

Advanced freeze valves for energy production and conversion systems using molten salts

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DTU Physics Department of Physics



Mateusz Pater

Advanced freeze valves for energy production and conversion systems using molten salts

PhD thesis

Copenhagen, 2023

This thesis is submitted in partial fulfillment of the requirements for the PhD degree at the Technical University of Denmark. The work has been carried out as part of an industrial PhD project funded by Innovation Fund Denmark (grant number 9065-00260) at the Department of Physics, Section of Radiation Physics at the Technical University of Denmark and at the host company, Seaborg Technologies between May 2020 and May 2023.

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Abstract (English)

Molten salts are being increasingly considered for use in energy production and conversion systems, as well as in energy storage systems. Nuclear reactors and concentrated solar power plants have been utilizing or intending to utilize molten nitrites, fluorides, and chlorides. This industrial PhD project adds on to the research on these salts with a focus on a new alternative, molten sodium hydroxide.

A nitrite-based solar salt and sodium hydroxide are investigated in two different thermal convection loops equipped with freeze valves. The molten salt loops have been designed, assembled, and operated by the author to provide data for thermal hydraulics studies, analyses of melting and freezing, and corrosion measurements. The freeze valves, including a novel C-shaped design, are tested as integral safety components of the loops to inform the design of future facilities and ensure smooth operation of the loop experiments. Computational fluid dynamics models are created to validate the temperature data collected during the experiments of salt natural circulation and salt phase change. A numerical benchmark is created to compare capabilities of different codes to model salt phase change. Additionally, density and viscosity of molten sodium hydroxide are measured at very high temperatures to increase the understanding of the salt's behavior and aid modelling thereof.

Candidates for industrial development of mechanical and freeze valves for use in molten salt systems are compared. Past and ongoing research on freeze valves and molten salt loops is summarized, and a dedicated design approach is suggested. The holistic view at the molten salts allows for understanding of the complexity of the molten salt based systems, and for making correct decisions with respect to the design of such systems, taking into account thermal hydraulics, material compatibility issues, and the influence of corrosion products.

Abstract (Dansk)

Smeltede salte overvejes i stigende grad til brug i energiproduktions- og konverteringssystemer samt i energilagringssystemer. Atomreaktorer og koncentrerede solkraftværker har brugt eller har til hensigt at udnytte smeltede nitritter, fluorider og chlorider. Dette erhvervs-ph.d.-projekt supplerer forskningen i disse salte med fokus på et nyt alternativ, smeltet natriumhydroxid.

Et nitritbaseret solsalt og natriumhydroxid bliver undersøgt i to forskellige varmekonvektionsloop udstyret med fryseventiler. De smeltede saltsloop bliver designet, monteret og styret af forfatteren for at indsamle data til termiske hydrauliske undersøgelser, analyser af smeltning og frysning og korrosionsmålinger. Fryseventilerne, inklusive et nyt C-formet design, bliver testet som integrerede sikkerhedskomponenter i loopene for at informere designet af fremtidige anlæg og sikre en jævn drift af loopforsøgene. Computational fluid dynamics-modeller bliver skabt for at validere temperaturdataene indsamlet under eksperimenterne med saltsvarmekonvektion og saltfaseændring. Et numerisk benchmark bliver skabt for at sammenligne forskellige softwares muligheder for at modellere saltfaseændringer. Derudover bliver massefylde og viskositet af smeltet natriumhydroxid målet ved meget høje temperaturer for at øge forståelsen af saltets adfærd og hjælpe med at modellere det.

Kandidater til industriel udvikling af mekaniske og fryseventiler til brug i smeltede saltsystemer bliver sammenlignet. Tidligere og igangværende forskning i fryseventiler og smeltede saltsloop er opsummeret, og der bliver en dedikeret designtilgang foreslået. Det holistiske syn på de smeltede salte giver mulighed for forståelse af kompleksiteten af de smeltede saltbaserede systemer og for at træffe korrekte beslutninger med hensyn til designet af sådanne systemer, under hensyntagen til termisk hydraulik, materialekompatibilitetsproblemer og indflydelsen af korrosionsprodukter.

Acknowledgments

We have not inherited the Earth from our fathers. We have borrowed it from our children.

When I came across this quote at the age of 14, I instantly knew it was going to define my entire career. I strongly believed – and still do – that only with sustainable technologies can we make the world a better place. The decision to study nuclear physics and engineering was a no-brainer to me, as nuclear energy is sustainable, efficient, and intriguingly difficult to harness in a safe way. To bring new, clean energy technologies such as nuclear molten salt reactors to a higher readiness level became my professional goal. However, doing industrial research in the field of molten salts has not been a walk in the park. On the contrary, it has been quite a hike up. I would have never done it without both the mental support from my family and the words of encouragement and admiration from my partner, for which I am eternally grateful. I got where I am because of you, and I am very happy.

