodialyse (ED) hebben een belangrijk nadeel; het restproduct is een vloeibare afvalstroom met een hoog zoutgehalte (vergeleken met het beginproduct) die moet worden afgevoerd. De verwerking van deze afvalstroom brengt technische, economische en milieutechnische uitdagingen met zich mee. Door strengere milieueisen ten aanzien van het lozen van zilt afvalwater is het verwerken of reinigen van deze afvalstroom een enorme uitdaging voor het duurzaam maken van ontziltingstechnieken. Daarom wordt er op dit moment veel onderzoek gedaan naar de ontwikkeling van ontziltingstechnologieën waarbij **geen** vloeibare afvalstroom wordt geproduceerd (zero-liquid-discharge – ZLD).

Superkritische water ontzilting (super critical water desalination = SCWD) is een nieuwe ontziltingsmethode waarbij geen vloeibare afvalstroom wordt geproduceerd. Een uitgebreid literatuur overzicht van verschillende state-of-the-art ontziltingstechnologieën, hun voordelen en belangrijkste nadelen, evenals de motivatie voor het ontwikkelen van een ontziltingsproces zonder een zilte afvalwaterstroom als restproduct worden besproken in **Hoofdstuk 1**.

Het hoofddoel van het onderzoek dat beschreven wordt in dit proefschrift is het ontwikkelen, ontwerpen en bouwen van een SCWD proces op pilot plant schaal waarmee schoon drinkwater wordt geproduceerd met een vast zout als restproduct.

Om een SCWD proces te ontwerpen is het van groot belang om de fasen die aanwezig zijn onder superkritische water condities te kennen, en de invloed van de proces condities (druk en temperatuur) op de scheidingsefficiëntie en de totale energiebalans van het proces te begrijpen. In **hoofdstuk 2** worden visualisatie-experimenten van de faseovergang van NaCl-H₂O onder superkritische water condities als functie van temperatuur en druk uitgevoerd in kwarts capillairen.

Onder superkritische condities worden twee verschillende fasen, V-L en V-S, geconstateerd en daarnaast de overgangsfase V-L-S.

De overgang van V-L naar V-S werd gevonden bij een temperatuur van ongeveer 450 °C bij 250 bar en 475 °C bij 300 bar. Daarnaast werd de samenstelling van het fase-evenwicht NaCl-H₂O onder isobare condities bestudeerd in een lab opstelling. De resultaten van de visualisatie experimenten en de fase-evenwicht metingen laten zien dat het SCWD proces kan worden uitgevoerd in twee stappen: (i) een V-L scheiding om het superkritische water als product te scheiden van de vloeibare brine-fase bij 250/300 bar, en (ii) een V-S scheiding om het vaste zout te verkrijgen door het ‘flashen’ (verdampen) van het water uit de vloeibare brine-fase (een zeer geconcentreerde zoutoplossing, 50 wt.% bij 300 bar, 460 °C) naar atmosferische druk. Deze twee-traps methode is nodig om neerslag van zout in de 1^e-strap van het proces te voorkomen omdat dit verstoppingen van de apparatuur tot gevolg heeft en daarmee stilstand van de apparatuur.

Het SCWD proces met water bij 250 en 300 bar werd gesimuleerd in UniSim Design. De resultaten van de simulatie laten zien dat het uitvoeren van het SCWD proces bij 300 bar betere mogelijkheden voor warmte-integratie biedt en daarnaast leidt tot een verlaging in energieverbruik van 22% in vergelijking met operatie bij 250 bar. Een conceptueel ontwerp en een demonstratie op labschaal (12 g/hr) van het ‘proof-of-concept’ van het SCWD proces met een 3.5 wt.% NaCl-H₂O oplossing worden gegeven in **Hoofdstuk 2**.

Het SCWD proces is energie-intensief en warmte-integratie is daarom van essentieel belang om zoveel mogelijk energie terug te winnen en daardoor het proces ook commercieel haalbaar te maken. Het begrijpen van het warmteoverdrachts-mechanisme en het berekenen van de warmteoverdrachtscoëfficiënten voor stromend sub- en superkritisch water zijn van essentieel belang voor het ontwerp van de warmtewisselaar die nodig is voor de warmte-integratie. In **Hoofdstuk 3** zijn 2D-numerieke simulaties in COMSOL Multiphysics uitgevoerd om inzicht te verkrijgen in de warmtetransportmechanismen van verticaal stromend sub- en superkritisch water bij lage massadebiten. De resultaten laten zien dat het warmtetransport vooral

plaatsvindt door middel van een circulatie stroming (van wand naar de kern) die wordt veroorzaakt door een verschil in dichtheid tussen wand en bulk. Dit verschil is een direct gevolg van temperatuurgradiënten over de doorsnede van de buis. Uit de numerieke resultaten is een 1D Nusselt correlatie afgeleid om te worden ingebruikt voor ontwerp berekeningen. De 2D-model resultaten zijn gevalideerd met experimentele temperatuurmetingen.

In **Hoofdstuk 4** worden twee experimentele meetmethoden – lokaal en ruimtelijk gemiddeld – voor het bepalen van de warmteoverdrachtscoëfficiënt (HTC) van verticaal stromend sub- en superkritisch water gepresenteerd. Alleen de lokale meting heeft voldoende resolutie en nauwkeurigheid om het maximum in de HTC in de buurt van de pseudo-kritische temperatuur te detecteren. Verandering in massadebiet gaf geen waarneembaar effect op de HTC omdat voor de lage massadebieten in deze experimenten natuurlijke convectie het dominante warmte-overdrachtsmechanisme is. Een toename in druk leidt tot een afname van de gemeten HTC in de buurt van de pseudo-kritische temperatuur. Experimentele resultaten verkregen met de lokale meetmethode worden gebruikt om de in **Hoofdstuk 3** verkregen numerieke resultaten verder te valideren.

In **Hoofdstuk 5** worden het gedetailleerde design (en uitdagingen), materiaalselectie, besturing en procesbewaking, en experimentele resultaten van een eerste generatie modulaire pilot plant voor SCWD met een drinkwater capaciteit van 5 kg/uur, de eerste in zijn soort, gepresenteerd. Experimenten met een NaCl voeding (3.5 wt%) zijn succesvol uitgevoerd, waarbij de plant voor meerdere uren probleemloos in bedrijf was en een sluitende massabalans werd verkregen. De pilot plant produceert drinkwater (< 700 ppm zout) en vaste zoutkristallen (2 – 15 μm).

De uitkomsten van het onderzoek worden samengevat in **Hoofdstuk 6**. Ook worden hierin de bottlenecks van het huidige ontwerp besproken en suggesties voor verdere ontwikkeling van het SCWD proces gegeven. Voorbeelden hiervan zijn de optimalisatie van het flash proces en aanvullende testen met andere zouten en zoutmengsels. SCWD is op dit moment nog steeds energie-intensiever dan het conventionele MSF of MED. Een eerste evaluatie laat zien dat het daarom nog te duur is om als stand-alone drinkwater productietechniek te gebruiken. De

toegevoegde waarde van SCWD in combinatie met conventionele ontziltingstechnologieën als end-of-pipe oplossing moet verder worden onderzocht.

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Chapter 1

Introduction

1.1. World Water Scarcity Problem

Water is the basic substance of life on earth, and drinking water is becoming increasingly scarce (see Figure 1). Every sign suggests that it's getting worse and will continue to do so. Water shortages affect about 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. An increased demand for fresh water on the order of 64 billion m³ a year has been estimated based on the world's annual population growth of 78 million a year.²

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.³ Therefore, there is a very urgent need to obtain fresh water from these salt water streams. This can and has been achieved via desalination over the decades.

Figure 1. Global physical and economic water scarcity.⁴

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 (MSF) distillation, Multiple Effect Distillation (MED), Thermal Vapor Compression (TVC), Mechanical Vapor Compression (MVC)^{5, 6} and Reverse Osmosis (RO), while the minor processes include freezing, solar humidification, and electro dialysis (ED).⁷ See Table 1 for the capacities, energy consumption and product water quality of these conventional desalination processes.

1.2. Conventional Desalination Technologies

MSF distillation and RO are the most widely used desalination methods to obtain fresh water from salt water (sea water and brackish water) streams,⁸ and are therefore considered state-of-the-art desalination technologies. While other conventional desalination technologies such as MVC, ED are available commercially, their use are mainly on a smaller scale and in decentralized locations.⁸ These conventional desalination methods are generally categorized as water recovery processes.⁹

MSF distillation 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 A MSF unit is separated into different flash chambers with different pressures, and vaporisation/evaporation of salt water is realized by successively lowered pressures in each chamber. The salt water is heated, but not allowed to boil, reducing the precipitation of scale forming materials.⁷ The incoming salt water is pressurized and sent into a condenser where it encounters and exchanges heat (pre-heated) with the rising vapor. It then passes into a heater where the temperature is raised close to the boiling point by steam or fossil fuels. But, since a higher pressure is maintained, no boiling occurs. This high temperature in combination with successive pressure decrease in the individual chambers results in the flashing of the saline stream (see Figure 2). The condensate is collected as fresh water, while the non-evaporated saline stream exits the process as concentrated brine.

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 ratio (about 50%) and a waste brine stream (70 000 ppm TDS for sea water installations) which has to be dealt with.

Figure 2. Schematic of MSF desalination process.¹

Reverse Osmosis (RO) is a very appealing process for saline water desalination, and is becoming a leading method in the commercial desalination industry ⁷. An important factor that has influenced the advances of the reverse osmosis process is its lower energy consumption ($30 \text{ MJ}_{\text{el}}/\text{m}^3$ drinking water) compared to MSF distillation plants ($300 \text{ MJ}_{\text{th}}/\text{m}^3$ drinking water). Reverse osmosis is a semi-permeable membrane process in which a preferential material (water) is transported through the membrane against the osmotic pressure of the saline water feed (see Figure 3). RO plants are operated at 54 - 80 bar for sea water desalination and about 15 – 25 bar for brackish water treatment.¹

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 (0.5 wt.% saline feed) installations (BWRO), only a value of 35 – 50% is achieved for sea water installations (SWRO) due to the high osmotic pressure.⁸ Major drawbacks of the RO process are membrane fouling and the production of a waste brine stream^{10, 11} (60 000 ppm for sea water installations) which has to be subsequently dealt with.

Figure 3. Schematic of the RO process.¹

The brine streams from MSF distillation and RO processes are usually discharged in the ocean if the desalination plant is located close to the coast, otherwise, extra treatment steps (which could be expensive) are required if the plant is located inland. Extra treatment steps for managing brine concentrate include: deep well injection,¹² disposal in publicly owned treatment works,⁹ evaporation in natural and solar ponds,¹³⁻¹⁵ combined evaporation (for concentrating the brine) and crystallization (of the concentrated brine).^{15, 16} These extra treatment steps also come with shortcomings.

For deep well injection and disposal in publicly owned treatment works, there is the risk of the discharged brine polluting ground water sources.¹⁴ Evaporation in natural and solar ponds is limited by the amount of solar radiation available, and this technique is mostly restricted to arid and semi-arid regions. In addition, a large expanse of land will be required to treat large volumes of brine. For example, 2×10^6 m² of surface area is needed to treat 1000 m³/hr of brine.¹⁷ Combined evaporation and crystallization has been reviewed by Giwa et al.¹⁶ The authors concluded that while 100% salt recovery is theoretically possible with this treatment step, the economic cost of such route need to be thoroughly investigated.

Discarding the concentrated brine along with chemical agents (such as anti-scaling agents, anti-flocculants, anti-foaming agents, etc.) could lead to the destruction of marine lives.^{13, 18-20} Regulations regarding the discharge of waste brines into water bodies are becoming more stringent.²¹ In the United States for example, some states have already banned the practice of discharging waste brine streams in publicly owned treatment works.⁹ As a result of the increased fresh water demand and stricter regulations regarding the disposal/treatment of the waste brine streams from conventional desalination methods, the exploration of in-situ desalination methods, or combination of methods that allow for the treatment of salt water streams without the production of waste brine streams (zero liquid discharge – ZLD) will become inevitable.

Table 1. Capacity, Energy Consumption, and Product Water Quality of Conventional Desalination Processes.^{1, 22-25}

	MSF	MED	MVC	TVC	⁺SWRO	[~]BWRO
Unit size (m ³ product water/day)	50 000 – 70 000	5 000 – 15 000	100 – 3 000	10 000 – 30 000	up to 128 000	up to 98 000
Electrical energy (kW-h/m ³ product water)	2.5 - 5	2.5	7-12	2	4 – 6 [*]	1.5 – 2.5
Thermal energy (MJ/m ³ product water)	190 - 300	145 - 230	none	15	none	none
Product water quality (ppm TDS)	10 - 50	≈ 10	≈ 10	≈ 10	400 - 500	200 - 500

^{*}With energy recovery. ⁺Sea Water Reverse Osmosis. [~]Brackish Water Reverse Osmosis

1.3. ZLD Desalination Technology

While a lot of studies both on pilot plant and industrial scale has been carried out on conventional desalination processes,^{8, 10, 11, 26, 27} in areas of increased efficiency, and energy reduction, only few studies on ZLD processes are available in literature.^{9, 17, 28, 29} Leusbrock in his work¹⁷ explored the potential of using supercritical water (SCW) for the removal of inorganic salts from aqueous streams without the production of a liquid waste stream. The author measured the solubility of different inorganic salts in SCW and proposed conceptual process options on how SCW could be used to achieve desalination with ZLD. Salvador Cob²⁸ in her work used a combination of cation exchange (CIEX) as pre-treatment, Nano filtration (NF) and RO as main desalination methods with Eutectic Freeze Crystallization (EFC) as post treatment for the concentrate brine from the process in order to achieve ZLD. However, the author could only reach near ZLD with a maximum total system recovery of 98%. Lopez and Tremblay⁹ have carried out preliminary cost estimation for the desalination of ‘hypersaline feedstock’ using a Joule-heated SCW with ZLD in a commercial process simulator. The authors’ claim the approach is “expected to produce no contaminant liquid streams”, however, there is no real plant data to back up the authors’ claim.

In this thesis, a new desalination method that addresses the technical, economic and environmental challenges faced by conventional desalination methods regarding brine treatment and disposal, and allows for the production of water with zero liquid discharge is investigated and presented.

1.4. Objective and Outline of Thesis

Supercritical water desalination (SCWD) meets the challenge of waste disposal in desalination processes by producing drinking water and solids salt (so called zero liquid discharge, ZLD). The process offers a high water yield per pass (~93 wt.% for sea water feed concentration), and can handle high concentration salt streams that cannot be processed with conventional desalination methods. The main objective of the work described in this thesis is the development, construction and

operation of a pilot plant scale SCWD process for the treatment of salt-water streams with ZLD through a thorough investigation of its sub-systems.

The conceptual design of the SCWD process is introduced in chapter 2. The phases present under supercritical water (SCW) conditions have been investigated in quartz capillaries (0.13 mL) for a model NaCl – H₂O solution, and the phase equilibrium solubility of the model solution was studied under isobaric conditions in a lab-scale experimental apparatus (12 g/hr feed). The proof-of-concept of the SCWD process was also demonstrated in this chapter. Subsequently, a design of a two-stage separation step was carried out with a preliminary estimation of the energy requirement of the process.

Heat integration has been highlighted to be critical to the commercial success of the SCWD process. In chapter 3, heat transfer characteristics of SCW flow was studied in COMSOL Multiphysics with the aim of obtaining a correlation for the heat transfer coefficient of SCW at the low mass fluxes found in pilot plant scale SCW processes. Such a correlation can then be used to design heat exchangers required for heat integration. The obtained Nusselt correlation for heat transfer coefficient is validated with experimental measurements in a newly built set-up.

Chapter 4 introduces experimental methods for measuring heat transfer coefficients (HTCs) of water from sub- to supercritical conditions. Effects of increasing mass flow and pressure on HTC are shown. A comparison between the calculated HTCs using the proposed Nusselt correlation in chapter 3 and experimentally calculated HTCs is made.

Chapter 5 focuses on the design considerations and challenges, construction and commissioning of a first of its kind first generation modular pilot plant for SCWD with a capacity of 5 kg/hr drinking water. The detailed design, selection of materials of construction, operating procedure and control of the pilot plant as well as the first results are presented.

Chapter 6 highlights the most important findings of the work described in this thesis. In addition, some recommendations for future research on this subject before proceeding to industrial-scale application are proposed.

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Chapter 2

Design of a Process for Supercritical Water Desalination with Zero Liquid Discharge

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ABSTRACT

Conventional desalination methods have a major drawback; the production of a liquid waste stream that has to be disposed of. 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 with zero liquid discharge (ZLD). An experimental apparatus has been designed, built and operated to show the proof of principle of the SCWD process using NaCl-H₂O as a model solution. Next, a SCWD process with a two stage separation step has been designed. Enthalpy calculations for a 3.5 wt.% NaCl feed and experimental results show that the SCWD process operated at 460 °C and 300 bar will produce drinking water (750 ppm TDS) and salt crystals (2–5µm) with an estimated stand-alone thermal energy consumption of 450 MJ_{th}/m³ product water.

1. INTRODUCTION

Desalination, the process of removing excess salt from salt water streams to produce fresh water remains a viable means to abate the global challenge of water scarcity.¹ The continual research and development of desalination processes over the decades have resulted in a variety of commercial desalination methods. These processes can be classified into major desalting processes such as; Multi-Stage Flash Distillation (MSF), Multiple Effect Distillation (MED), Vapor Compression (VC) and Reverse Osmosis (RO), and minor desalting processes such as freezing, solar humidification, and electro dialysis, with respect to their installed capacities and commercial successes.² 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.³ Although this desalination method produces water of very good quality (approximately 50 ppm of TDS), it has two major drawbacks: (i) low fresh water to feed ratio (about 50% for sea water installations) and, (ii) the production of a waste brine stream (70 000 ppm TDS for sea water installations) which needs 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.² An important factor that has influenced the advances of the reverse osmosis process is its lower energy consumption ($30 \text{ MJ}_{\text{el}}/\text{m}^3$ drinking water³) compared to MSF plants ($300 \text{ MJ}_{\text{th}}/\text{m}^3$ drinking water³⁻⁶). Feed concentration affects the performance of RO plants. For example, while a yield (defined as ratio of fresh water produced to feed water) of 90 – 95% can be obtained for brackish water installations, only a value of 35 – 50% is achieved for sea water processing due to the high osmotic pressure.⁷ Drawbacks of the RO process include membrane fouling,⁸ and the production of a waste brine stream (~60 000 ppm for sea water installations) which contains anti-scaling agents and anti-flocculants.

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 local increased salinity and turbidity which could lead to negative impact on marine ecology.⁹ With the expected more stringent regulations regarding dilution in surface water,¹⁰ a new desalination method which avoids the production of concentrated brine stream needs to be investigated. In this paper, we present 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 a sea water installation).

Supercritical water (SCW) is defined as water at pressures and temperatures above the critical pressure ($P_c = 221.2$ bar) and critical temperature ($T_c = 374.15$ °C) of water. As water approaches the supercritical state, its properties change drastically. Such changes in properties include lower density, decreased viscosity, lower dielectric constant and diminished hydrogen bonding compared to water at ambient conditions.^{11,12} The changes in hydrogen bonding and dielectric constant make water lose its polarity and consequently its solvation ability for inorganic compounds/salts. The solubility of inorganic salts in water drops by several orders of magnitude when water enters the supercritical (SC) state. As a result inorganic salts precipitate to form solid salts within the supercritical water system.¹³⁻¹⁵ The diminished solubility of inorganic salts in supercritical water is the principle employed in the SCWD process.

A conceptual design for the SCWD process is shown in Figure 1. A high-pressure pump is required to pressurize the saline feed to pressures above the critical pressure of water. Because the process is energy intensive (approximately 2 GJ of energy is required to bring 1 m³ of water from room conditions - $P = 1.02$ bar, $T = 25$ °C - to supercritical conditions - $P_c = 221$ bar, $T_c = 375$ °C -). A heat exchanger that operates at sub- to supercritical water conditions is necessary to recover most of the energy supplied to the process. A heater that provides additional energy is required to bring the feed to the desired temperature necessary for separation. Key design challenges that have been identified are: (i) the controlled removal of 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. Solutions to these major challenges will be discussed subsequently in this paper.

In order to design a SCWD unit, it is essential to know the phases that are present at supercritical water conditions and understand the effect of process conditions (pressure and temperature) on separation efficiency. The phases present at supercritical conditions for a saline solution (sodium chloride - water is used as a model system) will be investigated in a small-scale quartz capillary tube. The effects of pressure, temperature and feed concentration on separation and energy requirements will also be studied. The results of these investigations will form the basis for the selection of a separation unit as well as help to identify the optimal operating conditions for a desired level of separation at minimum energy costs.

Figure 1. Conceptual design of the SCWD Process.

2. EXPERIMENTAL SECTION

2.1. Experiments and Procedures

The experiments are divided into two parts; visualization 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 °C). The focus is on sodium chloride (NaCl) since it is the main constituent of sea water.

2.1.1. Visualization Experiments

Armellini and co-workers^{16,17} have developed an experimental technique to examine phase behavior and precipitation in salt-water systems near and above the critical point of pure water and study salt nucleation and growth from supercritical water. Their experimental apparatus features an “optically accessible cell” made of Inconel 625 and sapphire windows. This experimental technique offers the advantage of conducting isobaric experiments, however it is expensive and could not be readily purchased.

To study the phases present at SC conditions for sodium chloride solution, visualization experiments will be carried out in quartz capillaries. This experimental technique was developed by Potic et al.¹⁸ to study thermochemical conversion of wet biomass at supercritical water conditions. This experimental method has several advantages: (i) an experiment can be conducted that is fast, cheap and safe, (ii) the quartz capillaries can withstand extremely high pressures (600 bar) and high temperatures (900 °C), (iii) quartz capillaries have no catalytic activity, and (iv) quartz is corrosion resistant.¹⁸ A major disadvantage is that isobaric measurements cannot be carried out with this experimental method. Due to the pressure-temperature relationship in isochoric systems, the pressure in the capillary increases as the temperature is increased. However, since water vapor pressure predominantly determine the overall pressure, the pressure in the quartz capillary can be controlled by the initial amount of solution in the capillary.¹⁸ The P-T relationship for water in a closed system¹⁹ is used to estimate the pressures in the capillary at the various recorded temperatures.