I thank all my supervisors and mentors for believing in my work and taking care of me: Bent, Christian, Andreas, Esben, Jacob, and especially Luca who has always stood by me and said exactly what I needed to hear.

Last but not least, my dear friends, colleagues, and fellow PhD students – you all have made my journey an unforgettable experience. Thank you for making my days in Denmark, at Seaborg, and at DTU always filled with love. Let this PhD thesis be a testament to my finest years so far.

List of Publications

IV

This document is composed of a PhD dissertation manuscript and four original scientific articles which are embedded in the body of the document and whose beginning and end are marked for clarity. Contents of the articles are excluded from this document's list of figures, nomenclature, and references, and should be treated as appendices placed within the body of the document. The papers constituting the author's scientific output created as a result of the PhD project are:

- Mateusz Pater, Bouke Kaaks, Bent Lauritzen, Danny Lathouwers, A numerical benchmark for modelling phase change in molten salt reactors. Manuscript submitted for publication in a scientific journal.
- Mateusz Pater, Bent Lauritzen, Esben Bryndt Klinkby, Jacob Groth Jensen, Luca Silvioli, Andreas Vigand Schofield, NS1 - A Natural Circulation Loop Facility for MSR Research, Conference Proceedings of the 19th International Topical Meeting on Nuclear Reactor Thermal Hydraulics, March 6, 2022. ISBN 9789076971261.
- Mateusz Pater, Christian R.H. Bahl, Esben Bryndt Klinkby, Andreas Vigand Schofield, Bent Lauritzen, Computational fluid dynamics model for a C-shaped sodium hydroxide freeze valve. Manuscript submitted for publication in a scientific journal.
- Laura Voigt, Mateusz Pater, James Amphlett, Daniela Schwarz, Christopher Giehl, Daniel John Cooper, Viscosity and density of molten sodium hydroxide at temperatures between 623 and 973 K. Manuscript submitted for publication in a scientific journal.

Table of Contents

Abstract	(English)I
Abstract	(Dansk)II
Acknowle	edgmentsIII
List of Pu	blicationsIV
List of Fig	guresVIII
List of Ab	breviationsXI
1. Intro	oduction1
1.1.	Background1
1.2.	Host company introduction7
1.3.	Research objectives8
1.4.	Outline of the thesis9
2. Valv	es for molten salts11
2.1.	Research procedure11
2.2.	Valve choice12
2.3.	Off-the-shelf valves14
2.4.	Materials lifetime
2.5.	Historical developments: mechanical valves21
2.5.3	1. ORNL in the 20 th century21
2.5.2	2. John Hopkins University
2.5.3	3. ORNL today
2.5.4	4. Sandia National Labs23
2.5.	5. Abengoa25
2.5.0	5. <i>CIEMAT</i> 26
2.5.	7. Bhabha Atomic Research Centre27
2.5.8	3. University of Wisconsin-Madison27

	2.6	5.	Historical developments: freeze valves			
	2.7	7.	Historical developments: hybrid valves			
	2.8	3.	Free	eze valve research today	42	
3	.	Pha	se ch	ange	52	
	3.1	L.	Phy	sical description	52	
	3.2	<u>2</u> .	Ana	lytical methods	54	
	3.3	3.	Nun	nerical methods	56	
4	.	Nun	neric	al benchmark	64	
	Int	rodu	uctio	n	64	
	A r rea	num acto	erica rs	I benchmark for modelling phase change in molten salt	65	
	Clo	osing	g rem	narks	108	
5	.	Rese	earch	n on molten salt loops	109	
	5.1	L.	Hist	orical ORNL loops	110	
	5.2	2.	Res	earch loops today	119	
	!	5.2.2	1.	ORNL	119	
	!	5.2.2	2.	Bhabha Atomic Research Centre	123	
	!	5.2.3	3.	Polytechnic University of Milan	126	
	5.2.4.		4.	SINAP	127	
	!	5.2.5	5.	University of Wisconsin-Madison	129	
	!	5.2.6	6.	TerraPower	133	
	5.3	3.	Loo	ps at Seaborg Technologies	135	
6	.	Loop	p des	ign process	137	
	6.1	L.	Rati	onale for building the loops	137	
	6.2	2.	Des	ign decisions based on the literature study	138	
6.3. Project managemen		Proj	ect management	140		
	6.4	1.	Goo	od engineering practice	147	
6.5.		Des	ign calculations	149		

	6.6. T	he role of procurement and manufacturing	. 153	
7.	NS1 lo	op facility	. 154	
	Introduc	tion	. 154	
	NS1 – A I	natural circulation loop facility for MSR research	. 155	
	Closing r	emarks	.178	
8.	MS1 lo	oop facility	. 179	
	Introduc	tion	. 179	
	Computa	tional fluid dynamics model for a C-shaped sodium hydroxic	le	
	freeze va	llve	. 180	
	MS1 ope	rations	. 229	
	Closing r	emarks	.233	
9.	NaOH	thermophysical and transport properties	. 234	
	Introduc	tion	.234	
	Viscosity between	and density of molten sodium hydroxide at temperatures 623 and 973 K	.235	
	Phase transition enthalpy			
	Closing r	emarks	.259	
1(0. Con	clusions	. 260	
	10.1.	Numerical models	.260	
	10.2.	Freeze valves and molten salt loops	.261	
	10.3.	Properties of NaOH	.263	
	10.4.	Recommendations	.263	
R	eferences		.267	

List of Figures

Figure 1. Scheme of molten salt reactor's circuits, adapted from [13]. Figure
courtesy of the Generation IV International Forum
Figure 2. Top view of the Molten Salt Reactor Experiment [14]. Photo courtesy of
the Oak Ridge National Laboratory
Figure 3. 110 MW molten salt tower CSP plant Crescent Dunes Solar Energy
Project. Cropped photo courtesy of Amble, CC BY-SA 4.0
Figure 4. Energy conversion scheme of a CSP plant, adapted from [15]4
Figure 5. Commercial water pipe freezing system [24]7
Figure 6. Stem-guided globe valve, adapted from [52]15
Figure 7. Bellows globe valve, adapted from [52]16
Figure 9. Molten salt valve installed in the Nitrate Salt Large Heat Transfer Loop
[36]
Figure 10. Resistance-heated freeze valve tested at the ORNL [91]. Photo courtesy
of the Oak Ridge National Laboratory
Figure 11. Induction-heated freeze valve tested at the ORNL [91]. Photo courtesy
of the Oak Ridge National Laboratory
Figure 12. Calrod-heated freeze valve tested at the ORNL [91]. Photo courtesy of
the Oak Ridge National Laboratory
Figure 13. ORNL's freeze valve test rig [91]. Photo courtesy of the Oak Ridge
National Laboratory
Figure 14. Freeze valve design used in the MSRE Engineering Test Loop [91], [93].
Figure courtesy of the Oak Ridge National Laboratory
Figure 15. Example of a horizontal freeze valve assembly [94]. Photo courtesy of
the Oak Ridge National Laboratory
Figure 16. Freeze valve used in the MSRE Engineering Test Loop [95]. Photo
courtesy of the Oak Ridge National Laboratory
Figure 17. MSRE freeze valve with an air jacket before assembling heaters and
cooling tubes [92]. Photo courtesy of the Oak Ridge National Laboratory
Figure 18. Location of freeze valves in the MSRE systems [90]. FFT is the fuel flush
tank used for cleaning of the MSRE fuel salt loop, and FD-1 and FD-2 are the fuel
drain tanks. Figure courtesy of the Oak Ridge National Laboratory
Figure 19. Hybrid drain valve intended for use in the Molten Salt Reactor
Demonstration Plant [102]. Figure courtesy of the Oak Ridge National Laboratory.

Figure 24. Cut of the model of the freeze plug grate with seven freeze plugs [110].
Figure 25. Decay heat design of the MSFR freeze valve studied by Shafer [111]44
Figure 26. Freeze valve implemented in FFFER [34]
Figure 27. Freeze valve tested in SWATH [34]46
Figure 28. Petal-shaped freeze plugs in the SWATH freeze valve [34]
Figure 29. Progression of melting of the paraffin-filled wedge-shaped freeze plug
[111]. The original size of the plug is marked in red and the top surface of the
molten paraffin is shown in green48
Figure 31. Tano Retamales' SWATH experiment prior to assembly, with the solid
FLiNaK exposed [116]
Figure 33. Enthalpy-temperature phase diagram for a pure substance, adapted
from [119]53
Figure 34. The melting contour obtained at different time steps in the experiment
and in the simulation of Anggara et al. [148]60
Figure 35. Phase state and velocity fields for the 2D volume of fluid model (V-2D)
and the 2D Boussinesq model (B-2D) at two different time steps [149]. The solid
state is shown in black61
Figure 36. Phase state and velocity fields obtained with the 3D Boussinesq model
and in the experiment [149]62
Figure 37. Photos of the melting front propagation in NaNO ₃ [150]. The left wall is
heated63
Figure 38. Natural circulation loop in a harp configuration used in the Molten Salt
Reactor Program [151]. Photo courtesy of the Oak Ridge National Laboratory 111
Figure 39. Thermal convection loops NCL-15 and NCL-16 prior to operation [152].
Photo courtesy of the Oak Ridge National Laboratory113
Figure 40. In-Pile Molten-Salt Loop No. 1 in the ORR [154]. Photo courtesy of the
Oak Ridge National Laboratory114
Figure 41. In-Pile Molten Salt Loop No. 2 in the ORR [154]. Photo courtesy of the
Oak Ridge National Laboratory115
Figure 42. Forced convection loop designed by the ORNL [156]. Figure courtesy of
the Oak Ridge National Laboratory116
Figure 43. Forced convection loop FCL-2b used for heat transfer coefficient
measurements [157]. Photo courtesy of the Oak Ridge National Laboratory 118
Figure 44. ORNL's Liquid Salt Test Loop [166]. Photo courtesy of the Oak Ridge
National Laboratory122
Figure 45. ORNL's thermal convection loop [162].
Figure 46. Model of the MSNCL [86]124
Figure 47. Photo of the MSNCL [86]125
Figure 48. Photo of the DYNASTY facility [163]126