In the experiments, a sodium chloride solution (3.5 wt.%, about the same amount present in sea water) was injected into a quartz capillary (*i.d* = 1 mm, *o.d* = 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 (see Figure 2). A thermocouple (TI-C) 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 interrelated.

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 °C with the initial liquid level used in these visualization experiments.

Figure 2. Schematic of apparatus for visualization experiments.

2.1.2. Phase Equilibrium Measurements

The visualization experiments present some insight to the phases present and phase changes that occur at supercritical conditions for a 3.5 wt.% sodium chloride solution. To determine the concentration of the salt in the phases observed in the visualization experiments, solubility measurements at phase equilibrium were carried out.

The equilibrium phase behavior of NaCl-H₂O system under supercritical water conditions has been investigated in the past. Olander and Liander,²⁰ Parisod and Plattner,²¹ Bischoff et al.,²² Sourirajan and Kennedy,²³ Armellini and Tester²⁴ have all investigated the phase behavior of NaCl-H₂O system under isothermal conditions at supercritical water pressures and temperatures. Bischoff and Pitzer,²⁵ and

Armellini²⁶ presented temperature-composition phase diagrams for NaCl-H₂O at 250 bar and 300 bar respectively by interpolating the isothermal data of several of the authors mentioned above. A recent study by Leusbrock et al.¹³ presents solubility data for sodium chloride in water at temperature and pressure ranges of 380 °C–420 °C and 180–235 bar respectively.

Although the solubility and equilibrium phase diagram of NaCl have been studied extensively, there are discrepancies (orders of magnitude in some cases) in the data reported in literature by different authors under the same experimental conditions (e.g. ²³ and ²⁶). In addition, extrapolating experimental data points beyond the experimental condition range can lead to possible errors. The SCWD process will operate under isobaric supercritical water conditions, interpolating isothermal data found in literature might lead to possible errors in the solubility of NaCl in the pressure and temperature range of interest to the process, therefore, it is decided to measure the solubility of NaCl in supercritical water at these process conditions in the vapor and liquid phase in one experiment. The apparatus was also used for the proof of concept of the separation method.

In order to determine the temperature-composition phase diagram of NaCl-H₂O under isobaric conditions, an experimental set-up that can be used to measure the solubility of salt in the vapor (supercritical) phase and liquid phase has been designed and built (see Figure 3). The experimental set up is a modification of the one used by Leusbrock et al.¹³. The design of the separator is similar to that used by Vogel et al.²⁷ to study the separation performance of various binary type I salt – water mixtures.

Pressures up to 400 bar were provided to the unit using a HPLC pump (LabAlliance series 1500, LabAlliance USA) with a volume flow rate of 0.01 – 12 mL/min and controlled with a back pressure regulator (TESCOM 26-1762-24-S, Tescom Europe GmbH & Co. KG, Germany, $C_v = 0.1$, accuracy $\pm 1\%$ of central pressure range). Electrical heating is provided in the pre-heater and oven. The pre-heater is used to raise the temperature of the pressurized feed from room temperature to about 250 °C. Due to the very corrosive nature of chloride containing feeds at subcritical temperatures,²⁸ Titanium grade 1 (Ethen Rohre GmbH, Germany) 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. Standard type K thermocouples (accuracy $\pm 0.75\%$) are installed in the pre-heater and oven to measure and control the temperatures therein. Thermocouples are also attached to the inlet (TI-2), middle (TI-3) and outlet (TI-4) of the separator to measure the temperatures at these points, and the average of the three temperatures is taken as the temperature in the separator. The mean absolute deviation of the temperatures recorded by the three thermocouples (TI-2, TI-3 and TI-4) is 2°C .

Figure 3. Schematic of Experimental Set-up for Phase Equilibrium Measurement.

The saline feed (3.5 wt.% NaCl) is prepared using demineralized water and pure sodium chloride (> 99.5% purity) from Sigma-Aldrich (Sigma-Aldrich Chemie, GmbH, Germany). 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°C , and further heating to the desired temperature is achieved in the oven via electrical

heating. Inside the separator in the oven, phase separation takes place with the supercritical phase (product water stream) leaving from the top while the liquid (brine) phase stays in the separator. The outgoing supercritical phase is cooled (with a fan), depressurized to room conditions, and collected for analysis. This is done at an interval of 20 minutes. The system is deemed to be in equilibrium when deviations in three consecutive solubility measurements are ± 0.001 wt.% (10 ppm).

When equilibrium is ascertained, the resulting liquid phase (brine) is collected, under experimental conditions (pressure and temperature), into a liquid collector (0.5 mL) with the aid of an air-controlled flow valve (see Figure 3). The salt concentration of the product water stream and the brine collected (after dilution with a known amount of demineralized water) are determined via conductivity measurement. Mass in and out of the experimental set-up were measured to ascertain if the mass balance is closed. The mass balance error was calculated to be less than 2% (relative standard error) on salt basis.

3. RESULTS: VISUALIZATION AND PHASE EQUILIBRIUM MEASUREMENTS

As the solution in the quartz capillary is heated (Figure 2), the pressure in the system increases with increasing temperature (the system is isochoric). Photographs taken during the visualization experiments are shown in Figure 4. At temperatures and pressures above the critical point of pure water ($T_c = 374$ °C, $P_c = 221$ bar), two distinct regions exist. At 380 °C (pressure equivalent of about 220 bar), the first bubbles appeared (Figure 4a) resulting in the formation of a vapor–liquid (V–L) region in the system. With continued heating, the existence of a V–L phase was observed, and as the temperature increases, the liquid level in the capillary decreases (Figure 4b), resulting in an increase in salt concentration in the liquid phase. At 450 °C (approx. 250 bar), a transition vapor–liquid–solid (V–L–S) region appears (Figure 4c), and the system enters a vapor–solid (V – S) region (Figure 4d). These observations are consistent with the behavior of a Type I salt-water system.²⁶

To check the effect of the feed concentration on separation, the experiment was repeated with sodium chloride solutions with initial concentrations of 1, 5 and 10

wt.%. The temperatures at which the phase transitions occurred remains unchanged, which suggests that the initial feed concentration has no effect on the degree of separation. However, the volume of liquid observed in the V – L region increases with an increase in initial concentration.

Figure 4. Photographs showing the phases present at different temperatures in SCW for 3.5 wt.% NaCl solution at start. In the enlargements the interface between the glass and liquid phase has been accentuated with a solid line.

The observations made in the visualization experiments are more evident in the solubility measurements as presented in Figure 5. This figure shows the results of solubility measurements for sodium chloride in the vapor phase and liquid phase at pressures of 250 and 300 bar and supercritical temperatures (380 – 500 °C). An important feature of the phase diagrams at these two pressures is the existence of a vapor–liquid phase region at temperatures above the supercritical temperature of pure water ($T_c = 374$ °C). The measurements presented in this study are in agreement

with the temperature-composition compilation of Bischoff and Pitzer²⁵ and the phase diagram of Armellini²⁶ obtained by interpolating isothermal data of several authors (see 2.1.2. Phase Equilibrium Measurements). The solubility results also show that drinking water within the set safe limit (1000 ppm TDS²⁹) can be produced within the V–L region. For example, at 300 bar and 460 °C, the quality of water produced is 750 ppm (see Figure 5). Thus, by controlling the temperature in the separator (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 – 50 wt.% at 300 bar, 460 °C –) to atmospheric pressure. The flashing experiment is discussed in the subsequent subsection.

During the phase equilibrium measurements, higher pressure and temperature fluctuations were observed at 250 bar (P fluctuation = ± 5 bar, T fluctuation = ± 3 °C) compared to 300 bar (P fluctuation = ± 1 bar, T fluctuation = ± 1 °C). The phase diagram shifts 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 °C, the concentration of NaCl at 250 bar is 400 ppm, while at 300 bar the concentration is 1000 ppm). These results reveal that a lower pressure of 250 bar favors better quality of produced water, however, an operating pressure of 300 bar favors system stability (low/no fluctuations in pressure and temperature).

Figure 5. Phase diagrams of NaCl at 250 bar (with photos of capillary experiment) and 300 bar, and supercritical temperatures, (— — compilation of Bischoff and Pitzer²⁵) and (- - - - estimated from Linke³⁰).

The effect of feed concentration on the solubility of NaCl in supercritical water was also investigated for solutions with initial concentrations of 1 and 10 wt.% respectively. The experiments were conducted at pressures of 250 and 300 bar, and temperatures of 380, 420, 450 and 500 $^{\circ}\text{C}$. No noticeable difference in solubility was observed when compared to the 3.5 wt.% solution experiments.

3.1. Flash Crystallization of 50 wt. % Brine Solution

A slight modification of the experimental set-up for phase equilibrium measurements (see Figure 3) has been carried out to enable us to simulate the crystallization of salt when the liquid phase (50 wt.% at 300 bar and 460 $^{\circ}\text{C}$) in the V-L region of the phase diagram is flashed to atmospheric pressure. In the modified set-up, the brine collector in Figure 3 was replaced with a nozzle (ID = 1.5 mm, Length = 160 mm) made from Incoloy 825. The experimental procedure is as described in section 2.1.2. Phase Equilibrium Measurements. The experiment was carried out at 300 bar, 460 $^{\circ}\text{C}$ and was also used for the proof of principle of this separation technique.

After phase equilibrium is ascertained, the pump is switched off for about 2-5 minutes to allow most of the vapor left in the separator to exit the system, all the while monitoring the temperature and pressure of the system. Afterwards, the air-

controlled valve is opened and the liquid phase collected in the separator under process condition is flashed to atmospheric pressure.

The SEM (Jeol JSM 5600 LV, at 5kV) photomicrograph of the NaCl salt which was used to prepare the feed solution as well as that of the solids obtained after the flash experiment is shown in Figure 6. The feed particles shown in Figure 6a are crystalline with sizes ranging from 200 - 700 μm . The salt obtained from flashing the 50 wt.% brine from 300 bar, 460 $^{\circ}\text{C}$ to atmospheric pressure, shown in Figure 6b is comprised of small particles (size range: 2 to 5 μm) clustered together. At higher magnification, no pores were revealed on the surface of the particles, indicating a crystalline structure. Particle sizes of the crystals will guide the choice and design of the cyclone to separate the salt from the steam.

(a)

(b)

Figure 6. SEM photomicrographs of particles of (a) NaCl feed, (b) NaCl obtained from flashing the brine solution.

4. PROCESS SIMULATION

Preliminary process simulations with water in the commercial process simulator, UniSim Design Suite 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) required 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 5, guide the choice of temperature. As such, 440 °C is chosen as the operating temperature (for phase separation) at 250 bar, while 460 °C is chosen as the system temperature at 300 bar.

The simulation process flow diagram (PFD) of the conceptual design (Figure 1) with the stream table at 300 bar is shown in Figure 7. The feed is pressurized and enters a counter-current 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 the separation is added. The outlet stream (#3) is split (TEE-101) into 93% (mass basis) supercritical product water (#4) and 7% concentrated liquid (#5), mimicking the V–L separation. Stream #4 is cooled by using it to preheat the feed. Further cooling and depressurization are done in the cooler (E-102) and relief valve (RV-100) respectively.

Figure 7. PFD of preliminary simulation based on water at 300 bar in UniSim Design.

The performance of the heat exchanger (E-100) and the duty of the heater (E-101) are of interest. In order to make a fair comparison between the two pressures, the duty, logarithmic temperature difference (LMTD) and overall heat transfer coefficient (U) of the heat exchanger (E-100) are set to the same value (see Table 1) for the two simulations. The minimum approach temperature (ΔT_{min}) is the minimum temperature difference between the hot stream and the cold stream in a heat exchanger. ΔT_{min} is a constraint in heat exchanger design that prevents a thermodynamic violation (for example temperature cross between the hot and cold stream). Heuristic put the limitation on ΔT_{min} at 10 °C for shell and tube heat exchangers for effective heat transfer.³¹ Hence, the area of the heat exchanger in the simulations was selected to obtain a ΔT_{min} greater than 10 °C.

Important results of the simulation are shown in Table 1. ΔT_{min} in the heat exchanger at a pressure of 300 bar is higher than that at 250 bar. Since ΔT_{min} of 10 °C is allowed, this implies a better heat integration potential for the process at 300 bar.

Table 1. UniSim Design Simulation Output.

P (bar)	250	300	300*
E-100 duty ($\text{GJ}_{\text{th}}/\text{m}^3$ product water)	2.5	2.5	2.5
E-100 $\Delta T_{\min}$ ($^{\circ}\text{C}$)	<u>15</u>	<u>20</u>	<u>15</u>
E-100 LMTD ($^{\circ}\text{C}$)	46	46	33
U ($\text{W}/\text{m}^2\cdot^{\circ}\text{C}$)	1000	1000	1000
A (m^2)	0.15	0.15	0.21
T_#3 ($^{\circ}\text{C}$)	440	460	460
E-101 duty ($\text{MJ}_{\text{th}}/\text{m}^3$ product water)	<u>670</u>	<u>520</u>	<u>410</u>
P-100 power ($\text{MJ}_{\text{el}}/\text{m}^3$ product water)	40	50	50

*Simulation results for a pilot unit (5. DESIGN OF A PILOT UNIT)

In addition, the extra heating (E-101 duty) required to raise the temperature of the pre-heated stream (#2) from the heat exchanger to the desired operating temperature is lower (22% reduction) when the process is operated at 300 bar compared to operating at 250 bar. For system stability, heat integration potential and lower energy consumption, we have selected 300 bar as the operating pressure of the SCWD process.

A final process simulation of the SCWD process at 300 bar was then carried out utilizing the heat integration potential at 300 bar by increasing the heat exchange area from 0.15 to 0.21 m^2 , this reduces the minimum approach temperature from 20 to 15 $^{\circ}\text{C}$ and the thermal energy consumption from 520 to 410 $\text{MJ}_{\text{th}}/\text{m}^3$ product water (see Table 1, last column, 300*).

The process design and simulation in UniSim was carried out using the properties of pure water neglecting the influence of the salt present on the process, especially

the heat exchanger performance (complications such as possible temperature cross in the heat exchanger) and the energy required by the process. The effects of the presence of salt in solution on the system was checked by modeling the heat exchanger (E-100) using the P-T- X_{NaCl} -h correlation developed by Driesner³² for a 3.5 wt.% NaCl solution (feed concentration for the SCWD process) at 300 bar.

Figure 8. Temperature Profile of Heat Exchanger E-100 from UniSim for water (a) and temperature profile calculated for 3.5 wt.% NaCl (b) using the P-T- X_{NaCl} - Enthalpy correlation of Driesner³².

The temperature profiles in the heat exchanger (E-100) for the simulation in UniSim with water and for modeling a 3.5 wt.% NaCl solution are shown in Figure 8(a) and (b) respectively. The profile for the two cases follow similar trend, and there is no temperature cross in the heat exchanger for the 3.5 wt.% case. A slight reduction in the heat exchanger duty (E-100 duty), the minimum approach temperature (E-100 $\Delta T_{\min}$) was observed with the presence of salt (see Table 2). Also, a 10% increase in the thermal energy required by the process (E-101 duty) was found for the 3.5 wt.% NaCl case. Although the presence of 3.5 wt.% NaCl in solution does have some slight effects on the heat exchange and energy requirement of the process, the simplification in the UniSim simulation with pure water is a good approximation for the real system. However, the thermal energy requirement obtained in the 3.5 wt.% case will be taken as the thermal energy needed for the SCWD process.

Table 2. Effect of the presence of salt on simulation results.

P = 300 bar	UniSim (H₂O)	3.5 wt.% NaCl
E-100 duty (GJ/m ³ product water)	2.5	2.3
E-100 ΔT_{min} (°C)	<u>15</u>	<u>12</u>
A (m ²)	0.21	0.21
E-101 duty (MJ/m ³ product water)	<u>410</u>	<u>450</u>

In real sea water systems, there is potential for other salts such as CaSO₄ and MgSO₄ to precipitate on the walls of the heat exchanger due to their very low solubilities at the conditions in the heat exchanger (sub to supercritical conditions). In the concentrated brine the solubility of these salts will be increased,³³ but if this will be sufficient to avoid solid formation needs to be investigated. How the scaling can be handled will be the focus of subsequent research on the pilot plant.

5. DESIGN OF A PILOT UNIT

A proposed process design for the SCWD process for producing 10 kg/hr of drinking water is shown in Figure 9 with the stream properties table added. The feed stream is pressurized and heated up to a pressure of 300 bar and a final temperature of 460 °C in the separator. At these supercritical conditions, the stream is separated into a vapor (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 475 °C in order to prevent salt crystallization (see phase diagram, Figure 5) in the separator, which could lead to equipment blockage 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 with that to 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 for the heated feed stream (#3) to be brought to the desired operating temperature is provided in the heated separator.

Figure 9. Proposed Process Design of a Pilot unit for the SCWD Process.

Kritzer²⁸ and Marrone and Hong³⁴ 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 will be operating in such environment, therefore, Titanium grade 1 has been chosen as material of construction for the shell and tube.

The highly concentrated brine stream (#7) is moved into a crystallizer 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-pressurized to obtain drinking water of about 750 ppm TDS (safe limit for drinking water is 1000 ppm³⁴). This pilot plant has been designed and is under construction. A subsequent paper (to be published) will report the results of measurements and performance of the pilot plant.

The estimated thermal energy consumption for this process is about 450 MJth/m³ drinking water, taking heat integration into account. The expected investment and operational costs direct the research to using the SCWD process as a post-treatment step for other conventional desalination methods.

6. CONCLUSIONS

A design of a pilot plant unit for the supercritical desalination of salt-water streams with zero liquid discharge has been presented. The phases present at supercritical conditions for a NaCl 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 °C at 250 bar, and 475 °C at 300 bar.

The phase equilibrium of NaCl–H₂O has been studied under isobaric conditions in a lab-scale experimental set-up. Solubility of NaCl in the vapor phase in the V–L region was found to decrease with increasing temperature and increase with increasing pressure. In addition, the phase equilibrium curve shifts upwards and becomes narrower at the higher pressure of 300 bar. All results obtained are in agreement with literature (see Figure 5).

A lab-scale unit has been designed, built and operated at 300 bar and 460 °C to demonstrate the proof of principle of the SCWD process. A vapor phase (750 ppm NaCl) and a concentrated liquid phase (50 wt.% NaCl) were obtained under the process condition. The 50 wt.% brine was then flashed to atmospheric pressure to produce fine salt crystals of 2–5 µm clustered together.

The SCWD process has been simulated in UniSim Design at 250 and 300 bar pressure with pure water only to mimic the process. Operating the SCWD process at 300 bar pressure has been found to offer better heat integration potential as well

as a 22% reduction in thermal energy consumption compared to 250 bar. As a result, 300 bar has been selected as the operating pressure of the SCWD process.

A SCWD process with a two-stage (V-L at 300 bar, 460 °C and V-S at atmospheric pressure) separation step has been designed for the production of 10 kg/hr drinking water (~750 ppm TDS) without the production of any waste stream (ZLD), as opposed to the conventional MSF and RO processes. The stand-alone thermal energy consumption is estimated at 450 MJ_{th}/m³.

NOMENCLATURE

A = area, m²

h = specific enthalpy, kJ/kg

$i.d$ = inside diameter, mm

LMTD = logarithmic mean temperature difference, °C

$o.d$ = outside diameter, mm

P = pressure, bar

ppm = parts per million

SEM = scanning electron microscope

T = temperature, °C

TDS = total dissolved solids

X_{NaCl} = mole fraction of sodium chloride

U = overall heat transfer coefficient, W/m², °C

V-L = vapor-liquid

V-L-S = vapor-liquid-solid

ZLD = zero liquid discharge

Greek Symbol

ΔT_{min} = minimum temperature approach, °C

Subscripts

c = critical

el = electrical

min = minimum

th = thermal

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Chapter 3

Heat Transfer to Sub- and Supercritical Water Flowing Upwards in a Vertical Tube at Low Mass Fluxes: Numerical Analysis and Experimental Validation

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ABSTRACT

Heat transfer to supercritical water (SCW) flowing upwards in a vertical heated tube at low mass fluxes ($G \leq 20 \text{ kg/m}^2\cdot\text{s}$) has been numerically investigated in COMSOL Multiphysics and validated with experimental data. The turbulence models - essential to describe local turbulence - in COMSOL have been checked under conditions where empirical heat transfer correlations are available, and it is concluded that the Shear-Stress Transport (SST) turbulence model gives the most accurate results. Numerical results obtained show a buoyancy induced circulation of the fluid resulting from gravitational force acting on density gradients as well as a thin thermal boundary layer with a steep temperature gradient at the inner wall and a flat temperature profile in the bulk fluid. The heat transfer coefficient of SCW is enhanced near the pseudo-critical temperature (T_{pc}), and is deteriorated at temperatures above T_{pc} . A new heat transfer correlation has been developed and validated with experimental data.

1. INTRODUCTION

Supercritical water (SCW) has found many applications in the last decades and the range of applications keep growing with time. Several applications are based on SCW being a “green” solvent, its properties being tunable by changes in temperature and pressure, and its solvation behaviour for a variety of substances.¹ SCW has been used as a reaction medium for the conversion of biomass to hydrogen and natural gas,^{2,3} liquid fuels,⁴ for the total oxidation of hazardous materials (supercritical water oxidation –SCWO-)⁵⁻⁸ as well as organic synthesis. SCW has been proposed as a coolant for nuclear reactors allowing for high heat transfer and increased thermal efficiency.⁹ SCW also has potential in desalination for the production of drinking water with zero liquid discharge.¹⁰

Supercritical water processes are energy intensive (about 2 GJ of energy is required to bring 1 m³ of water from atmospheric conditions, $P = 1.02$ bar, $T = 25$ °C, to supercritical conditions, $P_c = 221$ bar, $T_c = 375$ °C). In order to make supercritical water processes a commercial success, heat integration is required to regain as much energy as possible from the process. To achieve this, the feed stream is heated by the supercritical product stream in a heat exchanger that operates at sub- to supercritical water conditions. In this heat exchanger, the feed will turn supercritical and the product stream will become liquid (subcritical) resulting in significant changes in properties such as the density, viscosity, heat capacity and thermal conductivity (see Figure A-1 in Appendix A), which significantly influence the heat transfer characteristics.¹¹

Currently, most research on SCW heat transfer is focused on using SCW as a coolant in large scale nuclear reactors, which requires high mass fluxes ($G > 200$ kg/m².s).^{9,12-15} However, for designing pilot plant scale SCW processes – such as supercritical desalination¹⁰ and supercritical water gasification³ – it may be required to know the heat transfer characteristics of SCW at low mass fluxes (typically $G \leq 20$ kg/m².s). At these low mass fluxes (mostly laminar flows – $Re < 2300$), heat transfer may be either deteriorated or enhanced due to natural convective forces, which do not play an important role at high mass fluxes (turbulent flows).¹⁵

To the best of our knowledge, the work of Withag et al.¹⁶ is the only work on heat transfer to SCW at low mass fluxes reported in literature. Withag et al.¹⁶ performed experiments and carried out 2D numerical simulations on supercritical water flowing upward in a vertical tube with mass fluxes ranging from 6.6-10.0 kg/m².s in COMSOL Multiphysics using the low-Reynolds $k - \varepsilon$ model. Although the numerical simulation correctly predicted the shape of the temperature profile measured in their experimental apparatus, the experimental values were over-predicted.