Figure 49. Model of the DYNASTY loop [163]	128
Figure 51. UW's high-temperature forced convection loop [36]	130
Figure 52. Nitrate Salt Large Heat Transfer Loop at UW [36]	131
Figure 53. Nitrate Salt Materials Loop at UW [36].	132
Figure 54. TerraPower's microloop design, adapted from [165]	134
Figure 55. Flow chart for Phase 0 of a loop build project	141
Figure 56. Flow chart for Phase A of a loop build project.	142
Figure 57. Flow chart for Phase B of a loop build project	143
Figure 58. Fragment of a Gantt chart for MS1 Phase A showing dependencies	of
tasks. Elements lying on the critical path are marked in red	146
Figure 59. ARTA grid used for guidance in risk management, adapted from [18	80].
	147
Figure 60. One of the first CFD models of the molten solar salt circulating in N	IS1.
Velocity field in the middle plane	151
Figure 61. One of the first CFD models of molten NaOH circulating in MS1.	
Temperature distribution in the middle plane with the temperature shown al	oove
390 °C and below 460 °C	152
Figure 62. MS1 with locations of all thermocouples marked.	230
Figure 63. Chosen temperature measurements taken during the loading	
procedure	231
Figure 64. Temperature measurements from all thermocouples showing the	
approaching of MS1's steady state conditions.	231
Figure 65. Salt drained from the loop after 300 h of exposure, solidified	232
Figure 66. Samples of the loop after cutting.	232

x

List of Abbreviations

2D	Two-Dimensional
3D	Three-Dimensional
CFD	Computational Fluid Dynamics
CIEMAT	Centro de Investigaciones Energéticas,
	Medioambientales y Tecnológicas
	(Center for Energy, Environmental,
	and Technological Research)
CMSR	Compact Molten Salt Reactor
CSP	Concentrated Solar Power
DN	Diametre Nominal (Nominal Diameter)
DTU	Danmarks Tekniske Universitet
	(Technical University of Denmark)
FFFER	Forced Fluoride Flow for Experimental
	Research
HTF	Heat Transfer Fluid
HTR	High Temperature Reactor
MSFR	Molten Salt Fast Reactor
MSNCL	Molten Salt Natural Circulation Loop
MSR	Molten Salt Reactor
MSRE	Molten Salt Reactor Experiment
OD	Outside Diameter
ORNL	Oak Ridge National Laboratory
ORR	Oak Ridge Research Reactor
PCM	Phase Change Material
PTFE	Polytetrafluoroethylene
R&D	Research and Development
SINAP	Shanghai Institute of Applied Physics
SWATH	Salt at WAll: Thermal excHanges
TUD	Technische Universiteit Delft (Delft
	University of Technology)
UW	The University of Wisconsin-Madison

1. Introduction

1.1. Background

Currently, the most widely used primary energy sources are oil, coal, and gas [1], all of which are associated with high greenhouse gas emissions and environmental pollution [2]. In light of the climate crisis, it is paramount that diverse clean energy sources supersede fossil fuels across the globe. Rapid reductions in greenhouse gas emissions are required now if the world is to slow down the global warming within two decades and limit it to 1.5 °C at the end of the century [3]. To mitigate the effects of the climate crisis, renewable energy sources, such as hydro, wind, and solar, should be introduced on a large scale.

Intermittent renewable energy sources cannot provide a base load and need to be supported by energy storage systems to ensure energy security [4]. Nuclear power can supply a base load where it is not possible to utilize renewable energy sources. It is, moreover, recognized by the International Energy Agency as low-emission and enabling a transition from a carbon-intensive industry to a net-zero industry [5].