In general, essential insights into the heat transfer characteristics as well as an engineering correlation for heat transfer in supercritical water at these low mass fluxes necessary for designing heat transfer equipment especially for pilot scale supercritical water processes are lacking. The objective of this work is to provide these insights by numerical simulation and experimental validation. First, a 2D model is set up in a commercial CFD package, COMSOL Multiphysics 5.0 (which we hereafter denote as COMSOL) and calculations are performed to check if the model can accurately describe temperature profiles and heat transfer for flow conditions with known Nusselt correlations (see Appendix A). Next, 2D simulations are performed for up-flow of water in a heated vertical tube under sub- and supercritical conditions to calculate the flow patterns, temperature profiles as well as heat transfer coefficients. The influence of mass flux and tube diameter on heat transfer characteristics are investigated. The results of the 2D model for the up flow in a heated tube are validated with experiments in a newly designed apparatus. Finally, a 1D Nusselt correlation for engineering design is proposed and validated with experimental results.

2. THEORETICAL BASIS

2.1. Governing Equations

The equations that describe a steady, compressible two-dimensional flow follows from the laws of conservation of mass, momentum and energy.^{17,18} The mass and momentum equations, Eqs.1 and 2 respectively, represent the steady state

compressible Reynolds Averaged Navier-Stokes (RANS) equations for turbulent flows.

$$\nabla \cdot (\rho \mathbf{u}) = 0 \quad (1)$$

$$\begin{aligned} \rho(\mathbf{u} \cdot \nabla) \mathbf{u} = \nabla \cdot (-p\mathbf{I}) + \nabla \cdot \left[(\mu + \mu_T)(\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3}(\mu + \mu_T)(\nabla \cdot \mathbf{u})\mathbf{I} \right] \\ - \nabla \cdot \left(\frac{2}{3}\rho k\mathbf{I} \right) + \mathbf{F} \end{aligned} \quad (2)$$

The volume force vector, $\mathbf{F}$, accounts for the gravity force that act downwards in the z-direction.

$$\mathbf{F} = \begin{bmatrix} F_r \\ F_z \end{bmatrix} = \begin{bmatrix} 0 \\ -\rho g \end{bmatrix} \quad (3)$$

The conservation of energy is described by:

$$\rho C_p \mathbf{u} \cdot \nabla T = \nabla \cdot (\lambda_{eff} \nabla T) \quad (4)$$

where λ_{eff} is the effective thermal conductivity.

2.2. Turbulence Modelling

Although the radial-averaged Reynolds number for the low flux SCW heat transfer model is expected to be below 2300 (i.e. laminar flow), some local turbulence is expected due to the increased flow near the wall caused by natural convection induced by the gravity force acting on the significant change in density (see Figure A-1 of Appendix A) around the pseudo-critical temperature (temperature at maximum C_p ; see Figure A-1 of Appendix A). Metais and Eckert¹⁹ have shown that transition to turbulence may occur at Reynolds numbers as low as 200 for natural convection induced flows. It is therefore necessary to include an accurate turbulence model in the COMSOL simulations.

In order to determine which turbulence model will best represent our system, preliminary simulations were carried out in COMSOL in three flow regimes for which correlations are available in literature: laminar and turbulent flows under normal temperature and pressure conditions, and turbulent supercritical water flow (see Figures A-3, A-4 and A-5 of Appendix A for the results). The Shear-Stress

Transport (SST) turbulence model was found to give the most accurate results in these flow regimes, and was therefore chosen as the turbulence model for further simulations.

The SST model combines the robustness of the $k - \varepsilon$ turbulence model in the bulk of the fluid and the $k - \omega$ turbulence model in the near-wall region. In addition, the SST model utilises a y^+ -insensitive (where y^+ is the near-wall grid resolution) wall treatment which has been found to improve its predictive accuracy for general industrial applications while eliminating the user influence in grid generation.²⁰ Accurate solutions require $y^+ < 1$.²¹ For more information on the SST model, see the book of Versteeg and Malalasekera¹⁸, Menter et al.²⁰ and the COMSOL CFD user guide.²¹

The heat flux in Eq.4 is modelled using the Kays-Crawford heat turbulence model.²² The turbulence model takes into account the contribution of turbulent fluctuations to the temperature field. See Kays et al.²² for detailed explanation of the Kays-Crawford heat turbulence model.

2.3. Natural Convection

Natural convection or free convective flow is induced by buoyancy forces. When temperature differences are introduced through boundaries maintained at different temperatures, the resulting density differences will induce motion; hot fluid tends to rise, cold fluid tends to fall.²³ When both forced and natural convection are present in a system, this is called mixed convection.¹⁵ There are two types of mixed convection: (i) aiding flow, when natural convection acts in the same direction as forced convection, and (ii) opposing flow, where natural convection acts in the opposite direction to forced convection.¹⁵ In this work only aiding flow will be considered. This means that heated flows are always flowing upwards. Natural convection is modelled with Eq.3 as part of the RANS equation.

2.4. Properties of Water in the Critical and Supercritical region

The thermo-physical properties of water are estimated with industrial formulations of the IAPWS (International Association for the Properties of Water and Steam).^{11,24,25} These formulations, based on experimental data, calculate the desired properties in the critical region with an error as given in Table 1. Thermo-

physical properties of water as functions of temperature and pressure are shown in Figure A-1 of Appendix A. The temperature at the maximum value of C_p is called the pseudo-critical temperature, T_{pc} and it is pressure dependent. At 270 bar, $T_{pc} = 392$ °C and at 300 bar, $T_{pc} = 402$ °C. The physical properties of the fluid are imported to the COMSOL model using the Matlab implementation of the IAPWS formulations called *XSteam*.²⁶

Table 1. Error of the IAPWS formulations with experimental data at 300 bar for 327 °C < T < 527 °C.

Property	Error	Source
C_p	3%	IF-97 ¹¹
ρ	0.2%	IF-97 ¹¹
μ	3%	IAPWS Viscosity ²⁵
λ	2%	IAPWS Thermal conductivity ²⁴

2.5. Discretization and Boundary Conditions

A 2D-axisymmetrical geometry is constructed in COMSOL. Dimensions of the test sections are given in Table 2 and a schematic is shown in Figure 1. The water inlet is placed at the bottom of the tube. The inlet velocity is given as a parabolic laminar flow profile, and a uniform inlet temperature is set. An inlet region (10 cm, from $z = -10$ cm to $z = 0$ cm) is assigned to put some distance between the model boundary and the physics domain to improve model stability.²¹ A linearly increasing temperature profile is specified at the outer walls (insulated from the environment) with the exception of the experimental validation simulations (section 5.) where the outer wall temperature profiles obtained from the experiments are specified. The outlet is defined as a pressure boundary with the pressure specified. And the tube inner wall has been modelled with the no-slip boundary condition for fluid flow.

The numerical grid is 2D-axisymmetrical and consists of triangular elements. It is refined near the heated wall and expands towards the centre of the tube. Near-wall cells are 0.008 mm in size and grow to 0.5 mm at the centre of the tube (see Table A-1 and Figure A-2 of Appendix A for grid sensitivity analysis). A near-wall resolution, y^+ value of 0.4 has been used in the simulations.

Table 2. Parameters for 2D heated tube model.

Mass flux, G (kg/m ² .s)	3.0, 7.0, 20.0
Pressure, P (bar)	300
Inlet temperature, T_{in} (°C)	27, 127, 327
Outer wall temperature, T_{ow} (°C)	177-527, 377-527
Tube diameter, d_t (cm)	1, 2, 4
Inlet Reynolds number, Re_{in}	200 - 2000
Tube Reynolds number, Re_t	200 - 9000
Grashof number, Gr	$3 \times 10^6 - 9 \times 10^{10}$
Prandtl number, Pr	0.67 - 3.6

Figure 1. Geometry of the heated tube (base case) model.

The heated tube model simulation with $G_t = 7 \text{ kg/m}^2 \cdot \text{s}$, $d_t = 1 \text{ cm}$, $T_{in} = 327 \text{ °C}$ and $T_{ow} = 377 - 527 \text{ °C}$ will from hereon be referred to as *the heated tube base case*.

2.6. Post-Processing

The post-processing of the results consists mainly of averaging the 2D solutions which are functions of the r - (radial) and z - (axial) directions to obtain 1D results which are dependent only on the z -direction.

The average temperature of the fluid is determined by the mixing cup temperature and is calculated using Eq.5.

$$T_{mc}(z) = \frac{\int_{R_i}^{R_o} 2\pi r \cdot G(r, z) \cdot C_p(r, z) \cdot T(r, z) \cdot dr}{\int_{R_i}^{R_o} 2\pi r \cdot G(r, z) \cdot C_p(r, z) \cdot dr} \quad (5)$$

The other temperature that is important is the temperature of the fluid at the inside wall T_{iw} . The 1D averaged fluid properties are evaluated at the operating pressure

and $T = T_{mc}$, resulting in ρ_{mc} , $C_{p,mc}$, etc. since they are a strong function of temperature around the critical point.

The following dimensionless numbers are defined:

$$Nu = \frac{h \cdot d_t}{\lambda} = \frac{\phi''_{h,w} \cdot d_t}{(T_{iw} - T_{mc}) \cdot \lambda_{mc}} \quad (6)$$

$$Re = \frac{G \cdot d_t}{\mu_{mc}} \quad (7)$$

$$Pr = \frac{C_{p,mc} \cdot \mu_{mc}}{\lambda_{mc}} \quad (8)$$

$$Gr = \frac{g \cdot \beta_{mc} \cdot (T_{iw} - T_{mc}) \cdot d_t^3 \cdot \rho_{mc}^2}{\mu_{mc}^2} \quad (9)$$

where $\beta_{mc} = \frac{-1}{\rho_{mc}} \left(\frac{\partial \rho}{\partial T} \right)_p$

3. EXPERIMENTAL SECTION

In order to validate the results of the 2D COMSOL simulations as well as the proposed 1D Nusselt correlation, an experimental apparatus has been designed and constructed. Temperature measurements at different radial and axial positions in water flowing at sub- and supercritical conditions has been obtained. A detailed description of the apparatus as well as validation results is provided in this section.

3.1. Experimental Apparatus

The schematics of the experimental apparatus is shown in Figure 2. The main part of the apparatus consists of a stainless steel tube (with an inner diameter of 2.14 cm, outer diameter of 3.41 cm and length 154 cm) fitted with 8 aluminum heating blocks that keep the tube outer wall at a pre-set temperature. The heating blocks are insulated from the environment with stone wool to reduce heat losses.

Pressures up to 400 bar were provided to the tube with a high pressure pump (LEWA diaphragm pump LDC1, LEWA Herbert Ott GmbH & Co KG, Germany, max. P, 400 bar, max. flow 25.0 L/hr) and controlled with a back pressure regulator (TESCOM 26-1762-24A, Tescom Europe GmbH & Co. KG, Germany, $C_v = 0.14$).

The uncertainty in pressure was 0.3% (0.9 bar at 300 bar), while the uncertainty in mass flow measurement was 1%. The water is pre-heated by an electric heater (T-C1 is for temperature control, and T-S1 is for the set safety temperature) until the desired inlet temperature is attained. The water is heated as it flows upwards in the tube with the aid of the aluminium heating blocks. Each heating block can be set to a desired temperature (by adjusting T-C2), and the temperature at the tube outer wall in each heating block section is measured at the top and bottom parts of the section with T2 and T1 respectively. The experimental apparatus can be operated at pressures up to 350 bar, and temperatures up to 500 °C.

Nine thermocouples (Ti1-Ti9), held at different predefined radial positions, but at the same axial position by a movable thermocouple holder measure the radial temperature profile in the tube at different heights. All temperatures were measured using standard type-K thermocouples (uncertainty in temperature measurement is 0.4% of measured value in °C, while the relative difference of measured values between thermocouples is 0.2 °C).

At the tube outlet, the water is cooled to a temperature below 70 °C (temperature limit of the back pressure regulator) with a shell and tube water cooler and then depressurised. Mass in and out are weighed to ensure mass balance closure. Temperatures (outer wall and inside the heated tube) are monitored and recorded (at steady state) with the aid of PicoLog data acquisition program.

3.2. Experimental Procedure and Test Conditions

At the start of each measurement, the thermocouple holder is moved to the desired axial position then the pump is switched on. The desired operating pressure in the tube is attained by adjusting the air-controlled back pressure regulator (BPR). A cold test is carried out to check for leakages. Then the pre-heater is turned on and adjusted to obtain the desired inlet temperature. Thereafter, the heating blocks are switched on and set to the desired values. The outer wall temperatures as well as the temperature inside the tube are monitored with the aid of PicoLog data acquisition program. When steady state is attained (fluctuations of not more than 1 °C in all measured temperatures over a period of 10 minutes), the data is recorded. At the end of data acquisition, the apparatus is depressurised and cooled. The thermocouple

holder is then moved to the next measurement position (axial) and the procedure described above is repeated.

Measurements are carried out at tube axial positions 24, 44, 64, 84, 104, 124 and 144 cm respectively. Test conditions are summarized in Table 3. The test cases are modelled in COMSOL with tube dimensions, mass flow, pressure, inlet temperature and outer wall temperature profile (all obtained from experiment) as model input parameters and stainless steel chosen as tube material.

Table 3. Test conditions for validation of 2D COMSOL model and proposed 1D Nusselt correlation.

	Case A	Case B
$\dot{m}$ (kg/hr)	4.1	8.0
G (kg/m ² .s)	3.2	6.2
P (bar)	300	300
T_{in} (°C)	104	86
T_{ow} (°C)	210-399	211-398

Figure 2. Schematics of the heated tube experimental apparatus.

4. RESULTS OF 2D COMSOL SIMULATIONS

4.1. Heated Tube Base Case Model

Results of the heated tube base case ($G = 7 \text{ kg/m}^2\cdot\text{s}$, $d_t = 1 \text{ cm}$, $T_{in} = 327 \text{ }^\circ\text{C}$ and $T_{ow} = 377 - 527 \text{ }^\circ\text{C}$) are presented and discussed. The obtained velocity profile (streamlines) and the variation of the axial mass flux along the tube radius at

different axial positions for the steady state simulation are shown in Figure 3(a) and Figure 4 respectively.

Figure 3. Velocity streamlines (m/s) of the heated tube base case (a) and the base case without volume force (Eq.3) in the RANS equation (b): Fluid is $r = 0 - 0.5$ cm, wall is $r = 0.5 - 0.7$ cm.

Figure 3a shows three regions: (i) a stagnant zone around the center of the tube (in the region $0 < r < 0.15$ cm and $0 < z < 30$ cm), (ii) an adjacent circulation zone and (iii) a flow region with a growing momentum boundary layer at the near-wall region. At the beginning of the heat transfer area ($z = 0$ cm), the incoming fluid comes in contact with the circulating and/or stagnant bulk and is (abruptly) transported to the wall. As the fluid comes into contact with the heated wall surface, a boundary layer is formed due to the actions of buoyancy forces which drag the fluid along the wall leaving a mostly stagnant region in the bulk of the fluid.

Along the length of the heated tube, an increased upward velocity near the wall (about 10 x the inlet velocity) is observed. This is a direct result of the fluid near the wall heating up and consequently significantly decreasing density compared to the bulk fluid. This results in a vertical force accelerating the fluid in the upward

direction near the wall, and thus decreasing the velocity in the bulk. Natural convection induced circulation flow from the wall into the bulk of the fluid and back creates mixing. This circulation flow is reflected in the negative axial mass fluxes at $z = 20, 40$ and 60 cm as shown in Figure 4.

Figure 3b shows the velocity streamlines for the same simulation without the volume force (Eq.3) as part of the RANS equation. The velocity profile obtained is that of a laminar flow without the influence of natural convection with the maximum velocity at the centre of the tube, and the lowest velocity at near-wall region (see Figure 6b for the surface temperature plot). We can conclude that the flow pattern in Figure 3a is a buoyancy-induced motion resulting from volume forces acting on density gradients which arise from temperature gradients in the fluid.

Jackson and Hall²⁷ have provided a general criterion (Eq.10) for when the influences of buoyancy become negligible for supercritical fluids in vertical flows. Above the proposed limit, the higher the value for $Gr/Re^{2.7}$ the larger the influence of buoyancy.

$$\frac{Gr}{Re^{2.7}} < 10^{-5} \quad (10)$$

Figure 4. Variation of axial mass flux along the tube radius at different axial positions for the heated tube base case.

Figure 5 shows that the values of $Gr/Re^{2.7}$ obtained for the base case simulation are much higher than the proposed limit of Jackson and Hall²⁷ indicating a dominant influence of buoyancy.

Figure 5. Variation of $Gr/Re^{2.7}$ along the tube length for the heated tube base case.

The surface plots of the temperature profile are shown in Figure 6a for the heated tube base case and Figure 6b without the volume force as part of the RANS equation. In Figure 6a, a flat temperature profile (absent in Figure 6b) is observed in the bulk indicating that the buoyancy-induced circulation flow increases mixing in the fluid bulk. In addition, a thermal boundary layer of about 0.2–0.5 mm (the boundary layer grows thicker away from the circulation zone) from the heated surface with a steep temperature gradient is observed. The radial temperature profile can be seen more clearly in Figure 7. The temperature from the outer tube wall to the tube center at three different axial position is plotted against the tube radial coordinates. A radial temperature gradient is observed only in the thermal boundary layer close to the tube inner wall. The temperature gradient in the thermal boundary layer as well as the thickness of the boundary layer is observed to increase as the fluid moves away from the circulation zone.

Figure 6. Temperature profile of the heated tube base case (a) and the base case without volume force (Eq.3) in the RANS equation (b). Fluid is $r = 0 - 0.5$ cm, wall is $r = 0.5 - 0.7$ cm.

Figure 7. Radial temperature profiles at $z = 20, 60$ and 80 cm respectively for the heated tube base case.

Heat transport in the fluid domain is by convection and conduction (turbulent and non-turbulent contributions). The non-turbulent conductive ($\phi_{h,cond}''$), turbulent conductive ($\phi_{h,T}''$) and convective ($\phi_{h,conv}''$) heat fluxes are defined in Eqs. 11, 12 and 13 respectively. Figure 8 shows the variation of the contributions of the convective and conductive heat fluxes to the total radial heat flux along the radius at different axial positions. Positive values depict heat flux towards the wall, while negative values denote heat flux towards the tube center. While the fluid in the thermal boundary layer ($0.45 < r < 0.5$ cm) is heated by thermal conduction and convection in the radial direction, very close to the wall ($r = 0.495$ cm), heat is primarily transferred to the fluid by non-turbulent conduction. Away from the thermal boundary layer towards the center of the tube, radial heat transport is primarily due to convection.

$$\phi_{h,cond}'' = -\lambda \cdot \nabla T \quad (11)$$

$$\phi_{h,T}'' = -\lambda_T \cdot \nabla T \quad (12)$$

$$\phi_{h,conv}'' = \rho \cdot \mathbf{u} \cdot \left(H - \frac{P}{\rho} \right) \quad (13)$$

Figure 8. Radial heat flux variation over the radius at different axial positions for the heated tube base case (See Eqs.11-13 for definitions of the heat fluxes): positive values denote the direction is towards the wall, while negative values denote the direction is towards the center of the tube.

Figure 9 shows the heat transfer coefficient (HTC), tube inner wall temperature and the tube centre (bulk) temperature as function of the axial position. The HTC is observed to go through a peak ($2750 \text{ W/m}^2\cdot\text{K}$) at $T_{iw} = 402^\circ\text{C}$ and $T_b = 389^\circ\text{C}$, then decreases rapidly to about $300 \text{ W/m}^2\cdot\text{K}$. This shows a deteriorated heat transfer in SCW laminar flow at temperatures above the pseudo-critical temperature. Above the pseudo-critical temperature, the properties of supercritical water becomes more gas-like under isobaric conditions. This might account for the deteriorated heat transfer coefficient obtained at these temperatures.

Figure 9. Bulk temperature, tube inner wall temperature and HTC profile as function of axial position for heated tube base case.

4.2. Effect of Mass Flux

The effect of mass flux was investigated for 3, 7 and 20 kg/m².s in a tube diameter of 1 cm, inlet temperature of 327 °C and linearly increasing wall temperature of 377-527 °C. The velocity streamlines are shown in Figure 10 (see Figure A-6 in Appendix A for the axial mass flux plots). As the mass flux (and consequently mass flow since tube diameter is constant) increases, the sizes of the circulation zone and stagnant zone decrease.

Figure 11 shows the values of $Gr/Re^{2.7}$ to be higher than the proposed limit of Jackson and Hall²⁷ (Eq.10) for all mass fluxes investigated, indicating that buoyancy effects are present. However, the influence of buoyancy decreases with increasing mass flux.

Figure 10. Velocity streamlines (m/s) for mass fluxes $3 \text{ kg/m}^2\text{s}$ (a), $7 \text{ kg/m}^2\text{s}$ (b) and $20 \text{ kg/m}^2\text{s}$ (c) for $d_t = 1 \text{ cm}$, $T_{in} = 327 \text{ }^\circ\text{C}$ and $T_{ow} = 377\text{-}527 \text{ }^\circ\text{C}$: Fluid is $r = 0 - 0.5 \text{ cm}$, wall is $r = 0.5 - 0.7 \text{ cm}$.

Figure 11. Variation of $Gr/Re^{2.7}$ along the tube length for the different mass fluxes and tube diameters.

As shown in the dimensionless radial temperature plot at tube axial positions 20 and 60 cm respectively (Figure 12), there is no substantial influence of mass flux (in the range considered in this work) on the dimensionless radial temperature profile of

the fluid. We can conclude that for the flow conditions investigated, the reduction in the influence of buoyancy noticeable in the velocity profiles (decrease in the circulation zone with increasing mass flux in Figure 10) is not substantial enough to affect the dimensionless radial temperature profile with respect to the thickness of the boundary layer (see Figure 12), which could explain the observation that the HTC is only marginally affected by the mass flux (see Figure A-7, Appendix A). Increasing the mass flux increases the temperature difference between bulk and wall at almost constant inner wall temperature (see Figure 12) which follows directly from the energy balance including a "constant" HTC (constant HTC with respect to mass flux, see Figure A-7, Appendix A).

Figure 12. Dimensionless radial temperature profiles for the different mass fluxes at $z = 20$ and 60 cm respectively for $d_t = 1$ cm, $T_{in} = 327$ °C and $T_{ow} = 377$ - 527 °C.

4.3. Effect of Tube Diameter

The influence of tube diameter on the flow profile is shown in Figure 13 for the conditions described in the figure caption (see Figure A-8 of Appendix A for the axial mass flux plots). Increasing the tube diameter while maintaining the same mass flux leads to an increase in the sizes of the circulation and the stagnant zones respectively. Figure 11 shows the variation of $Gr/Re^{2.7}$ over the tube length. An

increase in the influence of buoyancy on the fluid flow is observed with increase in tube diameter.

The dimensionless radial temperature plot (Figure 14) shows a decrease in the dimensionless thermal boundary layer with increase in tube diameter, however, the absolute thermal boundary layer thickness, taking the tube diameter into account (0.2-0.5) hardly changes. The constant absolute thermal boundary layer thickness explains the marginal influence of the tube diameter on the HTC (see Figure A-9, Appendix A).

Figure 13. Velocity streamlines (m/s) for tube diameters 1 cm (a), 2 cm (b) and 4 cm (c) for $G = 7 \text{ kg/m}^2\cdot\text{s}$, $T_{in} = 327^\circ\text{C}$ and $T_{ow} = 377\text{-}527^\circ\text{C}$.

(a)

(b)

Figure 14. Dimensionless radial temperature profiles for the different tube diameters at $z = 20$ and 60 cm respectively for $G = 7$ kg/m².s, $T_{in} = 327$ °C and $T_{ow} = 377$ - 527 °C (a) and with the near-wall region enlarged (b).

4.4. Nusselt Correlation

Nusselt numbers calculated from the 2D COMSOL model are fitted to other dimensionless numbers (Gr , Re , Pr) and fluid properties. The model parameters used in the simulations and dimensionless numbers that have been used for the data fitting are shown in Table 2.

We have fitted our data to the correlation proposed by Mokry et al.⁹:

$$Nu = a \cdot Gr^b \cdot Pr^c \cdot Re^d \cdot \left(\frac{\rho_w}{\rho_{mc}}\right)^e \cdot \left(\frac{C_{p,w}}{C_{p,mc}}\right)^g \cdot \left(\frac{\lambda_w}{\lambda_{mc}}\right)^f \cdot \left(\frac{\mu_w}{\mu_{mc}}\right)^h \quad (14)$$

Which includes the effect of forced convection (Re), natural convection (Gr) and fluid properties (Pr), as well as a correction factor based on the difference in physical properties between the fluid in the bulk (mixing cup average) and the fluid at the wall. In Eq.14, $a - h$ represent the fit parameters. The Nusselt fit obtained for the heated tube (Nu_t) is shown in Eq.15.

The effect of diameter in Reynolds and Grashof has been taken into account in the Nusselt correlation for the heated tube by fitting to results obtained from simulations for 3 tube diameters (1, 2 and 4 cm respectively).

$$Nu_t = \frac{h_t d_t}{\lambda_{mc,t}} = 0.78 \cdot Gr^{0.34} \cdot Re^{-0.26} \cdot Pr^{-0.07} \cdot \left(\frac{C_{p,w}}{C_{p,mc}}\right)^{0.20} \cdot \left(\frac{\rho_w}{\rho_{mc}}\right)^{0.23} \quad (15)$$

The Nusselt correlation fits within $\pm 20\%$ (Figure 15).

Figure 15. Nusselt correlations parity plot for SCW flow in a heated tube at low mass fluxes. Data used: $d_t = 1$ cm, $G = 3, 7$ and 20 kg/m².s; $d_t = 2$ cm, $G = 3$ and 7 kg/m².s; $d_t = 4$ cm, $G = 3$ and 7 kg/m².s; P , T_{in} and T_{ow} are listed in Table 2. Number of data points = 238028.

5. EXPERIMENTAL VALIDATION RESULTS

In this section, the validation of the 2D COMSOL model and the 1D Nusselt correlation for the test cases are discussed.

5.1. Validation of 2D COMSOL Model

The radial temperature profiles for cases A and B at tube length 44 cm and 84 cm are presented in Figure 16. The experimental results show a flat radial temperature profile in the fluid with a steep gradient at the near-wall region. The comparison of the numerical simulation results with the experimental data shows good agreement. This proves that the 2D COMSOL model correctly describes the radial temperature profiles for SCW flow at low mass fluxes.

Figure 16. Comparison of radial temperature profiles obtained from 2D COMSOL simulation with experimental data for test cases A (a), (b) and B (c), (d).

5.2. Validation of 1D Nusselt Correlation and Predictive Accuracy of COMSOL

The derived 1D Nusselt correlation for the heated tube model has been validated. A 1D heated tube has been modelled with the test conditions listed in Table 3 as input parameters. In the 1D model, the heated tube is divided into sections. The steady state heat balance for each section reads:

$$\dot{H}_{out} = \dot{H}_{in} + \dot{Q}_{wall} \quad (16)$$

The heat flow through the wall, $\dot{Q}_{wall}$ is calculated as:

$$\dot{Q}_{wall} = UA_{sec}(T_{ow} - T_{mc}) \quad (17)$$

where A_{sec} , is the heat transfer area of each section and U , is the overall heat transfer coefficient given as:

$$\frac{1}{U} = \frac{d_t \ln(d_{ow}/d_{iw})}{2\lambda_w} + \frac{1}{h_t} \quad (18)$$

where d_{iw} is the inner tube diameter, d_{ow} , the outer tube diameter and λ_w , is the temperature-dependent thermal conductivity of the stainless steel wall.

The heat transfer coefficient of the fluid in the tube (h_t) is obtained from the derived Nusselt correlation, Eq.15. The 1D heated tube model was solved iteratively.

The results of the 1D validation for cases A and B are presented in Figure 17 and Figure 18 respectively. In addition to the experimental results and the prediction from the proposed Nusselt correlation, predictions obtained using: the VDI heat atlas²⁸ correlation (Eq.19) for free convection, the Sieder-Tate¹⁷ correlation (Eq.21) for forced convection, the correlation of Mokry et al.⁹ (Eq.22) for turbulent supercritical water flow and results of 2D COMSOL simulations are also shown. The Sieder-Tate¹⁷ correlation was chosen as it is one of the most widely used HTC for forced convection while the VDI heat atlas²⁸ and Mokry et al.⁹ HTC correlations were chosen because they are one of the most recent and experimentally validated correlations for the free convection and turbulent SCW flow respectively.

$$Nu = \frac{h_t \cdot R}{\lambda} = 0.52 \cdot (Gr^* \cdot Pr)^{0.25} \quad (19)$$

where Gr^* is defined as :

$$Gr^* = \frac{g \cdot \beta \cdot (T_{iw} - T_{in}) \cdot R^4 \cdot \rho^2}{\mu^2 \cdot L} \quad (20)$$

The reference temperature for the properties is $\frac{1}{2}(T_{iw} + T_b)$.

$$Nu = \frac{h_t \cdot d_t}{\lambda} = 1.86 \cdot \left(Re \cdot Pr \cdot \frac{d_t}{L} \right)^{1/3} \cdot \left(\frac{\mu_b}{\mu_w} \right)^{0.14} \quad (21)$$

$$Nu = \frac{h_t \cdot d_t}{\lambda} = 0.0061 \cdot \overline{Pr}_b^{0.684} \cdot Re_b^{0.904} \cdot \left(\frac{\rho_w}{\rho_b} \right)^{0.564} \quad (22)$$

Results obtained with the Sieder-Tate and Mokry correlations significantly underestimate the experimental data. These correlations derived for turbulent flows where forced convection is the governing mechanism for heat transport are not suitable for low mass fluxes where natural convection governs the heat transport mechanism.

Although the VDI correlation performed much better than the forced convection correlations, it also under-predicts the measured temperature profiles. The VDI correlation has been derived for free convective flows under normal conditions of pressure and temperature and therefore cannot be applied to flows at sub- and supercritical conditions. However, we have shown that it is a good first estimate.

Figure 17. Experimental outer wall and mixing cup temperatures, and mixing cup temperature obtained from various Nusselt correlation for case A.

Figure 18. Experimental outer wall and mixing cup temperatures, and mixing cup temperature obtained from various Nusselt correlation for case B.

The comparison of the experimental data with the predicted mixing cup temperature obtained from the proposed Nusselt correlation and the results of the 2D COMSOL simulations show a good match.

6. CONCLUSIONS

A numerical study has been carried out in COMSOL Multiphysics CFD package to provide more insights into heat transfer characteristics of supercritical water flow at low mass fluxes ($G \leq 20 \text{ kg/m}^2 \cdot \text{s}$) in a heated tube. Using the SST turbulence model and including the volume force (to model natural convection) in the RANS equation are essential to accurately describe the flow. The 2D numerical results have been used to derive a 1D Nusselt correlation that can be used for quick engineering calculations. The numerical results and the proposed Nusselt correlation have been validated with experimental data.

An increased upward fluid velocity (about 10 times the inlet velocity) near the wall with a decreased velocity of the fluid in the bulk was observed. Buoyancy-

induced circulation resulting from volume force (gravitational force) acting on density gradients (a direct consequence of temperature gradients) is created. Radial heat transport in the boundary layer is by conduction and convection, while away from the boundary layer, heat is primarily transferred by convection. The heat transfer coefficient goes through a maximum as the temperature of the fluid approaches the pseudo-critical temperature, and then decreases rapidly at temperatures above the pseudo-critical temperature.

It was shown that the influence of buoyancy on the size of the induced circulation stream decreases with increasing mass flux (for the same diameter, inlet conditions and outer wall temperature profile) and increases with increasing tube diameter (for the same mass flux, inlet conditions and outer wall temperature profile) for the flow conditions investigated in this work. The mass flux and tube diameter only have a marginal effect on the HTC which could be explained by the simulation results which show that the mass flux and tube diameter only have a slight influence on the thickness of the thermal boundary layer.

Radial fluid temperatures of SCW flow at low mass fluxes in a heated tube have been successfully measured in a newly designed experimental apparatus at different axial positions. The numerical results are in good agreement with our experimental data. Temperature profiles obtained by using the proposed Nusselt correlation in a 1D heated tube model have been compared to our experimental data and widely used correlations for free and forced convection published in literature. The results of the proposed Nusselt correlation and the 2D COMSOL model for the heated tube show a good match with our experimental data.

NOMENCLATURE

A	heat transfer area (m^2)	Greek symbols	
C_p	isobaric heat capacity (J/kg.K)	β	thermal expansion coefficient (K^{-1})
CFD	Computational fluid dynamics	ε	turbulent dissipation rate (m^2/s^3)
d	diameter (m)	μ	dynamic viscosity (Pa.s)
$\mathbf{F}$	volume force ($\text{kg/m}^2.\text{s}^2$)	μ_T	turbulent viscosity (Pa.s)
g	gravitational constant (m/s^2)	ρ	density (kg/m^3)
G	mass flux ($\text{kg/m}^2.\text{s}$)	ϕ_h''	heat flux (W/m^2)
Gr	Grashof number	ω	turbulence frequency (s^{-1})
h , HTC	heat transfer coefficient ($\text{W/m}^2.\text{K}$)	λ	thermal conductivity (W/m.K)
H	enthalpy (J/kg)	Subscripts	
$\dot{H}$	rate of change of enthalpy (W)	avg	average
I	identity tensor	b	bulk
k	turbulent kinetic energy (J/kg)	c	critical
L	tube length (m)	cond	conductive
Nu	Nusselt number	conv	convective
p	relative pressure (Pa)	eff	effective
P	absolute pressure (Pa)	in	inlet
Pr	Prandtl number	iw	inner wall
$\dot{Q}$	heat flow (W)	mc	mixing cup average
r	radial coordinate (m)	ow	outer wall
R	tube radius (m)	pc	pseudo-critical
Re	Reynolds number	sec	section

SCW	supercritical water	t	tube
SST	shear-stress transport	T	turbulent
T	temperature ($^{\circ}\text{C}$)	w	wall
$\mathbf{u}$	velocity vector (m/s)		
U	overall heat transfer coefficient ($\text{W}/\text{m}^2\cdot\text{K}$)		
y^+	Near-wall grid resolution		
z	axial coordinate (m)		

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Appendix A

Supporting Information for Chapter 3

Figure A-1. Some selected properties of water showing variations around the pseudo-critical region at 270 and 300 bar. Temperature at maximum C_p is called the pseudo-critical temperature, $T_{pc} = 402$ °C at 300 bar.

Table A-1. Total number of elements with corresponding grid size for the 2D COMSOL mesh analysis

Number of Elements	Near wall grid size (mm)	Maximum grid size in bulk (mm)
44688	0.8	1.0
124857	0.08	1.0
419565	0.012	0.75
608499	0.008	0.5
1677552	0.004	0.25

Figure A-2. Mesh convergence for the 2D COMSOL SST model showing the ratio of the average axial velocity to the inlet velocity ($u_{z,avg}/u_{in}$) at axial position 30 cm (a) and the outlet (b) for the heated tube base case.

Table A-2. Parameters for low P-T turbulent water and turbulent SCW flow validation.

Parameter	Low P-T Laminar	Low P-T Turbulent	Turbulent SCW flow (Mokry et al. ¹)	Unit
P	1.013	1	270, 300	bar
G	1	1091	769	kg/m ² .s
u_{in}	0.001	1.1	1.1	m/s
d_t	2.0	1.0	1.0	cm
t	0.3	0.3	0.3	cm
L	100	70	50	cm
Re_{in}	25	16800	91750	
T_{in}	27	40	327	°C
T_{ow}	77	90	377 - 527	°C

Figure A-3. Nu validation for laminar flow under low P-T conditions. $Nu = 3.66$ for constant wall temperature in circular tubes.

Figure A-4. Nu validation for turbulent flow under low P-T conditions. Dittus-Boelter correlation: $Nu = 0.023 \cdot Re^{0.8} \cdot Pr^{0.4}$.

Figure A-5. Nusselt validation of COMSOL (SST turbulence model) with the correlation of Mokry et al.¹ for SCW flow at high mass fluxes at 270 bar (a) and 300 bar (b).

Figure A-6. Variation of axial mass flux along the tube radius at different axial positions for mass fluxes 3 kg/m².s (a), 7 kg/m².s (b) and 20 kg/m².s (c) for $d_t = 1$ cm, $T_{in} = 327$ °C and $T_{ow} = 377-527$ °C.

Figure A-7. HTC as function of T_b for mass fluxes 3 kg/m².s, 7 kg/m².s and 20 kg/m².s respectively for $d_t = 1$ cm, $T_{in} = 327$ °C and $T_{ow} = 377$ -527 °C.

Figure A-8. Variation of axial mass flux along the tube radius at different axial positions for tube diameters 1 cm (a), 2 cm (b) and 4 cm (c) for $G = 7$ kg/m².s, $T_{in} = 327$ °C and $T_{ow} = 377$ -527 °C.

Figure A-9. HTC as function of T_b for tube diameters 1 cm, 2 cm and 4 cm respectively for $G = 7 \text{ kg/m}^2 \cdot \text{s}$, $T_{in} = 327 \text{ }^\circ\text{C}$ and $T_{ow} = 377\text{-}527 \text{ }^\circ\text{C}$.

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Chapter 4

An Experimental Study of Heat Transfer to Sub- and Supercritical Water Flow in a Vertical Tube at Low Mass Fluxes

ABSTRACT

We have measured the heat transfer coefficient (HTC) of supercritical water (SCW) flow in a vertical heated tube at low mass fluxes ($G < 10 \text{ kg/m}^2\text{s}$) at 250 and 300 bar with bulk fluid temperatures ranging from 200 to 470 °C. To the best of our knowledge, we are the first to observe that at low mass fluxes, the HTC goes through a profound maximum near the pseudo-critical temperature, as also observed for high mass fluxes ($G > 500 \text{ kg/m}^2\text{s}$). Spatially-averaged measurement and a local (direct) measurement techniques were used, and it was found that only the local technique had enough resolution and accuracy to detect the maximum in HTC. Experimental results showed that at low mass fluxes, increasing the mass flow has negligible effect on the HTC indicating that natural convection is the dominant heat transfer mechanism. Decreasing the pressure leads to enhancement of heat transfer with an increased peak in HTC near the pseudo-critical temperature, T_{pc} . The pressure effect is associated with the larger changes in the density as a function of temperature with decreasing pressure in the pseudo-critical region. Our CFD based Nusselt correlation derived for a pressure of 300 bar showed good predictive power for the HTC measured at 300 bar with the local measurement technique.

1. INTRODUCTION

Supercritical water (SCW) has found many applications in the process industry due to its unique properties, such as; tunability of properties by changes in pressure and temperature, and solvation behavior for a number of organic and inorganic compounds. These applications range from the use of SCW as a reaction medium for the conversion of biomass to gaseous and liquid fuels,¹⁻³ for the total destruction of hazardous materials (supercritical water oxidation – SCWO –)⁴⁻⁷ and for desalination with zero liquid discharge.⁸ SCW processes have a high energy demand, and as such heat integration is requisite to their commercial success. Accurate predictions of heat transfer coefficients of SCW over a wide range of operating conditions are essential to the design of heat exchangers required for heat integration.

Most of the experimental and numerical studies on heat transfer to SCW flow have been carried out in the turbulent flow regime ($G \geq 200 \text{ kg/m}^2\text{s}$) typically found in supercritical water-cooled nuclear reactors (SCWR) and supercritical pressure boilers. These investigations (mainly focused on the critical region) reveal a rapidly increasing heat transfer coefficient (HTC) with a maximum at a temperature around the pseudo-critical temperature (T_{pc}) at the particular operating pressure.^{9, 10} The authors attribute the ‘unusual behavior’ of the HTC in the pseudo-critical region to the rapid change in physical properties of supercritical fluids in this region as small changes in temperature lead to large changes in fluid properties (see Figure 1). Although several researchers⁹⁻¹³ have proposed empirical correlations to calculate HTC for turbulent water flow under supercritical conditions, there are differences (up to factor 2 in some cases) in the values of HTCs calculated with these correlations.^{10, 14}

For laminar SCW flow (low mass fluxes, $G \leq 20 \text{ kg/m}^2\text{s}$) generally found in pilot plant scale supercritical water processes, where natural convection plays a significant role in the heat transport mechanism, experimental data as well as correlations on HTCs are lacking. Therefore, systematic and reliable experimental data in this flow regime are needed. In addition, it is of interest to know if the HTCs of SCW at low mass fluxes exhibit the same behavior (enhanced with a maximum)

near the pseudo-critical temperature as observed for high mass fluxes. The observed trend in the measured HTC at low mass fluxes are compared to literature HTC data at high mass fluxes in an attempt to obtain a better understanding of the heat transport mechanism.

We have carried out a numerical investigation on heat transfer to SCW flow at these low mass fluxes and proposed a new heat transfer correlation for sub- to supercritical water flowing upward in a vertical tube¹⁵. The focus of this paper is to present experimental data on HTC of sub- and supercritical water in buoyancy-aiding flow (upward flow in a heated tube) in this flow regime. Two experimental methods to measure HTC: spatially-averaged and local measurement methods and their respective calculation procedures are presented. The experimental HTC data obtained with these two methods are compared to HTC calculated with literature correlations obtained via similar technique: the VDI¹⁶ correlation for the spatially-averaged method, and our Nusselt correlation¹⁵ for the local method.

Figure 1. Profiles of selected thermophysical properties of water at 300 bar (Temperature at maximum C_p is called the pseudo-critical temperature, $T_{pc} = 402$ °C at 300 bar): ρ = density, C_p = specific heat capacity, μ = viscosity, and h = specific enthalpy.

2. EXPERIMENTAL APPARATUS

The schematic of the experimental apparatus is shown in Figure 2. A detailed description of the experimental apparatus is provided in this section.

The main part of the apparatus consists of a stainless steel tube (with an inner diameter of 2.14 cm, outer diameter of 3.41 cm and length of 154 cm) fitted with 8 aluminum heating blocks that keep the tube outer wall at a pre-set temperature. The heating blocks are insulated from the environment with stone wool to reduce heat losses. Pressures up to 400 bar were provided to the tube with a high pressure pump (LEWA diaphragm pump LDC1, LEWA Herbert Ott GmbH & Co KG, Germany, max. P, 400 bar, max. flow 25.0 L/h) and controlled with a back pressure regulator (TESCOM 26-1762-24A, Tescom Europe GmbH & Co. KG, Germany, $C_v = 0.14$). The uncertainty in pressure was 0.3% (0.9 bar at 300 bar), while the uncertainty in mass flow measurement was 1%. The water is pre-heated by an electric heater (T-C1 is for temperature control, and T-S1 is for the set safety temperature) until the desired inlet temperature is attained. The water is heated as it flows upwards in the tube with the aid of the aluminum heating blocks. Each heating block can be set to a desired temperature (by adjusting T-C2), and the temperature at the tube outer wall in each heating block section is measured at the top and bottom parts of the section with T2 and T1 respectively. The experimental apparatus can be operated at pressures up to 350 bar, and temperatures up to 500 °C.