Both energy storage and advanced nuclear power can take advantage of molten salts to perform their functions. Molten nitrate, chloride, and fluoride salts have been used in the energy industry due to their favorable properties [6]–[9]. These molten salts require high temperatures (up to a few hundred degrees) to remain liquid. Higher temperatures of a medium lead to the increased efficiency of an energy conversion system [10], which ultimately increases the system's sustainability. The salts boil only at temperatures higher than a thousand degrees, and remain in their liquid state under atmospheric pressure [11], which eliminates the risks inherent in pressurized systems such as steam explosions and the release of unwanted material into the environment.

Molten salts are used in innovative nuclear molten salt reactors (MSR, see Figure 1 and Figure 2) which, albeit never commercialized, have been proven to operate successfully. MSRs are a subject of research and are being developed by several companies worldwide, with an intended market entry

at the end of this decade [12]. Molten salts are used in MSRs as both coolants and fuel carriers, where the fissile elements are integral parts of the salt. The salt is circulated through a reactor core where thermal energy is produced and subsequently transferred to another medium to convert it to other forms of energy.





Another application of molten salts is concentrated solar power (CSP) plants (see Figure 3) where a molten salt is used as a heat transfer fluid (HTF) and as a thermal energy storage medium. In general, a CSP plant converts solar



Figure 2. Top view of the Molten Salt Reactor Experiment [14]. Photo courtesy of the Oak Ridge National Laboratory.



Figure 3. 110 MW molten salt tower CSP plant Crescent Dunes Solar Energy Project. Cropped photo courtesy of Amble, CC BY-SA 4.0.

energy to electricity by focusing multiple solar beams onto a receiver which heats up, and this heat can be further used to convert water into steam that moves an electric generator [15], see Figure 4. The HTF that transports the thermal energy between the receiver and the steam generator can be a molten salt, which is more economically viable than other HTFs [16].



Figure 4. Energy conversion scheme of a CSP plant, adapted from [15].

An energy storage solution can be placed between the receiver and the steam generator of a CSP plant in order to modulate the power output and release the energy when it is not produced. Storage is of the utmost importance to the transformation of the energy industry from fossil fuelbased to renewable-based energies [15], with the storage enabling a response to sudden changes in demand. The efficiency of such storage systems can reach above 90%, with the efficiency of energy conversion from heat to electricity being less than 50% [16]. Molten salt CSP plants are designed to supply a base load, similarly to coal or nuclear power plants. This is unprecedented, considering the variability of solar and wind – and molten salt CSP plants can in addition respond to fluctuating demand by releasing stored energy when economically advantageous.

Salt-based systems face a challenge due to salt's aggressive chemistry [12]; in many cases commonly used materials are not compatible with hightemperature molten salts and cannot withstand such an environment for extended periods. Control of the molten salt's flow and certain safety functions of circuits based on molten salts require the use of valves. Conventional mechanical valves that are wetted by molten salts corrode easily, and customized valves made with corrosion-resistant materials, sometimes including exotic alloys, are required in such systems. However, these valves need frequent maintenance and replacement [17], which lowers the capacity factor of CSP plants, and might be infeasible in radioactive circuits of MSRs. Leakage or inability to reopen a closed molten salt valve are amongst the common issues.

Conventional nuclear power plants utilize many heavily engineered safety features to maintain high levels of safety at all times, but the problem with the majority of them is that they rely on an external source of energy, e.g. diesel generators are used to propel emergency cooling water pumps [18], [19]. This is where MSRs are superior to widely used pressurized water reactors, as MSRs' safety is inherent in the nature of salts. The necessity of keeping salts at high temperature to maintain their liquid state is another important aspect. When the salts leak out of the reactor, they solidify at a rapid pace due to the relatively low temperature of the environment. A salt's solidification process encapsulates fission products within the salt, not allowing them to escape [12]. Advanced reactor designers aim to take full advantage of the passive safety and inherent safety features which allow for simplification of the reactor design and a considerable increase in safety [20].

To avoid the issue of a molten salt valve corroding or sticking closed, a freeze valve can be used in place of a mechanical shut-off valve [21]. Freeze valves perform a function of closing and opening a passage for molten salt from one part of a system to the other without any moving components needing to be wetted by the salt. The principle of operation is based on solidification and melting of a salt plug that is purposefully formed in a dedicated part of the piping to block flow. Coolers and heaters are placed on the outer side of the piping, and so are not influenced by a corrosive salt. In MSRs, freeze valves can be used as passive safety components which lead to a nuclear chain reaction ceasing without the use of any external source of power in case of an accident. These valves are included in designs of advanced nuclear reactors that rely on passive safety in contrast to widely used active means of ensuring safety, which can be prone to failure [22], [23].