Figure 2. Schematic of the experimental apparatus. (Figure adapted from Odu et al.¹⁵).

Nine thermocouples (Ti1-Ti9, see Figure 3), held at different predefined radial positions, but at the same axial position by a movable thermocouple holder measure the radial temperature profile in the tube at different heights. All temperatures were measured using standard type-K thermocouples (uncertainty in temperature measurement is 0.4% of measured value in °C, while the relative difference of measured values between thermocouples is 0.2 °C).

At the tube outlet, the water is cooled to a temperature below 70 °C (temperature limit of the back pressure regulator) with a shell and tube water cooler and then depressurized. Mass in and out are weighed to ensure mass balance closure. Temperatures (wall and inside the heated tube) are monitored and recorded (at steady state) with the aid of PicoLog data acquisition program.

3. EXPERIMENTAL METHODS, CALCULATION PROCEDURES AND NUSSELT CORRELATIONS

The two experimental techniques: the spatially-averaged and local measurement methods with their calculation procedures are described in detail in this section. In order to ascertain the reliability of the experimental results, the experimental apparatus has been validated for laminar flow of liquid water at 2.5 bar with a generally accepted heat transfer correlation available in literature. For all experiments, the fluid is demineralized water, the tube is heated, and the tube orientation is vertical with upward fluid flow. The Nusselt correlations used for HTC calculations are also presented in this section. Experimental error calculations are shown in Appendix B-II.

3.1. Spatially-averaged Experimental Procedure

In the spatially-averaged experimental procedure, the heated tube axial length is divided into sections, with measuring points at the inlet and outlet to each section. The radial temperature profiles inside the heated tube with the outer wall temperatures are measured at 7 axial positions: 24, 44, 64, 84, 104, 124 and 144 cm from the inlet under SCW conditions. Figure 3a and b show the schematic and the image of the movable thermocouple holder and the thermocouples arrangement respectively. The thermocouple holder is made from stainless steel (SS 316) with diameter 6 mm and length 182 cm. The radial temperature profile inside the tube is measured with nine (Ti1-Ti9) 0.5 mm diameter standard type-K thermocouples. Due to limitations imposed by the construction of the thermocouple holder, thermocouples Ti6 and Ti9 (see Figure 3a) are not touching the inner wall, but are at 0.17 and 0.83mm from the inner wall respectively.

Demineralized water is used in these experiments to avoid fouling and corrosion of the experimental apparatus. At the start of each measurement, the thermocouple holder is moved to the measuring axial position then the pump is switched on. The desired operating pressure in the tube is attained by adjusting the air-controlled back pressure regulator (BPR in Figure 2). A cold test is carried out to check if the apparatus is leak-tight. Then the pre-heater is turned on and adjusted to obtain the desired inlet temperature. Thereafter, the heating blocks are switched on and set to the desired values. The outer wall temperatures as well as the temperature inside the tube are monitored and recorded with the aid of PicoLog data acquisition program. When steady state is attained (fluctuations of not more than 1 °C in all measured temperatures over a period of 10 minutes), the data is recorded. At the end of data acquisition, the apparatus is depressurized and cooled. The thermocouple holder is then moved to the next measurement position and the procedure described above is repeated.

Figure 3. Schematic (a), and picture (b) of the thermocouple holder and thermocouples for measuring the radial temperature profile in the tube for the spatially-averaged method.

Table 1. Parameters for the Validation Experiment, Spatially-Averaged and Local Measurement Methods.

Validation		Spatially-Averaged Method				Local Method
		Case A	Case B	Case C	Case D	
$\dot{m}$ (kg/h)	9.4	8.0	8.0	11.4	11.4	4.1, 8.0
G (kg/m ² .s)	7.2	6.2	6.2	8.8	8.8	3.2, 6.2
P (bar)	2.5	300	300	300	300	250, 300
T_{in} (°C)	55	86	282	72	203	25-350
T_{ow} (°C)	75-92	211-398	337-398	198-393	294-396	250-490
Re	300-500	390-2100	1300-2360	460-2520	1350-2740	650-3250
Gr	(3-4)x10 ⁵	(3-6)x10 ⁸	(2-4)x10 ⁸	(2-6)x10 ⁸	(3-6)x10 ⁸	3x10 ⁷ -2x10 ⁹

3.1.1. Calculation Procedure for the Spatially-Averaged Method

Temperature measurements for the validation experiment have been taken at axial positions 24, 84 and 144 cm from the inlet. While for the SCW flow experiments, temperatures have been measured at axial positions: 24, 44, 64, 84, 104, 124 and 144 cm from the inlet. Due to the inability to experimentally measure the flow profile in the tube, a flat radial velocity profile is assumed and the mixing cup temperature, T_{mc} at each measurement position is calculated using the radial temperature measured at this position with Eq.1. The T_{mc} calculated in this manner is very close to the bulk temperature and is slightly lower in value compared to the T_{mc} calculated using the true radial velocity profile.¹⁵

Figure 4. Schematic of the calculation procedure for the spatially-averaged method.

The specific heat capacities are obtained at the pressure and measured temperatures using XSteam¹⁷ (the Matlab implementation of the IAPWS formulations¹⁸⁻²⁰). The calculation scheme is shown in Figure 4.

$$T_{mc}(z) = \frac{\int_{R_i}^{R_o} 2\pi r \cdot C_p(r, z) \cdot T(r, z) \cdot dr}{\int_{R_i}^{R_o} 2\pi r \cdot C_p(r, z) \cdot dr} \quad (1)$$

For the validation experiment at normal pressure and temperature conditions, z_1 is fixed as the inlet ($z = 0$), while z_2 is the tube length at each measuring point; 24, 84 and 144 cm respectively. While for the SCW flow experiments, the tube axial length is divided into 5 sections: 24 – 64 cm, 44 – 84 cm, 64 – 104 cm, 84 – 124 cm, and 104 – 144 cm with z_1 and z_2 being the tube length at the inlet and outlet of each section respectively.

The quantity of heat transferred into each section is calculated from the enthalpy change in the section using Eq.2. The enthalpies of water into and out of each section are obtained at the pressure and mixing cup temperature using XSteam.¹⁷

$$\dot{Q} = [h(z_2) - h(z_1)] * \dot{m} \quad (2)$$

where $\dot{m}$ is the mass flow rate in kg/s through the tube and h is the specific enthalpy of the fluid in J/kg.

Next, the overall heat transfer coefficient based on the tube outer area, U_o is calculated as follows:

$$U_o = \frac{\dot{Q}}{A_o * \Delta T_{lm}} \quad (3)$$

where A_o and ΔT_{lm} are the heat transfer area based on the tube outer diameter and the logarithmic mean temperature difference given by Eqs.4 and 5 respectively.

$$A_o = \pi d_o \Delta z \quad (4)$$

$$\Delta T_{lm} = \frac{(T_{ow,2} - T_{mc,2}) - (T_{ow,1} - T_{mc,1})}{\ln \left[\frac{(T_{ow,2} - T_{mc,2})}{(T_{ow,1} - T_{mc,1})} \right]} \quad (5)$$

The spatially-averaged heat transfer coefficient, HTC_{ln} is then calculated as:

$$HTC_{ln} = \frac{1}{\frac{d_i}{d_o} \left[\frac{1}{U_o} - \frac{d_o \ln \left(\frac{d_o}{d_i} \right)}{2\lambda_t} \right]} \quad (6)$$

where d_o , d_i and λ_t are the outer diameter, inner diameter and thermal conductivity of the tube respectively. And, $\lambda_t(T) = 1.22 \cdot T^{0.432}$ with the temperature, T in Kelvin (from ²¹).

The HTC values calculated with the spatially-averaged method are tube section-averaged values. Parameters for the validation and SCW experiments using the spatially-averaged experimental technique are listed in Table 1.

3.2. Local Experimental Method and Calculation Procedure

In the local experimental technique a modification was made to the experimental apparatus. Two 0.5 mm holes were drilled from the outer wall of the stainless steel tube to depths of 3.35 and 5.35 mm respectively at tube axial position 100 cm. Standard type-K thermocouples (0.5 mm diameter) are inserted into these holes (T_{w1} and T_{w2} in Figure 5) and also welded to the outer wall (T_{ow} in Figure 5) at this axial position to measure the radial wall temperature profile. In addition, the measuring end of the thermocouple holder as well as the thermocouples arrangement was modified to allow for the local measurement of the tube inner wall temperature. The schematic and image of the thermocouples arrangement for the local experimental method is shown in Figure 6. The length and diameter of the thermocouple holder and the standard type-k thermocouples for temperature measurement remain unchanged. However, the measuring end of the thermocouple holder has been equipped with a spring that pushes thermocouples Ti-5 and Ti-8 in Figure 6 against the wall (on opposite sides) to ensure that the tube inner wall temperature can be measured. The measured tube inner wall temperatures can then be compared to the values obtained with Eq.7.

$$T_{iw} = T_{w1} - \left[\frac{\ln\left(\frac{r_i}{r_1}\right)}{\ln\left(\frac{r_2}{r_1}\right)} * (T_{w1} - T_{w2}) \right] \quad (7)$$

$$\phi_h'' = -\lambda_t * \left[\frac{(T_{w1} - T_{w2})}{\ln\left(\frac{r_2}{r_1}\right) * r_i} \right] \quad (8)$$

$$HTC_{loc} = \frac{\phi_h''}{(T_{iw} - T_{mc})} \quad (9)$$

The inner wall temperature, T_{iw} (Eq.7) and the radial heat flux, ϕ_h'' (Eq.8) are estimated from the measured wall temperatures (T_{w1} and T_{w2}) by applying the Fourier's law of heat conduction in a cylinder.²² The heat transfer coefficient of the fluid is calculated with Eq.9. T_{mc} is the mixing cup temperature calculated with Eq.1 (a flat radial velocity profile in the tube is assumed).

To start measurement, the thermocouple holder is moved to the desired axial position (100 cm) and the experimental procedure follows as described for the spatially-averaged method in section 3.1.

Figure 5. Schematic of the calculation procedure for the local method.

Figure 6. Schematic (a), and picture (b) of the thermocouple holder and thermocouples for measuring the radial temperature profile in the tube for the local method.

The fluid inlet temperature and the heating block temperatures are adjusted to obtain the different bulk temperatures. The change in heating block temperature changes the heat flux through the wall to the fluid for each measurement in the local measurement method. For the higher mass flow ($G = 6.2 \text{ kg/m}^2 \cdot \text{s}$), in order to obtain similar bulk temperatures as in the lower mass flow ($G = 3.2 \text{ kg/m}^2 \cdot \text{s}$) the inlet temperature and the heating block temperatures were increased.

3.3. Nusselt Correlations

Nusselt correlations used in this paper to evaluate the experimental data are described in this section.

A Nusselt correlation that describes heat transfer in mixed convection for buoyancy aiding flow (up flow in a heated tube or down flow in a cooled tube) is given by Bird et al.²² as:

$$Nu_{mixed} = \frac{HTC_{mixed} \cdot d_i}{\lambda} = \sqrt[3]{Nu_{free}^3 + Nu_{forced}^3} \quad (10)$$

where, Nu_{free} and Nu_{forced} are Nusselt correlations for free and forced convection defined in Eq.11¹⁶ and Eq.14²² respectively for laminar flows.

$$Nu_{free} = \frac{HTC_{free} \cdot d_i}{\lambda} = 1.04 \cdot (Gr_s^* \cdot Pr)^{1/4} \quad (11)$$

the modified Grashof number, Gr_s^* and Prandtl number, Pr are given as:

$$Gr_s^* = \frac{g \cdot \beta \cdot (T_{iw} - T_{in}) \cdot r_i^3 \cdot \rho^2}{\mu^2} \cdot \frac{r_i}{L} \quad (12)$$

$$Pr = \frac{C_p \cdot \mu}{\lambda} \quad (13)$$

$$Nu_{forced} = \frac{HTC_{forced} \cdot d_i}{\lambda} = 1.86 \cdot \left(Re \cdot Pr \cdot \frac{d_i}{L} \right)^{0.33} \cdot \left(\frac{\mu_b}{\mu_w} \right)^{0.14} \quad (14)$$

where T_{iw} and T_{in} are the inner wall and inlet temperatures respectively, and μ_b and μ_w are the viscosities of the fluid in the bulk and at the wall respectively. C_p , ρ , μ and λ are the specific heat capacity, density, viscosity and thermal conductivity of the fluid obtained at the reference temperature, $\frac{1}{2}(T_{iw} + T_{in})$. The VDI¹⁶ Nusselt correlation for free convection (Eq.11) has been obtained with a method similar to the spatially-averaged method. Therefore, the experimental HTC's obtained with the spatially-averaged method will be compared to calculated HTC's from the VDI correlation.

Our proposed correlation¹⁵ shown in Eq.15 has been obtained from COMSOL simulations using the local method calculation procedure. Experimental HTC's obtained with the local method are compared to the calculated HTC's from this correlation.

$$Nu_t = \frac{HTC \cdot d_i}{\lambda_{mc}} = 0.78 \cdot Gr^{0.34} \cdot Re^{-0.26} \cdot Pr^{-0.07} \cdot \left(\frac{C_{p,w}}{C_{p,mc}} \right)^{0.20} \cdot \left(\frac{\rho_w}{\rho_{mc}} \right)^{0.23} \quad (15)$$

$$Re = \frac{G \cdot d_t}{\mu_{mc}}$$

$$Pr = \frac{C_{p,mc} \cdot \mu_{mc}}{\lambda_{mc}}$$

$$Gr = \frac{g \cdot \beta_{mc} \cdot (T_{iw} - T_{mc}) \cdot d_t^3 \cdot \rho_{mc}^2}{\mu_{mc}^2}$$

where T_{iw} and T_{mc} are the tube inner wall and mixing cup temperatures respectively. The thermophysical properties of the fluid ($C_{p,mc}$, μ_{mc} , ρ_{mc} , λ_{mc} and β_{mc}) are evaluated at the mixing cup temperature.

In order to analyze the accuracy and precision of the correlation against our experimental data, the average error and the standard deviation are calculated. The average error (e_{av}) and the standard deviation (σ) are defined as follows:

$$e_{av} = \frac{\sum_{i=1}^n e}{n} \quad (19)$$

$$\sigma = \sqrt{\frac{\sum_{i=1}^n (e - e_{av})^2}{n - 1}} \quad (20)$$

where n is the number of data points and the error, e is defined as:

$$e = \frac{Nu_{calc.} - Nu_{expt.}}{Nu_{expt.}} \quad (21)$$

4. RESULTS AND DISCUSSION

4.1. Validation of the Experimental Apparatus

The experimental apparatus has been validated by taking a well-established flow problem, to see if our measurements are in line with an accepted and widely validated empirical correlation. The validation experiment has been carried out using the spatially-averaged method and the experimental conditions are presented in Table 1.

Figure 7a shows the measured radial temperature profile at two axial positions, 24 and 84 cm respectively. The radial temperature profile is flat in the bulk with a temperature gradient close to the wall. This shows that although the flow is laminar with respect to the Reynolds number, there is turbulence introduced to the system by natural convection. This observation is consistent with the numerical results obtained from our previous work.¹⁵ Figure 7b shows the experimental and theoretical HTC as a function of the tube length for the validation experiment. The contributions of free and force convection to the aggregate heat transfer coefficient are also shown. It is evident from Figure 7b that free convection is the dominant heat transfer mechanism, and that the experimental results are in good agreement with the literature correlation, which is based on experimental data.

Figure 7. Radial temperature profiles at axial positions 24 and 84 cm (a), and HTC as a function of axial position (b) for the validation experiment.

4.2. Spatially-Averaged Measurement Method for SCW Flow

The temperature profiles and HTC for SCW flowing upwards in a vertical heated tube using the spatially-averaged method are discussed in this section. In addition, the experimental HTCs are compared with calculated HTCs obtained from the VDI correlation for free convection in buoyancy aiding flow (Eq.11). Note that the bulk

and inner wall temperatures at the outlet are lower than T_{pc} (402 °C at 300 bar) for all the cases studied and presented.

The cases investigated with the spatially-averaged method are defined in Table 1.

For all the cases investigated, the set-point temperature of the heating blocks was the same. However, the pre-heater temperature was increased for cases B and D in order to increase the flow inlet temperature. Figure 8 shows the profiles of the outer wall, inner wall, fluid mixing cup and bulk temperatures respectively along the length of the tube for the cases investigated with the spatially-averaged method. Experimental results show that for constant pre-heater and heating block temperatures, the wall temperature is significantly increased with a decrease in the mass flow (comparing cases A and C, and cases B and D). When the inlet temperature is increased (comparing cases A and B, and cases C and D), all temperatures shift upwards.

For all the cases, the mixing cup and bulk temperatures are very close to each other. This is a result of the radial temperature profile which shows a steep temperature gradient close to the wall and a flat temperature profile in the bulk fluid.

Figure 8. Tube outer wall, tube inner wall, fluid mixing cup and fluid bulk temperature profiles as a function of axial position for cases A, B, C and D – spatially-averaged method-.

Figure 9 shows the HTC_s calculated from the temperature profiles as a function of the fluid bulk temperature for the different cases (defined in Table 1) using the spatially-averaged method as well as the calculated HTC_s using the VDI correlation, Eq.11. While VDI correlation predicts the order of magnitude of the HTC correctly, it fails to describe effects of experimental parameters such as the inlet temperature (compare cases A and B; cases C and D). In addition, there is no appreciable difference in the measured HTC_s for the different flows (cases A and C; cases B and D) and different inlet temperatures (cases A and B; cases C and D) within the experimental error. The measured HTC values for the two flow rates and inlet

temperatures vary between 1250 – 2500 W/m²K (average value of 1800 W/m²K and average experimental error of 12%) with no clear effect of the bulk temperature. It is known that for high mass fluxes the HTC starts to increase at temperatures lower than T_{pc} (from 350 °C in some instances) before going through a maximum near the T_{pc} .⁹ This trend of the HTC vs T_b is only clearly observed for case B and not for the rest of the cases investigated. In order to investigate if this is indeed not the case for low mass fluxes, like our spatially-averaged data suggest, we decided to develop another experimental method that measures locally and can reach higher temperatures as it might be possible that the absence of the effect of T_{pc} with the spatially-averaged method is an artefact of the method itself.

Figure 9. HTC profile as function of bulk temperature for cases A, B, C and D – spatially-averaged method- and VDI correlation (Eq.11).

4.3. Local Measurement Method for SCW Flow

The results of the locally measured HTCs are presented in this section.

4.3.1. Radial Temperature Profile

The measured radial temperature profiles in the fluid and inside the tube wall are shown in Figure 10. A temperature gradient is observed in the thermal boundary layer close to the wall, while a flat temperature profile is observed from this thermal boundary layer (< 0.5 mm from the tube inner wall) to the bulk of the fluid. This is consistent with the numerical solution we obtained in our previous work.¹⁵ The wall temperature measured inside the tube (with the thermocouple probe) was found to be slightly lower than the predicted inner wall temperature from T_{w1} and T_{w2} (using Eq.7). This difference is due to the construction of the type-K thermocouple sensor. The sensor has a length of 0.5 mm from the tip of the thermocouple, therefore, the measured inner wall temperature is actually the average of the true inner wall temperature and the temperature of the fluid in the region 0.5 mm from the wall. For further calculations, the predicted tube inner wall temperature (Eq.7) is taken as the inner wall temperature, T_{iw} .

Figure 10. Measured radial temperature profiles at $z = 100$ cm: $G = 6.2 \text{ kg/m}^2\text{s}$, $T_{ow} = 256^{\circ}\text{C}$, $T_b = 238^{\circ}\text{C}$ (a), and $G = 3.2 \text{ kg/m}^2\text{s}$, $T_{ow} = 414^{\circ}\text{C}$, $T_b = 404^{\circ}\text{C}$ (b).

4.3.2. Effects of Mass Flux and Pressure on Heat Transfer

The variations of the HTC plotted against the bulk temperature showing the effects of mass flux and pressure are shown in Figure 11(a) and (b) respectively (see Figure B-1 – 2 in Appendix B-I for the plot of HTC against bulk enthalpy, used

frequently in literature to represent HTC data). The results show that the HTC increases and goes through a maximum at temperatures in the neighborhood of $T_c < T_b < T_{pc}$ and then rapidly decreases at temperatures above T_{pc} (385 °C at 250 bar and 402 °C at 300 bar).

Figure 11. HTC as a function of bulk temperature showing the effect of mass flux (a), and the effect of pressure (b) for the local method.

The increased HTC and maximum value near the pseudo-critical temperatures has been observed in studies conducted by several authors^{9, 10, 12, 14, 23-26} on heat transfer to SCW flows at high mass fluxes. Yamagata et al.⁹ attributed this behavior to the large changes in the physical properties of the fluid produced by small changes in temperature “across the section” of the tube. In our previous work¹⁵ (Chapter 3), we identified the dominant physical property to be density and concluded that the increase in HTC near the pseudo-critical temperature is due to buoyancy-induced mixing resulting from the gravitational force acting on the large density gradients (a direct consequence of temperature gradients) along the cross-section of the tube. Above the pseudo-critical temperature, SCW becomes more gas-like, and this

accounts for the very low (compared to other temperatures) heat transfer coefficients obtained at these temperatures.

The effect of mass flux has been investigated at 3.2 and 6.2 kg/m²s respectively. Figure 11(a) shows the effect of flow is negligible at these low mass fluxes and flow conditions studied in this work. This can be attributed to the heat transfer mechanism being predominantly by natural convection. This is consistent with the simulation results obtained in Chapter 3 (Figure A-7, Appendix A) on the influence increased mass flux on HTC at low mass flux SCW flow.

The effect of pressure on heat transfer to SCW flow has been investigated at 250 and 300 bar respectively. Figure 11(b) shows that the effect of pressure on heat transfer is mainly in the region of the pseudocritical temperature, T_{pc} . Furthermore, the measured maximum HTC value is reduced from 6000 W/m²K to 5000 W/m²K when the pressure is increased from 250 bar to 300 bar. In addition, the temperature at which the maximum HTC is measured shifts to the right at a higher pressure. This trend is consistent with the findings of Taklifi et al.²⁶, Shen et al.²³, and Wang et al.²⁴ on the effect of pressure on heat transfer to turbulent SCW flows. The increased HTC peak value observed with a decrease in pressure is linked to the larger change in the thermophysical properties (especially ρ and C_p) of water with decreasing pressure in the pseudocritical region.

(a)

(b)

Figure 12. Temperature difference between the inner wall and bulk temperature, $T_{iw} - T_b$, and heat flux, ϕ_h'' vs bulk temperature, T_b at 300 bar for the local method.

The plots of the temperature difference between the inner wall and bulk temperature, $T_{iw} - T_b$ and the heat flux, ϕ_h'' against the bulk temperature, T_b for the local method at 300 bar are shown in Figure 12. As stated in section 3.2., the fluid inlet

temperature and the heating block temperatures were increased at the higher mass flow ($G = 6.2 \text{ kg/m}^2.\text{s}$) in order to obtain similar bulk temperatures as in the lower mass flow ($G = 3.2 \text{ kg/m}^2.\text{s}$). Increasing the heating block temperature (and consequently outer wall temperature) leads to an increase in the heat flux through the wall. The increase in heat flux leads to a corresponding increase in the temperature difference between the wall and the tube bulk (Figure 12 (a) and (b)), and consequently no increase in the HTC at the two flows investigated. This trend is inconsistent with the findings of Yamagata et al.⁹ for SCW flow at very high mass fluxes, where the authors found that increasing the heat flux lead to a decrease in the HTC, especially near the pseudo-critical temperature. It appears increasing the heat flux has no influence on the HTC for SCW flow at low mass fluxes.

4.3.3. Assessment of Nusselt Correlations

The experimental Nusselt numbers are compared to the calculated Nusselt numbers using our proposed correlation, Eq.15 in Figure 13. The average error and standard deviation of the calculated Nusselt against the experimental Nusselt are -3.4% and 18.1% respectively.

Figure 13. Comparisons of experimental Nusselt numbers with calculated Nusselt numbers using Eq.15. $n = 62$.

Our CFD based Nusselt correlation captures 90% of the data within $\pm 25\%$ of the error margin. For 300 bar, the pressure at which it is derived, our proposed correlation shows a good match with the experimental data. However, our Nusselt correlation (derived from data at 300 bar) is unable to capture most of the experimental data obtained at 250 bar, showing that the pressure/temperature dependency of natural convection is difficult to capture in an engineering correlation.

While empirical Nusselt correlations are able to satisfactorily predict HTC's for constant thermophysical property flows over a wide range of flow conditions (pressure, temperature, etc.), the drastic property changes SCW undergoes near the critical region make such empirical correlations inadequate for SCW flows. Empirical correlations for SCW do not fully reflect all observed phenomena, and are thus case dependent and may produce unreliable results if flow conditions differ from those under which they were developed, as shown in Figure 13 for our proposed Nusselt correlation.

4.4. Comparison of the Two Measurement Methods

Evaluation of the results of the experimental methods (Figure 9 and Figure 11) shows that the HTC's obtained with the spatially-averaged method are lower than those obtained with the local method within the same pressure and temperature ranges. The measured HTC values using the spatially-averaged experimental method vary between $1250 - 2500 \text{ W/m}^2\text{K}$, with an average value of $1800 \text{ W/m}^2\text{K}$ at 300 bar and temperatures below the T_{pc} . However, at the same pressure, a constant HTC value of $3000 \text{ W/m}^2\text{K}$ was measured with the local measurement method at temperatures below the T_c with an enhancement and a peak ($5000 \text{ W/m}^2\text{K}$) near the T_{pc} .

While it appears that the spatially-averaged method is giving wrong results, this is not the case. The spatial-averaging dampens out the HTC peak, and the absolute HTC values obtained are a function of definition used for the HTC (see Appendix B-I).

5. CONCLUSIONS

Two experimental methods – a spatially-averaged and a local method - to measure HTC of SCW flow at low mass fluxes in a vertical heated tube have been presented. The absolute values of the measured HTCs for the two methods are a function of the definition used for the HTC and as such a function of the measurement method. We have found that only the local measurement method had enough resolution and accuracy to detect a maximum in HTC near the T_{pc} as reported for SCW flow at very high mass fluxes by several authors.^{9, 23, 24, 26}

Due to the dominance of natural convection as heat transport mechanism at these low mass fluxes, no noticeable effect of an increase in mass flux on heat transfer coefficient was observed. However, an increase in pressure was shown to decrease the magnitude of the measured maximum HTC value in the region of the T_{pc} .

Our CFD based Nusselt correlation derived for a pressure of 300 bar showed good predictive power for the HTC measured at 300 bar with the local measurement technique. However, our proposed correlation is unable to capture most of the experimental data obtained at 250 bar, showing that the pressure/temperature dependency of natural convection is difficult to capture in an engineering correlation for SCW flow.

NOMENCLATURE

A	heat transfer area (m ²)	Greek symbols	
C_p	isobaric heat capacity (J/kg.K)	β	thermal expansion coefficient (K ⁻¹)
d	diameter (m)	μ	dynamic viscosity (Pa.s)
e	error	ρ	density (kg/m ³)
g	gravitational constant (m/s ²)	ϕ_h''	heat flux (W/m ²)
G	mass flux (kg/m ² .s)	ω	turbulence frequency (s ⁻¹)
Gr	Grashof number	λ	thermal conductivity (W/mK)
Gr_s^*	modified Grashof number	Δ	difference
HTC	heat transfer coefficient (W/m ² K)	σ	standard deviation error
h	specific enthalpy (J/kg)	Subscripts	
L	length (m)	av	average
$\dot{m}$	mass flow (kg/h)	b	bulk
n	number of data points	c	critical
Nu	Nusselt number	calc	calculated
P	absolute pressure (Pa)	exp	experimental
Pr	Prandtl number	i	inside
$\dot{Q}$	heat flow (W)	in	inlet
r	radial coordinate (m)	iw	inner wall
R	tube radius (m)	lm	logarithmic mean
Re	Reynolds number	mc	mixing cup average
SCW	supercritical water	o	outside
SWCO	supercritical water oxidation	ow	outer wall

SCWR	Supercritical water cooled reactor	pc	pseudo-critical
T	temperature ($^{\circ}\text{C}$)	w	wall
z	axial coordinate (m)		

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Appendix B

Supporting Information for Chapter 4

APPENDIX B - I

In order to get a better understanding and explain the observed trend of lower values of experimental HTC measured with the spatially-averaged method compared to those measured with the local method, a COMSOL simulation of the test conditions of case C (spatially-averaged measurement method. See Table 1) was carried out, with the inlet flow rate and conditions as well as outer wall temperatures as input for the simulation. From the results of the COMSOL simulation, the HTC was the calculated using the spatially-averaged (Eq.6) and local (Eq.9) methods respectively.

The HTC values calculated from the COMSOL simulation result using the two calculation schemes (see Figure 4 and Figure 5 respectively) as well as the experimental HTC values for case C using the spatially-averaged method with their corresponding heat fluxes are shown in Figure B-I - (a) and (b) respectively. The plots show that for the same simulation data (and by extension experimental data), while the HTC values calculated using the spatially-averaged method differ from the values obtained with the local method, the corresponding heat fluxes are of the same order of magnitude. These results indicate that the HTC values calculated from simulation data, and by extension experimental data is not a constant characteristic of the fluid medium, but a function of how the HTC is defined. This is point is also emphasized in section 14.1 of the book of Bird, Stewart and Lightfoot.²²

(a)

(b)

Figure B-I - 1. HTC profile (a), and Heat flux profile (b) as function of bulk temperature for COMSOL simulation of spatially-averaged experimental method case C.

Figure B-I - 2. HTC as a function of bulk enthalpy showing the effect of mass flux (a), and the effect of pressure (b) for the local method.

APPENDIX B - II

The experimental error calculations are shown in this appendix. The propagation error method of Berendsen²⁷ is used.

Local Experimental Method

The propagation of error for the HTC's measured with local experimental technique is shown below.

The possible error in radial position measurement (with a Vernier caliper), $e(r) = 0.05$ mm.

The error in temperature measurement, $e(T) = 1.0$ °C.

Relative error between temperatures, error in ΔT , $e(\Delta T) = 0.2$ °C

Error in predicted inner wall temperature, T_{iw} (Eq.7) calculation:

$$e(T_{iw}) = \sqrt{e(A)^2 + e(T)^2} \quad (22)$$

Where $e(A)$ is defined as:

$$e(A) = \frac{\ln\left(\frac{r_i}{r_1}\right)}{\ln\left(\frac{r_2}{r_1}\right)} * (T_{w1} - T_{w2}) * \sqrt{\left(\frac{e(B)}{\frac{\ln\left(\frac{r_i}{r_1}\right)}{\ln\left(\frac{r_2}{r_1}\right)}}\right)^2 + \frac{2 * e(\Delta T)^2}{(T_{w1} - T_{w2})^2}} \quad (23)$$

Where $e(B)$ is defined as:

$$e(B) = \frac{\ln\left(\frac{r_i}{r_1}\right)}{\ln\left(\frac{r_2}{r_1}\right)} * \sqrt{\left(\left(\frac{e(C)}{\ln\left(\frac{r_i}{r_1}\right)}\right)^2 + \left(\frac{e(D)}{\ln\left(\frac{r_2}{r_1}\right)}\right)^2\right)} \quad (24)$$

$e(C)$ and $e(D)$ are defined as:

$$e(C) = \sqrt{\left(\left(\frac{e(r)}{r_i}\right)^2 + \left(\frac{e(r)}{r_1}\right)^2\right)} \quad (25)$$

$$e(D) = \sqrt{\left(\left(\frac{e(r)}{r_2}\right)^2 + \left(\frac{e(r)}{r_1}\right)^2\right)} \quad (26)$$

Error in heat Flux, ϕ_h'' (Eq.8) calculation:

$$e(\phi_h'') = \phi_h'' * \sqrt{\left(\frac{e(\lambda_t)}{\lambda_t}\right)^2 + \left(\frac{e(E)}{\frac{(T_{w1} - T_{w2})}{\ln\left(\frac{r_2}{r_1}\right) * r_i}}\right)^2} \quad (27)$$

Where $e(\lambda_t)$ and $e(E)$ are defined as:

$$e(\lambda_t) = |1.22| * T^{0.432} * |0.432| * \frac{e(T)}{T} \quad (28)$$

$$e(E) = \frac{(T_{w1} - T_{w2})}{\ln\left(\frac{r_2}{r_1}\right) * r_i} * \sqrt{\frac{2 * e(\Delta T)^2}{(T_{w1} - T_{w2})^2} + \left(\frac{e(F)}{\ln\left(\frac{r_2}{r_1}\right) * r_i}\right)^2} \quad (29)$$

Where $e(F)$ is defined as:

$$e(F) = \ln\left(\frac{r_2}{r_1}\right) * r_i * \sqrt{\left(\left(\frac{e(D)}{\ln\left(\frac{r_2}{r_1}\right)}\right)^2 + \left(\frac{e(r)}{r_i}\right)^2\right)} \quad (30)$$

Error in HTC_{loc} (Eq.9) calculation:

$$e(HTC_{loc}) = HTC_{loc} * \sqrt{\frac{2 * e(\Delta T)^2}{(T_{iw} - T_{mc})^2} + \left(\frac{e(\phi_h'')}{\phi_h''}\right)^2} \quad (31)$$

Spatially-Averaged Method

The propagation of error for the HTC_s measured with spatially-averaged experimental technique is shown below.

The possible error in diameter measurement (with a Vernier caliper), $e(d) = 0.05$ mm.

The error in temperature measurement, $e(T) = 0.2$ °C.

Relative error between temperatures, error in ΔT , $e(\Delta T) = 0.2$ °C.

The error in length measurement, $e(z) = 0.1$ cm

Error in ΔT_{lm} (Eq.5) calculation:

$$\begin{aligned}
 &e(\Delta T_{lm}) \\
 &= \Delta T_{lm} \\
 &\quad * \sqrt{\frac{2 * e(\Delta T)^2}{G^2} + \frac{e(\Delta T)^2 * \left(\left(\frac{e(\Delta T)}{(T_{ow,2} - T_{mc,2})} \right)^2 + \left(\frac{e(\Delta T)}{(T_{ow,1} - T_{mc,1})} \right)^2 \right)}{H^2}} \quad (32)
 \end{aligned}$$

$$G = (T_{ow,2} - T_{mc,2}) - (T_{ow,1} - T_{mc,1}) \quad (33)$$

$$H = \ln \left[\frac{(T_{ow,2} - T_{mc,2})}{(T_{ow,1} - T_{mc,1})} \right] \quad (34)$$

Error in U_o (Eq.3) calculation:

$$e(U_o) = U_o * \sqrt{\left(\frac{e(d)}{d_o} \right)^2 + \left(\frac{e(z)}{\Delta z} \right)^2 + \left(\frac{e(\Delta T_{lm})}{\Delta T_{lm}} \right)^2} \quad (35)$$

Error in HTC_{lm} (Eq.6) calculation:

$$e(HTC_{ln}) = HTC_{ln} * \sqrt{\left(\frac{e(I)}{I}\right)^2} \quad (36)$$

$$I = \frac{d_i}{d_o} * \left[\frac{1}{U_o} - \frac{d_o \ln\left(\frac{d_o}{d_i}\right)}{2\lambda_t} \right] \quad (37)$$

$$e\left(d_o \ln\left(\frac{d_o}{d_i}\right)\right) = d_o \ln\left(\frac{d_o}{d_i}\right) * \sqrt{\left(\frac{e(d)}{d_o}\right)^2 + \frac{\left(\frac{e(d)}{d_o}\right)^2 + \left(\frac{e(d)}{d_i}\right)^2}{\left(\ln\left(\frac{d_o}{d_i}\right)\right)^2}} \quad (38)$$

$$e(I) = I * \sqrt{\left(\frac{e(d)}{d_o}\right)^2 + \left(\frac{e(d)}{d_i}\right)^2 + \frac{\left(e(U_o)\right)^2 + \left(e\left(d_o \ln\left(\frac{d_o}{d_i}\right)\right)\right)^2}{\left[\frac{1}{U_o} - \frac{d_o \ln\left(\frac{d_o}{d_i}\right)}{2\lambda_t}\right]^2}} \quad (39)$$

Chapter 5

A First Generation Pilot Plant for Supercritical Water Desalination (SCWD): Design and First Results

ABSTRACT

Supercritical water desalination (SCWD) is a technology that allows for the treatment of salt water streams without the production of a waste brine stream (zero liquid discharge). A first generation modular pilot plant for SCWD with a capacity of 5 kg/hr drinking water, the first of its kind, has been designed and constructed on the basis of thorough investigations of its subsystems. The detailed design, selection of materials of construction, operating procedure and control, and first experimental results are presented. Experiments with NaCl feed (3.5 wt.% solution) have been carried out successfully with the plant running for several hours without operational problems and with good mass balance closure (overall mass balance > 95 %). The pilot plant produces drinking quality water (< 700 ppm salts) and solid salt crystals (2-15 μm). Further tests with higher salt concentrations, other salts and mixture of salts are proposed to provide more data and insights for further refinement of the SCWD process.

1. INTRODUCTION

Many regions of the world suffer from water scarcity which negatively impacts the human and socio-economic developments in these regions. In order to meet the growing demands for potable water globally, desalination of sea and brackish water streams remains viable as the predominant technology. Desalination is the process of removing salts from salt water streams to produce potable water. There has been continual research and development of this process over the years, resulting in a variety of commercial desalination methods and large scale desalination plants. With respect to their installed capacities and commercial success, multi-stage flash (MSF), multi-effect distillation (MED) and reverse osmosis (RO) are the most widely used desalination methods to obtain fresh water from salt (sea and brackish) water streams.¹ These conventional desalination methods have a major drawback, the production of a waste brine stream (~60 000 and 70 000 ppm salts for seawater installations of RO and MSF respectively) which are usually discharged into the ocean if the desalination plant is located near the coast, otherwise extra treatment steps are required before discharge into surface water bodies if the plant is located inland.² Discharging the brine streams into the ocean has been shown to lead to increased local salinity and turbidity which could negatively impact marine ecology.³ In addition, the expected more stringent regulations regarding dilution in surface waters,⁴ has led to investigations in the direction of desalination with zero liquid discharge (ZLD).^{2, 5, 6} One of the methods through which ZLD can be achieved is the use of supercritical water for desalination.^{2, 5}

The solvation behavior and use of supercritical water ($P > 221.2$ bar, $T > 374.15$ °C) to remove inorganic salts from solutions has been studied by several authors.^{2, 5, 7-14} In our previous work,² we have explored the potential of supercritical water (SCW) in desalination and presented a supercritical water desalination (SCWD) process with zero liquid discharge. Using NaCl solution as model solution, we measured the phase equilibrium (Figure 1) and showed proof-of-principle of the SCWD process with a two stage separation step (V-L at supercritical water conditions and V-S at atmospheric pressure) in a small-scale laboratory apparatus.² In addition, we identified and discussed ways to tackle key design challenges; heat

integration, the controlled removal of salts under supercritical conditions, and selection of materials of construction. Furthermore, we proposed and presented a design for a two stage separation pilot plant scale SCWD process. In another paper,¹⁵ we have studied the heat transfer mechanism to SCW flow at the mass fluxes and conditions expected in the pilot scale SCWD process, and presented a validated heat transfer correlation that can be used to design heat exchangers for pilot scale SCW processes.

The findings of these investigations^{2, 15} have been used to design and build a 8 kg/h (saline feed) first generation SCWD pilot plant – the first of its kind. The pilot plant (design, properties and operating procedure) and the first experimental results (with 3.5 wt.% NaCl solution as model solution) obtained from it are presented in this work.

Figure 1. Phase diagram of NaCl-H₂O at 300 bar showing the heated path of a 3.5 wt.% feed (●) and the V - L separation at 460 °C into a supercritical vapor with 0.075 wt.% NaCl and a concentrated brine with 50 wt.% NaCl. (Figure adapted from Odu et al.²).

2. DESIGN CHALLENGES AND SOLUTIONS

The conceptual design of the SCWD process including the most essential equipment and operating conditions is shown in Figure 2. The SCWD pilot plant has been conceptualized as a modular plant consisting of a number of units. A high pressure pump required to pressurize the saline feed to the desired operating supercritical pressure, and a heat exchanger essential for heat integration to recover as much energy as possible from the process. A heater provides the additional energy to bring the feed to the desired operating temperature necessary for the first stage separation (V – L). The vapor (SCW) phase is separated from the concentrated brine (~50 wt.% at 300 bar and 460 °C) in the gravity separator. The concentrated brine is subsequently flashed into a cyclone to obtain steam and solid salt. The major challenges faced during the design of the SCWD pilot plant and how these challenges were tackled are discussed in this section.

Figure 2. Conceptual design of the SCWD process. (Figure adapted from Odu et al.²).

2.1. Heat Integration

SCW processes are energy intensive. Hence, in order to make these processes a commercial success, heat integration is essential to recover most of the energy put into the process. In the SCWD process, this is achieved by using the SCW product to heat up the feed (as shown in Figure 2) in a heat exchanger that can operate in sub-

to supercritical conditions. In this heat exchanger, the feed will go from sub-critical to SCW conditions while the product starting from a supercritical phase will become liquid. In order to design such a heat exchanger, insights into the heat transfer characteristics of SCW at the flow regime expected to be encountered in the SCWD pilot plant as well as an engineering correlation for heat transfer coefficient are required. We have investigated this subject in COMSOL Multiphysics (modeling) and validated the modeling results with experimental data.¹⁵ The findings are used in designing a double-pipe heat exchanger for the SCWD pilot plant. The performance of this heat exchanger will be presented and discussed in the results section.

2.2. Plugging of Vessels and Controlled Salt Removal

Early salt formation in the SCWD process could lead to a number of problems such as: (i) plugging of process vessels which will lead to increased down time, and (ii) reduction of the overall heat transfer coefficient if the salts are formed on the walls of the vessels, which can lead to increased operational (energy) costs. In order to prevent plugging of the process equipment, we have proposed a two stage separation step and shown the proof-of-principle in our previous work.² The concept of a two stage separation is to allow for the bulk of the feed to be dealt with in the V – L region of the phase diagram (see Figure 1) with a V – L gravity separator, then subsequently handle the salt formation downstream. For a 3.5 wt.% NaCl saline feed, 93% (on weight basis) of the feed is removed as SCW (drinking water quality, ~750 ppm TDS) at 300 bar and 460 °C in the V – L region. The concentrated brine that is left (~50 wt.%) can then be flashed batch-wise downstream to obtain steam and solid salt (see Odu et al.² for proof-of-principle).

Another challenge that arises is the controlled removal of salt when the highly concentrated brine is flashed from supercritical conditions to atmospheric pressure (V – S separation step). To achieve this, it is important that the temperature of the brine is maintained at the separation temperature (decrease in temperature leads to formation of solids, see L – S line in Figure 1) while the brine is transported as fast as possible to the flash vessel. This can be achieved by an isothermal storage of the brine followed by an adiabatic expansion through a capillary into a cyclone. The design and sizing of the capillary and cyclone will be presented later in this chapter.

2.3. Corrosion Potential and Material Selection

Corrosion has been identified as a key obstacle to the commercial success of SCW processes such as supercritical water oxidation (SCWO) and supercritical water gasification (SCWG).¹⁶⁻¹⁸ The high temperature and pressure conditions inherent to the SCWD process combined with the presence of salt could result in corrosion problems in the SCWD process. Therefore, attention has to be paid to the selection of the materials of construction for the SCWD process.

The hot sub-critical temperatures region has been identified as the maximum point of corrosion especially for chloride-containing feed streams due to the high density of the solution and the dissociated nature of the ions in solution.^{16, 19, 20} Marrone and Hong¹⁶ have reported that while corrosion is present at supercritical conditions, the potential for corrosion is greatly reduced compared to the sub-critical region. Due to the difference in corrosion potentials at sub-critical temperatures (and supercritical pressures) and supercritical conditions, the choice of material for the different parts of the pilot plant will be influenced by the process conditions (temperature and pressure) and the chemical environment (presence or absence of salt) in which they operate.