Conceptually, a freeze valve is intended to be placed under a reactor core where fission reactions take place and above a drain tank where the fuel salt

is stored in a way preventing fission. The freeze valve's temperature should be maintained below the salt's melting point, i.e. the valve is kept closed, with the use of a cooler, e.g. an air blower. When the reactor core overheats during an accident, the amount of surplus heat would be great enough to melt the solid plug and cause the fuel salt to fall into the drain tank due to gravity, thus reaching a safe state. During a total loss of power accident when the cooler stops working, the plug would heat up and ultimately melt, resulting in a core drain. If the freeze valve is to be opened immediately to force drainage, external heaters can be used to melt the solid salt inside the valve.

Freeze valves are very beneficial when isolation of different sections of a hydraulic circuit is needed and where no other means of isolation is available. To perform maintenance on some systems, it is common practice to drain the entire circuit, which results in a long downtime. Freezing a piece of a pipe instead could significantly shorten the maintenance shutdown and related costs. Commercial freeze valve technologies already exist for waterbased systems, where liquid nitrogen is used to freeze water inside a pipe [24] (see Figure 5). Similar techniques dedicated to molten salts could be used in both MSRs and CSP plants to increase their capacity factors and economics.

Phase change, specifically melting and solidification, are some of the focal points of research and development in both MSR and CSP technologies. Due to high temperatures required by the process to maintain the salt in a liquid state, freezing is an unwanted phenomenon and freeze protection is required when, for instance, molten salt CSP storage cools down overnight [25]. Salt solidification in a shell-and-tube heat exchanger due to excessive cooling can damage the tubing and make a power plant inoperable, as the salt expands during thawing. In freeze valves and drain tanks, on the other hand, the salt is expected to solidify, and the dynamics of this process should be understood in depth to design the system in an efficient way. As safety of both the environment and the asset depends on salt phase change, it is vital that this process is mastered, which involves not only deriving physicochemical description thereof, but also experimentation and computer modelling of phase change.



Figure 5. Commercial water pipe freezing system [24].

1.2. Host company introduction

Intense research and development in the field of molten salt chemistry, thermal hydraulics, and multiphysics is being conducted at Seaborg Technologies, a Danish start-up designing the Compact Molten Salt Reactor (CMSR). Based in Copenhagen, this company has received increasing attention over the last couple of years, and has scaled up to over 100 employees. The author has been pursuing an industrial PhD with Seaborg Technologies as a host company and the Technical University of Denmark as a host university.

The CMSR is a small modular reactor with a thermal power of 250 MW which utilizes molten fluoride and hydroxide salts to produce energy [26]. The heat from the reactor core is transported by molten salts towards a steam generator. Fission happens due to the presence of a moderator in the core, i.e. material that increases the probability of neutrons being captured by uranium within the fuel. Several CMSRs are placed on a barge located in the sea which can be towed to its final destination, where high-temperature steam can be used for production of electricity, hydrogen and ammonia, or for district heating.

Seaborg's solution is a direct answer to the increasing energy needs of developing countries in Southeast Asia where renewable energy sources are not reliable. Fossil fuels are one of the cheapest energy sources but the world cannot continue building more coal power plants if the climate crisis is to be combatted. Seaborg's Power Barges intend to outcompete coal economically while delivering clean and reliable energy to countries in need, reducing energy poverty at the same time.

1.3. Research objectives

This PhD project intended to develop advanced freeze valves to be used in molten salt based systems, with the primary focus being on Seaborg's CMSR. Two designs of freeze valves were tested in thermal convection loop facilities circulating different molten salts, which were designed and built by the author, with their behavior modelled numerically. As a result of the initial research, a knowledge gap relating to the usage of computational fluid dynamics (CFD) models for modelling of salt phase change was identified and bridged by creating a benchmark for a code-to-code comparison. Additionally, certain thermophysical and transport properties of Seaborg's hydroxide salt were measured to increase the accuracy of the models. Overall research objectives of the project were to:

- Identify and assess mechanical and freeze valve design candidates for industrial development while being optimized for high performance, compatibility with molten salts, and reliability.
- Identify distinguishing features of experimental facilities circulating molten salts and develop new facilities utilizing best practices.
- Improve the understanding of salt phase change physics.
- Experimentally validate CFD models of salt phase change in a freeze valve integrated with a molten salt loop.

1.4. Outline of the thesis

This document is divided into ten chapters and content of the following chapters is summarized here.

Chapter 2 introduces the reader to basic concepts and designs of valves that are used with molten salts. Historical and ongoing research and development (R&D) of mechanical, freeze, and hybrid valves is presented and discussed in detail. Issues inherent in the use of valves in molten salt service are analyzed and the need for more research underlined.

Chapter 3 describes the physics of phase change, which is a process utilized in the operation of a freeze valve. Mathematical and numerical approaches to describing and modelling phase change between the solid and the liquid state are discussed.

Chapter 4 includes one of the author's scientific articles on a numerical benchmark for comparing capabilities of various codes for modelling salt phase change in MSRs. The scarcity of experimental validation data is stressed.

Chapter 5 analyzes past and current research on molten salt loops which are test-beds for studying of: corrosion induced by molten salts, thermalhydraulics phenomena characteristic to a flow of molten salts, and molten salt valve operation. Various loop designs are compared and their experimental objectives discussed.

In Chapter 6, the author introduces the concept of utilizing thermal convection loops for studies of natural circulation, corrosion, and operation of freeze valves at Seaborg Technologies. The process of designing loops during the author's PhD project is detailed and relevant lessons learned summarized.

The first loop built by the author and the associated research work performed are described in Chapter 7 containing an original conference paper. A comparison of experimental data with CFD simulation results of natural circulation of a molten solar salt is presented and a preliminary analysis of a simple freeze valve's operability is carried out. The author's second loop is discussed in Chapter 8, with a great focus on the operation of a novel C-shaped freeze valve for use with molten sodium hydroxide. An experimental validation of a CFD model of freezing is a topic of a journal article being part of this chapter. The influence of impurities in the salt is taken into account in modelling of the salt's properties.

Chapter 9 discusses properties of sodium hydroxide and experimental measurements thereof performed during the project, and contains a journal article on new viscosity and density correlations that should improve modelling of Seaborg's hydroxide salt and freeze valves.

The last chapter lists conclusions of this project and recommendations for more advanced studies.

2. Valves for molten salts

A systematic literature review in the field of valves available for molten salt service has not been performed and published to date. It is vital to understand the state of the art in mechanical valves and research developments of freeze valve technology, which formulates the research question of the review presented in this chapter. This chapter focuses on specific examples of valves that have been used or proposed for use in molten salt service and is not intended to be a compendium on all valves that could be used with other fluids.

2.1. Research procedure

The procedure followed to find the references used in the literature review consisted of three parts. First, the ScienceDirect bibliographic database [27] was used to find existing molten salt valve literature reviews, with three different searches utilizing the default settings of the search engine. The search was conducted on February 7, 2022. The search terms were *literature review valve nuclear*, *literature review valve*, and *literature review nuclear*. 25 of the most relevant results for each search term were screened by reading the title and only one document satisfying the initial criterion was found.

The second part of the procedure utilized the default settings of Google Scholar [28] and DTU Findit [29] search engines. The search was conducted on February 8, 2022. Three separate searches with search terms *molten salt valve, valve molten salt,* and *valve salt* were performed in Google Scholar and one search with the term *"molten salt" AND valve* in DTU Findit. The first ten most relevant results from each search in Google Scholar and all 56 results from DTU Findit were screened by title. A total of 19 articles were retrieved.

In the third part of the procedure, the articles that were retrieved were skimmed by looking for the keyword *valve*. From the 20 articles retrieved in the two previous parts of the procedure, 16 were kept. While reading these

articles, five additional sources were found as citations. The author knew about additional resources that were not linked to any of the scientific databases that were also used in the review, most importantly *moltensalt.org* [30] which contained numerous Oak Ridge National Laboratory (ORNL) documents related to the MSR Program, and Delft University of Technology's (TUD) online repository [31]. Without having previously been introduced to these resources, it was not possible to easily reach research data pertaining to molten salt valve technologies, creating a cause for concern. This could be remedied through proper indexing of research institution materials, to ensure that works from bachelor's and master's theses and technical reports are readily available to researchers.

Additionally, a Google search for molten salt valves with off-the-shelf availability was conducted to understand which commercial solutions were available. The following sections discuss the results of the analyzed references and expand on the covered topics.

2.2. Valve choice

Valves are complex components made of multiple subcomponents - some of which are in direct contact with a process fluid through static and moveable interfaces, creating weak points in the system that are prone to leakage. It is not only the internal parts of the valve that can get damaged and leak, but also the end connections of the valve that are integrated with the system's piping in multiple ways, such as via a threaded connection, compression fittings, flanges, or welds, to name a few. Ensuring leaktightness while achieving the valve's function of flow throttling, shutting off the flow, or redirecting the flow over a range of temperatures, pressures, flow rates, and sometimes for a mixture of different phases is not a trivial task. It is of utmost importance when choosing a valve for a system that the system designer is aware of all process fluid parameters and characteristics, as well as the intended function of the valve, expected lifetime, dimensions, etc. In an MSR, different valves must carry out functions such as throttling of the flow of the coolant salt to the boiler and reheater. Another function could be shutting off the flow in fill, drain, and transfer pipes of the fuel salt, blanket salt (for breeder reactors), moderator salt (for liquid-salt moderated thermal reactors), and coolant salt systems [32]. There are many different valve designs, all of which can be manufactured using different materials depending on the end user's requirements.