The heat exchanger (see Figure 2) with saline feed flowing through will be operating in the sub-critical temperature regime, and as such in a very corrosive environment. In the very corrosive sub-critical region, Kritzer et al.²¹ and Marrone and Hong¹⁶ have reported that specialized materials like titanium and tantalum have much better corrosion resistance than Ni-based alloys, especially for chlorinated feeds. Other methods suggested by the authors^{16, 21} for corrosion control include lining the surface of the vessel with a high corrosion resistant, but expensive noble metals like gold and platinum. Considering cost and material properties such as the corrosion resistance and mechanical strength, grade 2 titanium has been chosen as the material of construction for the heat exchanger. In order to ensure that there is phase separation when the feed moves to the separator, a heater is installed between the heat exchanger and the separator to provide additional heating to attain the operating temperature required for phase separation. For ease of construction and

flexibility, the coiled tube running through the heater is made from grade 2 titanium as well.

The gravity separator will be operating under supercritical water conditions, an environment with a lower potential for corrosion. For the high temperature sections of SCWO systems, Marrone and Hong¹⁶ have proposed the use of nickel-based alloys “due to their combination of reasonably good corrosion resistance and high temperature strength under the widest range of conditions”. The gravity separator will be heated in an oven to keep the separator at the process temperature and maintain phase separation, therefore, the chosen material for the gravity separator should possess good and stable thermal properties in addition to a high resistance to corrosion. Due to its good mechanical and stable thermal properties over a wide temperature range as well as its exceptional resistance to corrosion, Incoloy 825 (a nickel-iron-chromium alloy with additions of molybdenum, copper, and titanium) was chosen as the material of construction for the gravity separator, cyclone and salt collector respectively.

We have made an educated selection of the materials of construction based on the available literature on corrosion in supercritical water processes. However, we have not conducted corrosion tests on the materials since the start of operation, and therefore we have no corrosion data to evaluate the performance of the selected materials.

3. THE PILOT PLANT

The pilot plant is designed and built at the high pressure laboratory of the University of Twente. It is placed in a concrete safety box, and controlled from outside this box. The pilot plant has been designed for a maximum capacity of 5 kg/hr of drinking water and can be operated up to a maximum temperature of 500 °C and a maximum pressure of 380 bar. A schematic diagram and picture of the pilot plant are shown in Figure 3 and Figure 4 respectively. In addition to the storage vessel for the saline feed, an additional vessel for water has been installed to facilitate the start-up and shut-down procedures. To monitor the mass flows in and out of the process, and calculate mass balance closure, all inflow and outflow vessels are placed on weighing balances. The pilot plant is modular built and consists of

different units, with the key units being: a high pressure pump, a double pipe heat exchanger, a heater, a gravity separator, a capillary and high temperature valve, and a cyclone with a solids collector. These units as well as the operating procedure of the pilot plant will be discussed in this section.

3.1. Key Units of the Pilot Plant

Pressurized saline feed is provided to the process by a high-pressure LEWA diaphragm pump LDC1 (LEWA Herbert Ott GmbH & Co KG, Germany). This pump can handle a wide variety of fluids, including saline solutions. The pump has a maximum capacity of 25.0 L/h (with an uncertainty of 1% in mass flow measurement), and a maximum operating pressure of 400 bar. The desired process pressure is set and controlled with a back pressure regulator, BPR-1 (TESCOM 26-1762-24A, Tescom Europe GmbH & Co. KG, Germany, $C_v = 0.14$).

Figure 3. Schematic of the SCWD pilot plant.

Figure 4. Photo of the SCWD pilot plant.

A double pipe heat exchanger (HEX) for heat integration has been designed, constructed and installed between the feed (#1) and SCW product stream (#4). The saline feed flows through the tube while the SCW product flows through the annular space between the inner and outer tubes in a counter-current manner. This configuration is to allow for easy cleaning in the event of fouling due to salt deposition. The inner and outer tubes of the heat exchanger (see Figure 5d) are made from grade 2 titanium, and the dimensions of the tubes are listed in Table 1.

Chapter 5

The double pipe heat exchanger has been wound into a spiral coil (diameter of 40 cm and height of 40 cm) for stability and compactness (see Figure 5d). In order to prevent the inner tube from touching the inner surface of the outer tube, a 0.5 mm titanium wire is wound on the outside of the inner tube before inserting it into the outer tube (see Figure 5f). The heat exchanger is insulated with 20 mm thick glass fiber thermal insulating rope to reduce heat losses to the environment.

To provide additional heating to raise the temperature of the feed to the process temperature, a heater is installed between the heat exchanger and the gravity separator. The heater is made up of a grade 2 titanium tube (see Table 1 for dimensions) through which the feed flows and a 2.5 kW aluminum block that provides the electrical heating. The heater tube has been wound into a spiral (diameter of 10 cm and height of 36 cm) around the aluminum heating block to make the unit compact.

The first stage V- L separation occurs in the gravity separator (Figure 5e) equipped with a dip-tube ($d_i = 3$ mm, $d_o = 5$ mm, $L = 20$ cm, grade 2 titanium) to bring the feed into the separator. The separator is made from Incoloy 825 with an inner diameter of 4 cm (wall thickness, $t = 2$ cm) and a height of 50 cm. The separator is placed in a 6 kW electric oven insulated from the environment. The SCW product exits through the top of the separator to the heat exchanger, while the concentrated brine settles to the bottom of the vessel. The brine (#5) is restricted to the gravity separator by a high pressure-high temperature valve (see Figure 5a).

Figure 5. Pictures of the flash valve (a), cyclone (b), capillary (c), the double-pipe heat exchanger (d), the gravity separator (e), and the internal construction of the heat exchanger (f).

Table 1. Dimensions and Materials of Process Units – See Appendix C for Detailed Design.

Unit	Description	Dimensions	Material	Volume (L)
HEX	Double pipe heat exchanger, spiral shape. $A_o = 0.079 \text{ m}^2$	$d_i = 3.0 \text{ mm}$	Inner tube – titanium	0.035
		$d_o = 5.0 \text{ mm}$		
		$L = 5.0 \text{ m}$		
	Volume is of annulus	$d_i = 6.22 \text{ mm}$	Outer tube – titanium	0.054
		$d_o = 9.52 \text{ mm}$		
		$L = 5.0 \text{ m}$		
Heater	Block heater for feed stream. Tube is spiral in Al block. $A_o = 0.071 \text{ m}^2$	$d_i = 3.0 \text{ mm}$	Tube - titanium	0.032
		$d_o = 5.0 \text{ mm}$		
		$L = 4.5 \text{ m}$		
Separator	Gravity separator	$d_i = 40 \text{ mm}$	Incoloy 825	0.628
		$d_o = 80 \text{ mm}$		
		$L = 50 \text{ cm}$		
Cooler-1	Water cooler $A_o = 0.028 \text{ m}^2$	$d_i = 4 \text{ mm}$	Inner tube – SS 316	0.019
		$d_o = 6 \text{ mm}$		
		$L = 1.5 \text{ m}$		
	Volume is of annulus	$d_i = 8.0 \text{ mm}$	Outer tube – copper	0.033
		$d_o = 10.0 \text{ mm}$		
		$L = 1.5 \text{ m}$		
3xCooler -2	Water cooler $A_o = 0.11 \text{ m}^2$	$d_i = 4 \text{ mm}$	Inner tube – SS 316	0.226
		$d_o = 6 \text{ mm}$		
		$L = 6.0 \text{ m}$		
	Volume is annulus	$d_i = 8.0 \text{ mm}$	Outer tube – copper	0.396
		$d_o = 10.0 \text{ mm}$		
		$L = 6.0 \text{ m}$		
Capillary	To flash brine into cyclone	$d_i = 3.0 \text{ mm}$	Titanium	0.002

		$d_o = 5.0 \text{ mm}$		
		$L = 24 \text{ cm}$		
Cyclone	Separation of solid salt particles from water vapor	$d_i = 20 \text{ mm}$	Incoloy 825	0.022
		$d_o = 40 \text{ mm}$		
		$L = 132 \text{ mm}$		
Salt collector	Salt storage vessel	$d_i = 40 \text{ mm}$	Incoloy 825	0.628
		$d_o = 80 \text{ mm}$		
		$L = 50 \text{ cm}$		

The high pressure-high temperature valve (flash valve) is made from a chromium-nickel based alloy creep resisting austenitic steel. With a high resistance to corrosion, and stable mechanical and thermal properties at very high temperatures and pressure (up to 600 °C and 1000 bar), this valve is well equipped to handle the potentially corrosive and the high instantaneous pressure drop (up to 299 bar) during the expansion of the concentrated brine in the second (V – S) separation step of the process. To keep the brine isothermal prior to expansion, the valve, with the capillary (see Figure 5c) is placed in a 1 kW electric oven. The valve is full open/close and pneumatically operated from outside the high pressure safety box.

The cyclone (see Figure 5b) and salt collector vessel are made from Incoloy 825 with their dimensions are listed in Table 1. These units are placed in a 6 kW oven with ceramic insulation to reduce heat loss to the environment. All temperatures and pressures shown in Figure 3 are measured with standard type-K thermocouples (uncertainty in temperature measurement is 0.4% of measured value in °C, while the relative difference of measured values between thermocouples is 0.2 °C) and a sputtered thin film type pressure transducers (accuracy is 0.25% full scale) respectively. Coolers (Cooler-1 and Cooler 2 in Figure 3) have been installed to cool the outlet flows (#6 and #11 in Figure 3) to temperatures below the temperature limit (70 °C) of the back pressure regulators (BPR-1 and BPR-2 in Figure 3).

3.2. Operating Procedure and Measurements

The pilot plant is operated in a combined mode (continuous and batch wise). The feed and the production of the SCW (< 700 ppm, drinking water quality) is continuous (~ 75 mins runtime for 3.5 wt.% feed) while the brine (~ 50 wt.% at 300 bar, 460°C) is collected batch wise during this period and then flashed in a few seconds by opening the flash valve. Prior to start-up, all fittings and connections are checked to ensure that they are tightly closed, and the valve connecting the gravity separator to the cyclone is closed. For start-up, demineralized water is pumped at 5 kg/h through the process with the heater and ovens switched on and set to the desired temperatures. The back pressure regulator (BPR-1) is adjusted to obtain the process operating pressure, and mass balance closure is checked with the outputs of the weighing balances to ensure there are no leaks. Once the desired operating conditions is attained and steady state is established (fluctuations of not more than 1°C and 2 bar in all measured temperatures and pressures respectively over a period of 30 mins), the 3-way valve is switched to the saline feed.

The saline feed is 3.5 wt.% NaCl solution prepared using demineralized water and high purity NaCl ($> 99.5\%$, from Sigma-Aldrich Chemie, GmbH, Germany). As the pressurized saline feed passes through the heat exchanger, it is pre-heated with the SCW coming from the gravity separator (see Figure 3). Additional heating to achieve the desired operating temperature is supplied by the heater to ensure there is phase separation as the feed enters the gravity separator. The concentrated brine stays in the separator while the SCW (drinking water quality) exits at the top and is cooled (while it is used to preheat the feed) in the heat exchanger. Additional cooling is provided for by installing an extra cooler (cooler-1 in Figure 3). The product water is then depressurized and analyzed online with a conductivity sensor (constructed in-house).

Using the solubility data in Figure 1 and making mass balance calculations for a 3.5 wt.%, 5 kg/h NaCl feed, it was estimated that the gravity separator will be half-filled with brine after 1 hour of operation at 300 bar and 460°C . Therefore, after running the plant for 1 hour, the pump is stopped and instantaneously, the high temperature-high pressure valve is opened to flash the concentrated brine through

the capillary ($d_i = 3$ mm, $L = 24$ cm, titanium) into the cyclone. The temperatures and pressures (indicators and points of measurements are shown in Figure 3) are monitored and recorded with PicoLog data acquisition program. Mass in and out of the plant are recorded and evaluated to ascertain mass balance closure.

4. EXPERIMENTAL RESULTS

An experimental run starts when the 3-way valve is switched from the water feed vessel to the salt feed vessel. All temperatures, pressures, mass flow rates, and online concentration measurements (see Figure 3 for measurements locations) are recorded during each run and later processed. The pressures in the separator and cyclone as well as the temperatures inside the separator (bottom part), valve inlet and capillary during an experimental run (Expt. VI, see Table 2) are shown in Figure 6. A constant pressure is maintained in the separator (293 ± 2 bar) and the cyclone (1 bar) respectively during the continuous part of the process prior to the expansion of the collected brine. Once the flash valve is opened, the liquid brine is discharged instantaneously from the separator. And as the last drop of brine exits the separator, the pressure in the separator decreases drastically, while the cyclone pressure increases as it encounters the flash products (see Figure 6a). In Figure 6b, the measured temperatures at the separator bottom, valve inlet, and capillary during the continuous mode are stable in value. When the flash valve is opened for the expansion of the brine, the temperature at the bottom of the separator decreases as the hot brine is emptied from the vessel, while the temperatures in the valve and capillary increases as they encounter the hot brine.

The flow rates of the saline feed and the SCW product of the experimental run during the continuous operation mode are presented in Figure 7a. The difference between the two flow rates corresponds to the accumulation rate of the concentrated brine in the separator. These flow rates are constant during the experimental run, indicating that the pilot plant can be operated with negligible fluctuations in the flow. Figure 7b shows that the salt concentration in the SCW product can be steadily measured during the test runs, indicating that the pilot plant runs in a steady state.

Figure 6. Pressures in the separator vessel and cyclone (a), and temperatures at the bottom of the separator, valve and capillary (b) plotted against the run time for Expt. VI (see Table 2).

Figure 7. Mass flow rates of the saline feed and SCW outflow (a), and NaCl concentration in SCW outflow (b) plotted against the runtime respectively for Expt. VI (see Table 2).

4.1. Mass Balances and SCW Product Concentration

The process conditions for the various experimental runs as well as the SCW product quality, brine concentration, and the overall mass balance closures for these runs are listed in Table 2. The reported salt concentrations in SCW for all experimental runs have been measured, while the concentration of salt in the brine phase have been calculated via the salt mass balance of the separator. The concentration of salt measured in the SCW product for all experimental runs are well below the recommended safe limit for drinking water (< 0.07 wt.%) by UNESCO.²² As shown in Table 2, an acceptable overall mass balance closure ($> 95\%$ for each experimental run) is obtained from the pilot plant data.

Table 2. Parameters for the Pilot Plant Experimental Runs.

Expt.	NaCl Feed	$\dot{m}$	Run time	Separator	Separator top (X ₁)	Separator bottom (X ₂)	SCW	Brine	Mass balance
	(wt.%)	(kg/h)	(min)	(bar)	(°C)	(°C)	(wt.%)	(wt.%)	(%)
I	3.46	5.26	71	298	452	444	0.068	47.0	101.5
II	3.46	5.27	69	296	455	451	0.054	48.6	99.7
III	3.46	5.26	83	297	459	455	0.049	52.8	98.4
IV	3.46	5.05	79	292	458	449	0.048	45.4	99.7
V	3.46	5.19	70	291	454	453	0.054	53.6	96.2
VI	3.50	5.00	89	293	456	440	0.048	45.5	96.0
VII	1.30	5.50	138	296	461	455	0.052	49.1	98.5

See Figure 3 for the locations of X1 and X2.

The measured salt concentrations in the SCW phase obtained from the pilot plant are compared with available literature data and models to check and validate the separation efficiency of the pilot plant. In order to make this comparison, a separation temperature is required. However, as shown in Table 2, there is a temperature gradient between the top and the bottom of the separator for some of the experimental runs. Since the separation already occurs at the top of the separator and the SCW product exits through the top of the separator before encountering the separator bottom, the temperature measured at the top of the separator is taken as the process separation temperature. This is the higher temperature in all experimental runs.

Figure 8 shows the comparison of the solubility of NaCl in the SCW product measured in the pilot plant to some selected data and models available in literature. The semi-empirical solvation model of Armellini & Tester,²³ the experimental data compilation of Bischoff & Pitzer²⁴ as well as the correlation of Driesner & Heinrich²⁵ have been chosen because the pilot plant process conditions (temperatures and pressures) are within their validity range. As shown in Figure 8, the solubility measurements from our pilot plant are in agreement with the model of Armellini & Tester.²³

The pilot plant results are compared with the solubility measurement results from our laboratory scale apparatus² (see Figure 1) in Table 3. From our previous work² and the works of other researchers²³⁻²⁵, an increase in temperature under isobaric condition, or a decrease in pressure under isothermal condition results in a decrease in salt concentration in the SCW phase and an increase in salt concentration in the brine phase. Although the pressures in the laboratory scale experiments and pilot plant tests are not the same, the results are consistent with the trends expected of the influence of pressure (under isothermal condition) on the solubility of salt in the SCW and brine phases respectively. From Figure 8 and Table 3, we can conclude that under similar process conditions, the results obtained from the pilot plant are consistent with the measurements obtained from our laboratory scale apparatus and they are in agreement with the solvation model of Armellini & Tester.²³

Figure 8. Comparison of the solubility of NaCl in SCW measured in the pilot plant with the semi-empirical solvation model of Armellini & Tester²³, compilation of Bischoff & Pitzer²⁴ and the model of Driesner & Heinrich²⁵.

Table 3. Comparison of Pilot Plant Results to Lab. Scale² Results.

Scale	Feed	$\dot{m}$	Pressure	Separator top	SCW	Brine
	(wt.%)	(kg/hr)	(bar)	(°C)	(wt.%)	(wt.%)
Lab	3.50	0.012	250	450	0.046	60.8
Pilot (I)	3.46	5.26	298	452	0.068	47.0
Lab	3.50	0.012	300	450	0.081	40.3
Lab	3.50	0.012	250	460	0.048	-*
Pilot (VII)	1.30	5.50	296	461	0.052	49.1
Lab	3.50	0.012	300	460	0.076	48.5

* No brine phase at 250 bar, 460 °C. At this condition, the system NaCl-H₂O is in the V – S region of the phase diagram – See ^{2, 23}.

4.2. Heat Exchanger Performance

The double-pipe heat exchanger installed in the pilot plant has a heat transfer area of 0.079 m². The performance of the heat exchanger for the different experimental runs has been evaluated and presented in Table 4. The heat exchanger works in accordance with the design with saline solution, and no salt deposition was observed.

The overall heat transfer coefficient (U), and heat loss ($\dot{Q}_{loss}$) have been calculated using Eqs.1 and 2 respectively.

$$U = \frac{\dot{Q}_c}{A_o \cdot \Delta T_{lm}} \quad (1)$$

$$\dot{Q}_{loss} = \frac{|\dot{Q}_h - \dot{Q}_c|}{\dot{Q}_h} \quad (2)$$

where A_o is the heat transfer area based on the outer diameter of the inner tube, ΔT_{lm} is the logarithmic mean temperature difference, $\dot{Q}_c$ and $\dot{Q}_h$ are the quantity of heat in J/s taken up by the cold stream and transferred from the hot stream respectively. $\dot{Q}_c$ and $\dot{Q}_h$ are calculated as follows:

$$\dot{Q}_c = \dot{m}_c \cdot [h_{c,out} - h_{c,in}] \quad (3)$$

$$\dot{Q}_h = \dot{m}_h \cdot [h_{h,out} - h_{h,in}] \quad (4)$$

where $\dot{m}_c$ and $\dot{m}_h$ are the mass flow rates of the cold and hot streams respectively in kg/s; $h_{c,out}$ and $h_{c,in}$ are the specific enthalpies of the cold stream at the outlet and the inlet respectively in J/kg; and $h_{h,out}$ and $h_{h,in}$ are the specific enthalpies of the hot stream at the outlet and the inlet respectively in J/kg. The enthalpies of the streams are calculated with the enthalpy correlation of Driesner²⁶ for the system NaCl-H₂O.

Table 4. Performance of the Heat Exchanger for the SCWD Pilot Plant.

Expt.	Cold Stream – Tube				Hot Stream – Annulus				Heat Exchanger		
	$\dot{Q}_c = 2.6 - 2.9 \text{ kW}$				$\dot{Q}_h = 3.4 - 3.5 \text{ kW}$				ΔT_{lm}	U	$\dot{Q}_{loss}$
	T_{in}	T_{out}	P_{in}	P_{out}	T_{in}	T_{out}	P_{in}	P_{out}			
	(°C)	(°C)	(bar)	(bar)	(°C)	(°C)	(bar)	(bar)			
I	23	402	291.3	288.4	440	38	298.2	287.2	25	1400	22
II	22	407	287.8	285.0	437	38	295.7	283.8	23	1640	17
III	23	407	289.4	286.5	438	39	296.6	285.2	23	1600	18
IV	21	407	285.8	283.0	437	37	292.3	281.7	22	1630	16
V	21	400	285.5	282.5	427	37	291.4	281.3	21	1600	21
VI	19	401	284.2	283.8	447	32	293.2	283.0	26	1400	23
VII	21	392	287.0	286.6	427	36	296.0	285.7	23	1500	22

The overall heat transfer coefficient, U of the heat exchanger has been measured as $1500 \pm 150 \text{ W/m}^2\text{.K}$ with losses of 16-23 %. The heat loss from the heat exchanger is considered relatively high, and could be further reduced by using a better insulation material and by switching the feed flow and SCW flow to the annulus and tube side respectively, to improve the efficiency of the heat exchanger and consequently, the overall energy efficiency of the pilot plant.

4.3. Expansion of the Concentrated Brine

The expansion of the concentrated brine (V – S separation step of the SCWD process) results in the production of steam and salt. After each experimental run, the precipitated salts were collected and analyzed. Figure 9 shows the SEM (Jeol JSM 5600 LV, at 5 kV) photomicrograph of the NaCl used to prepare the feed solution as well as the solids salt obtained from the salt collector after the expansion of the brine (45 wt.% for Expt. IV). The feed salt particles are crystalline in shape with sizes ranging from 200 – 500 μm (see Figure 9a). The salt particles obtained from the expansion of the 45 wt.% brine comprise of small sized (2 – 15 μm) particles clustered together. No pores were revealed on the surface of the salt particles at higher magnification, therefore we can conclude that the flashed salts have a crystalline structure. These findings are consistent with the results obtained from a lab-scale apparatus in our previous work² (Chapter 2).

(a)

(b)

Figure 9. SEM photos of NaCl particles used to prepare the 3.5 wt.% feed (a), and NaCl obtained from the expansion of the brine (b) for experimental run IV.

5. CONCLUSIONS AND OUTLOOK

A first generation modular pilot plant for supercritical water desalination (SCWD) with a maximum capacity of 5 kg/hr drinking water has been designed and constructed with the first results presented. Preliminary tests with NaCl feed solution (1.3 and 3.5 wt.% respectively) have shown that the pilot plant does run for several hours without operational problems with good mass balance closure. The produced water is of drinking quality and the flashing of the accumulated brine in the separator to atmospheric pressure works fine and results in (wet) solid salt and water vapor. The solubility of NaCl in the supercritical phase measured in the pilot plant agrees well with reported literature data and is consistent with the results obtained from our lab-scale experimental apparatus. The double-pipe heat exchanger installed for heat integration works in accordance with the design, with a measured overall heat transfer coefficient of $1500 \text{ W/m}^2\cdot\text{K}$.

Further testing is being carried out in the pilot plant to study the influence of process parameters and in the future to investigate other salts and mixture of salts. These additional results will provide necessary data and insights for further refinement of the SCWD process.

NOMENCLATURE

A	heat transfer area (m ²)	Greek Symbols	
<i>d</i>	diameter (m)	Δ	difference
<i>h</i>	specific enthalpy (J/kg)	ρ	density (kg/m ³)
HEX	heat exchanger	Φ	Volume flow (m ³ /s)
<i>L</i>	length (m)	Subscripts	
$\dot{m}$	mass flow (kg/h)	<i>c</i>	cold stream
MED	multi-effect distillation	<i>h</i>	hot stream
MSF	multi-stage flash	<i>ht</i>	heater
P	pressure (bar)	<i>i</i>	inner
$\dot{Q}$	heat flow (W)	<i>in</i>	inlet
RO	reverse osmosis	<i>L</i>	liquid
S_{NaCl}	solubility of NaCl (wt.%)	<i>lm</i>	logarithmic mean
SCW	supercritical water	<i>loss</i>	losses
SCWD	supercritical water desalination	<i>o</i>	outer
SCWG	supercritical water gasification	<i>out</i>	outlet
SCWO	supercritical water oxidation	<i>t</i>	terminal
SEM	scanning electron microscope	<i>v</i>	vapor
<i>t</i>	tube wall thickness (m)		
T	temperature (°C)		
TDS	total dissolved solids		
<i>u</i>	velocity (m/s)		
<i>U</i>	overall heat transfer coefficient (W/m ² K)		

Chapter 5

V - L vapor - liquid

V - S vapor - solid

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Appendix C

Detailed Design Calculations

APPENDIX C

An overview of the design consideration and assumptions for the sizing of equipment are given in this section.

The design of the process equipment has been based on the production of 5 kg/hr of drinking water and V-L separation at 300 bar and 460 °C. Making mass balance calculations for V-L separation at 300 bar and 460 °C (see Figure 1), 5.4 kg/hr of saline feed is required to produce 5 kg/hr of drinking water. The brine flow is 0.4 kg/hr (50 wt. % NaCl) resulting in 0.2 kg/hr salt and 0.2 kg/hr steam after flashing.

C-1. Heat Exchanger – Counter-current flow

Design calculation is based on heat duty equation,

$$\dot{Q} = U_o A_o \Delta T_{lm} = \dot{m}_c (h_{c,out} - h_{c,in})$$

$\dot{m}_c$ is the mass flow of the cold stream in kg/s, and $h_{c,in}$ and $h_{c,out}$ are the specific enthalpies of the cold stream at the inlet and outlet of the heat exchanger respectively in J/kg. $h_{c,in}$ and $h_{c,out}$ have been calculated using the correlation of Driesner²⁶ for NaCl solution.

U_o = Overall heat transfer coefficient based on outside tube heat transfer area, W/m²K.

A_o = Outside tube heat transfer area, m².

$$\Delta T_{lm} = \frac{(T_{h,in} - T_{c,out}) - (T_{h,out} - T_{c,in})}{\ln((T_{h,in} - T_{c,out}) / (T_{h,out} - T_{c,in}))}$$

Where $T_{h,in}$ and $T_{h,out}$ are the inlet and outlet temperatures of the hot stream, and $T_{c,in}$ and $T_{c,out}$ are the inlet and outlet temperatures of the cold stream respectively.

Values of $T_{c,in}$, $T_{c,out}$, and $T_{h,in}$ were fixed (see Table C-1 for values). $h_{h,out}$ was calculated by assuming all the heat transferred from the hot stream is absorbed from the cold stream:

$$\dot{m}_h (h_{h,in} - h_{h,out}) = \dot{m}_c (h_{c,out} - h_{c,in})$$

$\dot{m}_h$ is the mass flow of the hot stream in kg/s, and $h_{h,in}$ and $h_{h,out}$ are the specific enthalpies of the hot stream at the inlet and outlet of the heat exchanger respectively in J/kg. $h_{h,in}$ and $T_{h,out}$ have been calculated using the IAPWS formulation²⁷ for water and steam.

The inner and outer diameter of the inner tube was chosen based on standard issue titanium tube sizes available in the market that can withstand the high pressures (up to 300 bar) expected in the heat exchanger. The inner diameter of the shell (outer tube) was also chosen based on standard issue titanium tube size available in the market while maintaining equal mass fluxes through the tube and the shell annulus. Tube thickness was calculated based on the pressure and temperature requirements.

Table C-1. Calculation Parameters for Heat Exchanger Sizing.

	Parameter	Value
Based on process condition	$T_{h,in}$ (°C)	460
From Wagner et al. ²⁷	$h_{h,in}$ (kJ/kg)	2883.8
Calculated	$T_{h,out}$ (°C)	60
From Wagner et al. ²⁷	$h_{h,out}$ (kJ/kg)	276.2
Assumed	$T_{c,in}$ (°C)	20
From Driesner ²⁶	$h_{c,in}$ (kJ/kg)	112.8
Desired outlet temperature (assumed)	$T_{c,out}$ (°C)	430
From Driesner ²⁶	$h_{c,out}$ (kJ/kg)	2524.2
	$\dot{m}_c$ (kg/hr)	5.4
Inner tube	d_i (mm)	3.00
	d_o (mm)	5.00
	$\dot{m}_h$ (kg/hr)	5.0
Outer tube (Shell)	d_i (mm)	6.22
	d_o (mm)	9.52

Heat exchanger duty, $\dot{Q}$ was calculated as 3.6 kW, ΔT_{lm} was calculated as 35 °C. And, based on COMSOL calculations on heat transfer to sub- and supercritical water flow in a tube with the same dimensions as the chosen design, a U_o value of 1500 W/m²K was assumed resulting in a heat exchanger length of 4.4 m, which was rounded off to 5.0 m for the design.

C-2. Heater

The heater was designed to increase the temperature of the saline feed from 430 °C at the outlet of the heat exchanger to 460 °C to ensure the saline feed is already at the separation temperature when it enters the gravity separator.

We assume that there are negligible heat losses to the surrounding resulting in the equation:

$$\dot{Q} = U_o A_o \Delta T_{lm} = \dot{m}(h_{out} - h_{in})$$

$\dot{Q}$ = heater duty, W.

U_o = overall heat transfer coefficient based on outer area, W/m²K.

$\dot{m}$ = mass flow, kg/s

$$\Delta T_{lm} = \frac{(T_{ht}-T_{in})-(T_{ht}-T_{out})}{\ln((T_{ht}-T_{in})/(T_{ht}-T_{out}))}$$

h_{out} and h_{in} are the specific enthalpies of the fluid at the outlet and inlet of the heater in J/kg calculated using the correlation of Driesner²⁶ for NaCl solution. And, T_{ht} , T_{out} and T_{in} are the temperatures of the heater and of the fluid at the heater outlet and inlet respectively.

Table C-2. Calculation Parameters for Heater Sizing.

	Parameter	Value
Set as constraint	T_{ht} (°C)	470
From heat exchanger outlet (Assumed)	T_{in} (°C)	430
From Driesner ²⁶	h_{in} (kJ/kg)	2524.2
Based on process condition	T_{out} (°C)	460
From Driesner ²⁶	h_{out} (kJ/kg)	2800.0
	$\dot{m}$ (kg/hr)	5.4
Inner tube	d_i (mm)	3.00
	d_o (mm)	5.00

From our study on heat transfer in SCW in COMSOL¹⁵, we know that the HTC of water is greatly diminished ($< 500 \text{ W/m}^2\text{K}$) at temperatures above the pseudo-critical temperature (Temperature at maximum C_p , 402 °C at 300 bar). Therefore, U_o value of $250 \text{ W/m}^2\text{K}$ was assumed for the calculation of the area required for the desired level of heating.

In order to prevent solids formation on the inside wall of the tube, the heater temperature, T_{ht} should be below the transition temperature to the V – S region of the phase diagram (475 °C at 300 bar for NaCl – H₂O, see Figure 1). The heater temperature, T_{ht} was set at 470 °C.

This gives a ΔT_{lm} of 22 °C

Heater duty, $\dot{Q}$ was calculated as 0.4 kW, while the required heater length for the chosen diameter (see Table C-2) has been calculated as 4.5 m.

C-3. Gravity Separator

The function of the gravity separator is to remove the SCW product water which is then used for heat integration as well as storing the brine prior to flashing. The design of the gravity separator is illustrated in Figure C-3. A dip-tube brings in the feed to the separator (a mixture of vapor and liquid brine), the vapor (SCW) leaves through the outlet at the top of the vessel, while the concentrated brine settles to the bottom of the vessel under the action of gravity.

The sizing of the gravity separator is based on the methodology presented by Sinnott²⁸ and operating conditions of 300 bar and 460 °C.

Figure C-3. Gravity separator design.

$$D_v = \sqrt{\frac{4\Phi_v}{\pi u_s}}$$

D_v = minimum vessel inner diameter, m

Φ_v = vapour volumetric flow rate, m³/s

$$u_s = 0.15u_t$$

Where u_t is the settling velocity of the liquid droplets calculated as:

$$u_t = 0.07[(\rho_L - \rho_v)/\rho_v]^{0.5}$$

Where ρ_L and ρ_v are the liquid and vapour densities respectively in kg/m³.

Table C-3. Calculation Parameters for Gravity Separator Design.

	Parameter	Value
From Wagner et al. ²⁷	ρ_v (kg/m ³)	139
From Driesner ²⁶	ρ_L (kg/m ³)	1150
Design basis	$\dot{m}_v$ (kg/hr)	5.0
Design basis	$\dot{m}_L$ (kg/hr)	0.4
Calculated	Φ_v (m ³ /hr)	0.036
Calculated	u_t (m/s)	0.19
Assumed	Liquid hold-up (min)	60
Calculated	Liquid level in hold-up time (cm)	28

The minimum vessel diameter, D_v has been calculated as 2.1 cm. The gravity separator has been sized as follows:

$$d_i = 4 \text{ cm}$$

$d_o = 8 \text{ cm}$, thickness of 2 cm is sufficient to handle the high pressure and temperature

$$L = 50 \text{ cm}$$

Dip-tube length = 20 cm, This gives an allowance of 2 cm between the tip of the dip-tube and the liquid surface at liquid hold-up time of 60 mins. The dip-tube has an inner and outer diameter of 3.0 and 5.0 mm respectively.

C-4. Capillary

The design of the capillary was by trial and error. The dimensions are shown in Table 1.

C-5. Cyclone

The design of the cyclone follows from the methodology of Stairmand as stated in Sinnott.²⁸ Brine to be flashed to cyclone is 0.4 kg (~0.35 L) 50 wt.% NaCl solution at 300 bar and 460 °C for 60 mins liquid hold-up in the separator prior to flash. While the final flash conditions is assumed to be 10 bar, 180 °C. The estimated flash time is 45 sec, resulting in a flow rate of 0.00093 m³/s.

Following the design procedure highlighted in Sinnott,²⁸ an inlet feed velocity of 15 m/s was assumed, and the cyclone diameter and height have been calculated as 11 and 50 mm respectively. The cyclone dimensions was then scaled-up for a high gas flow rate cyclone. The cyclone has been designed with an inner diameter of 20 mm (with wall thickness of 10 mm) and height of 132 mm. The design of the cyclone is shown in Figure C-5. The dimension of the inlet to the cyclone results in a gas (steam) inlet velocity of 25 m/s.

Figure C-5. Design of cyclone for G - S separation.

C-6. Salt Collector

The salt collector has been designed as a pressure vessel with the same dimensions as the gravity separator. However, the salt collector has only one inlet and no outlet.

C-7. Coolers – Counter-current flow

C-7.1. Cooler-1 (see Figure 3)

Cooling product water from heat exchanger outlet ($\sim 40^\circ\text{C}$) to 25°C at 300 bar.

$$\dot{Q} = \dot{m}_{h,in}(h_{h,in} - h_{h,out})$$

$$\dot{m}_{h,in} = 5 \text{ kg/hr}$$

$$h_{h,in} = 193.9 \text{ kJ/kg at 300 bar, } 40^\circ\text{C. From IAPWS formulation of Wagner et al.}^{27}$$

$$h_{h,out} = 132.3 \text{ kJ/kg at 300 bar, } 25^\circ\text{C. From IAPWS formulation of Wagner et al.}^{27}$$

$$\dot{Q} = 86 \text{ W}$$

Utility is cooling water with $T_{in} = 18^\circ\text{C}$ and $T_{out} = 25^\circ\text{C}$.

$$\Delta T_{lm} = 11^\circ\text{C}$$

$$U_o = 300 \text{ W/m}^2\text{K (combination of cooling water and high pressure liquid water)}$$

$$\text{Calculated } A_0 = 0.026 \text{ m}^2$$

A cooler of heat transfer area, $A_0 = 0.028 \text{ m}^2$ (see Table 1 for dimensions and materials) has been designed.

C-7.2. Cooler-2 (see Figure 3)

Cooling saturated steam at 1 bar to liquid water at 25°C .

$$\dot{Q} = \dot{m}_{h,in}(h_{h,in} - h_{h,out})$$

$$\dot{m}_{h,in} = 0.27 \text{ kg/min (0.2 kg of steam was produced during the flash operation in 45 sec)}$$

$$h_{h,in} = 2675.8 \text{ kJ/kg at 1 bar, } 100^\circ\text{C. From IAPWS formulation of Wagner et al.}^{27}$$

$$h_{h,out} = 104.9 \text{ kJ/kg at 1 bar, } 25^\circ\text{C. From IAPWS formulation of Wagner et al.}^{27}$$

$$\dot{Q} = 11.4 \text{ kW}$$

The high cooling duty for cooler-2 is a direct consequence of the fast dynamic flash operation.

Utility is cooling water with $T_{in} = 18^\circ\text{C}$ and $T_{out} = 20^\circ\text{C}$.

$$\Delta T_{lm} = 30^\circ\text{C}$$

$$U_o = 1250 \text{ W/m}^2\text{K (combination of cooling water and condensing steam)}^{28}$$

$$\text{Calculated } A_0 = 0.30 \text{ m}^2.$$

A cooler of total heat exchange area, $A_0 = 0.33 \text{ m}^2$ ($3 \cdot A_0 = 0.11 \text{ m}^2$, see Table 1 for dimensions and materials) has been designed.

Chapter 6

Conclusions and Outlook

CONCLUSIONS

The supercritical water desalination (SCWD) process allows for the treatment of salt-water streams without the production of a waste stream (zero liquid discharge, ZLD) by utilizing the decreased solubility of inorganic salts in supercritical water (SCW). Compared to state-of-the-art conventional desalination methods such as reverse osmosis (RO) and multi-stage flash (MSF) distillation, SCWD offers the following potential advantages:

- (i) it meets the environmental challenges of waste brine disposal¹⁻⁴ encountered in the conventional processes,
- (ii) it offers a high water yield per pass (93 wt.% compared to 50 wt.% for RO and MSF for sea water installations), and
- (iii) it can handle high concentration salt streams that cannot be processed with conventional desalination methods.

The main objective of the research described in this thesis is the development and construction of a pilot plant scale SCWD process that produces drinking quality water and solids salt. The work presented in this thesis focuses on the process development (conceptual design of the process, lab-scale demonstration of the proof-of-concept, and selection of process operating pressure and temperature), design and construction of a pilot SCWD unit, and the first results from this pilot plant. In addition, detailed numerical modelling and experimental validation of heat transfer coefficient, which is essential for heat integration, are presented. From the work presented in this thesis, the following conclusions can be drawn.

Visualization experiments of the phase transition of model NaCl-H₂O in quartz capillaries confirmed that under supercritical water conditions, two distinct regions, V-L and V-S as well as a transition V-L-S are present. The transition temperature from V-L to V-S was found to be about 450 °C at 250 bar, and 475 °C at 300 bar respectively. In addition, the phase equilibrium solubility of NaCl-H₂O was studied under isobaric conditions in a lab-scale experimental setup at 250 and 300 bar respectively. The phase diagram (see Chapter 2, Figure 5) showed that the salt concentration in the supercritical vapor phase is of drinking water quality and

provided an operating window (pressure and temperature) to avoid salt precipitation in the early stage of the process.

The SCWD process was simulated in UniSim Design (using water) at 250 and 300 bar pressure. Simulation results showed that operating the SCWD process at 300 bar offers better heat integration potential as well as a 22% reduction in thermal energy consumption compared to operating at 250 bar. 300 bar was then selected as the operating pressure of the SCWD process.

The results of the visualization experiments supported by the phase diagram (see Chapter 2, Figure 5) showed that the SCWD process could be operated in two stages: (i) a V–L separator to remove the supercritical product water from the liquid phase at 250/300 bar, and (ii) a V–S separator to obtain the solid salt by flashing the liquid phase (a highly concentrated salt solution, 50 wt.% at 300 bar, 460 °C) to atmospheric pressure. The two-stage operation is necessary to avoid the potential of solids formation in the process equipment (particularly the separator) which could lead to equipment blockage and downtime. The proof-of-concept of two-stage separation for the SCWD process was demonstrated in a lab-scale (12 g/hr) apparatus using 3.5 wt.% NaCl-H₂O solution (Chapter 2).

The SCWD process is energy intensive (about 2 GJ of energy is required to bring 1 m³ of water from atmospheric conditions - $P = 1.02$ bar and $T = 25$ °C - to supercritical conditions - $P_c = 221$ bar and $T_c = 375$ °C -), therefore, in order to make it a commercial success and competitive with conventional desalination processes (such as MSF distillation, RO, etc.), heat integration is essential to regain as much energy as possible from the process. Heat integration is achieved by heating the feed stream with the SCW product stream in a heat exchanger. Understanding the heat transfer mechanism as well as knowing the heat transfer coefficient of sub- to supercritical water flow is required to design such a heat exchanger. As there are no available data or correlations for heat transfer coefficient of SCW at the low mass fluxes ($G \leq 20$ kg/m²s) typically found in pilot scale unit, 2D numerical simulations in COMSOL Multiphysics provided essential insights into the heat transport mechanism of SCW flow at low mass fluxes and was the basis for the developed 1D Nusselt correlation that can be used for engineering

design. The numerical results showed that the heat transport mechanism is primarily by buoyancy-induced circulation resulting from gravitational force acting on density gradients (a direct consequence of temperature gradients) across the cross-section of the tube. This circulation results in a flat radial temperature profile in the bulk of the fluid with a steep gradient in the thermal boundary layer at the wall. In addition, experimental measurements showed that the heat transfer coefficient go through a maximum ($> 3000 \text{ W/m}^2\text{K}$) as the temperature of the fluid approaches the pseudocritical temperature and then deteriorated rapidly ($< 500 \text{ W/m}^2\text{K}$) at temperatures above the pseudocritical temperature. The 1D Nusselt correlation for engineering design (developed with the numerical results) was validated with experimental measurements (Chapters 3 and 4). COMSOL is a powerful tool to investigate and understand the transport phenomena of complicated flows such as SCW flow.

The first of its kind, first generation modular pilot plant for SCWD with a capacity of 5 kg/hr drinking water was designed, constructed and operated. Experiments with NaCl feed (3.5 wt.% solution) were carried out successfully with the plant running for several hours without operational problems and with good mass balance closure (overall mass balance $> 95 \%$). The pilot plant produces drinking quality water ($< 700 \text{ ppm}$ salts) and solid salt crystals ($2\text{-}15 \text{ }\mu\text{m}$). The solubility of NaCl in the supercritical phase measured in the pilot plant agrees well with reported literature data and is consistent with the results obtained from our lab-scale experimental apparatus. The double-pipe heat exchanger installed for heat integration works in accordance with the design, with a measured overall heat transfer coefficient of $1500 \text{ W/m}^2\text{K}$ (Chapter 5).

With the pilot plant demonstration of the SCWD process introduced in this thesis, a new approach to tackle desalination in a sustainable way with Zero Liquid Discharge is provided.

OUTLOOK

In this thesis, we have shown the SCWD process, as a viable and working technology to treat salt water streams with zero liquid discharge from a lab-scale proof-of-concept unit (12 g/hr) to a pilot plant scale (5 kg/hr). Although the process works according to design and as intended, few issues need to be investigated further.

Optimization of the pilot plant especially the second stage flashing of the concentrated brine stream is highly recommended. The present design of the flash is based on trial and error, and is neither adiabatic nor isothermal. Future work should investigate the possibility and performance of an adiabatic or isothermal flash operation.

Further tests with higher salt concentrations, other salts and mixture of salts are proposed to provide more data and insights for further refinement of the SCWD process. In addition, the feasibility of fractional separation of salts from a salt mixture solution should be investigated.

The SCWD process is still energy intensive (even with very high level of heat integration, 150 MJ extra thermal energy is required per cubic meter of produced water compared to MSF distillation), and as such, a preliminary evaluation shows it is too expensive as a stand-alone water producing technology. The SCWD process will be best suited for a location with readily available low cost power or low cost high temperature heat source ($> 500\text{ }^{\circ}\text{C}$), e.g. combined heat and power (CHP) plants, ammonia production plants, etc. The added value of combining the SCWD process as end of pipe solution to conventional desalination methods to convert them to ZLD technologies should be explored.

Since the SCWD process can be used to process high salinity salt streams, the viability of the SCWD process in a salt manufacturing plant should be investigated. The steam produced during the flash operation of the concentrated brine could be used to provide some (or all) the heating requirements of the salt plant.

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Publications

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