Both standard (off-the-shelf) and custom-made mechanical valves have been used in molten salt service, predominantly in CSP plants and in research facilities [33]–[36]. The availability of existing valve solutions depends largely on the application. Different salts' melting points can vary between 50-1000 °C [11] and their intended service temperature must always be above the melting point plus a safety margin to avoid unwanted solidification. The operational temperature and the temperature difference between the cold and hot states are usually the limiters in terms of the material choice [17]. Valves must be able to lose neither their tightness nor their alignment due to thermal expansion from the room temperature to the operational temperature.

Most valves are able to withstand extremely high pressures quite easily, even up to 700 bar and more [37]–[39]. In CSP plants and MSRs, pressure levels in molten salt circuits are much lower than in chemical synthesis plants, oil production plants, or steam generators [12], [40]–[43], therefore the pressure is not of as much importance as in, for instance, pressurized water cooled nuclear reactors [44].

Another aspect to consider is the process fluid's chemistry which can lead to corrosion. Here, corrosion is understood as an overall degradative process resulting in a loss of a material caused by reactions of the material surface exposed to the surrounding environment. The environmental aspects include chemistry, radiation, and mechanical stress, each of which can induce and enhance corrosion. Depending on the corrosivity of the process fluid, the compatibility of the fluid with the materials building the valve can be quite limited. Special surface treatments and finishes, heat treatments, or the use of exotic materials may be required for specific applications [45]–[47]. Alternatively, the chemistry of the process fluid must be changed so that it is less corrosive with respect to the materials the valve is made of, for example by adding a reducing agent to the fluid [48]. The corrosion can result in cracks or plugs of the piping or deterioration of the material's properties. Additionally, metallic parts deprived of their protective oxide layers or other coatings, when in direct contact with each other at high

temperature and for a prolonged duration, can locally fuse and cause the valve's sealing surfaces to stick closed [17].

In a nuclear environment, irradiation damage must be taken into account in the valve choice and in the establishment of maintenance and replacement schedules. Any material that is exposed to high-energy radiation suffers damage in the form of lattice site displacements of atoms which can lead to element migration, creation of crevices, or embrittlement, all potentially resulting in cracks and loss of integrity [49]. It is noteworthy that corrosion and irradiation damage can be either enhancing or canceling each other to some extent [50], [51]. There is a research gap concerning the effects of irradiation on materials for new advanced nuclear reactors wetted by molten salts.

2.3. Off-the-shelf valves

There are multiple valve designs that can perform similar functions. To name a few for regulating (throttling) the flow, one can think of ball, needle, butterfly, plug, diaphragm, and globe valves – named after a feature of the mechanism that is in direct contact with the process fluid which is used for flow control (valve member), or after the historical shape of the valve body. In general, the working principle of a valve is that two surfaces are pressed together to form a tight seal. To study the behavior of valves for molten salt service, it is necessary to understand what the particular parts of the valve assembly are comprised of, as well as what materials they are made of and why. This will be discussed using the example of a stem-guided globe valve in two configurations: without (Figure 6) and with a bellows seal (Figure 7).



Figure 6. Stem-guided globe valve, adapted from [52].



Figure 7. Bellows globe valve, adapted from [52].

A globe valve utilizes a plug or a disc on a stem that is moved up and down in order to increase or reduce the size of the opening of a mating stationary ring seat, i.e. to throttle the flow. The seat is a part of the valve body, whereas the stem penetrates what is called a bonnet, which is a component whose function is to provide a leak-proof closure of the valve body. This is achieved with the use of a sealing mechanism called a packing that allows the stem to move and is responsible for leak prevention at the same time. The packing material is wearable and needs replacing during maintenance. Bellows valves use a packless design, where the bellows seal is a pleated metal tube connected to the stem and the bonnet. The folds allow the bellows to squeeze and straighten out with the stem's motion. The bellows creates an impenetrable seal, and in case of rupture, a standard packing placed above the bellows can maintain the valve's integrity. Adding a second bellows around the first one further increases robustness and can be used for balancing the pressure against the first seal with another fluid or for maintaining desired temperature conditions. Replacing a damaged bellows is an expensive and time-consuming process, however, the bellows seem to be more robust in the corrosive environment of molten salts than the packing rings.

There are alternatives to valves, where flow control can be achieved without any kind of a valve wetted by the primary process fluid. This can be achieved with the use of a *balanced pressure barometric leg* [32], in which the controlled differential gas pressure between the source of a fluid and the receiving reservoir allows for the fluid transfer. However, this method introduces limitations in the quantity of fluid that can be moved in each transfer, which is not a continuous process. Such a barometric leg cannot be used for large-scale industrial processes which are of main interest in the energy industry.

For off-the-shelf valve procurement for molten salt service, there are a small number of manufacturers offering different solutions marketed as molten salt valves. Table 1 summarizes some of the characteristics of their valves. There are also valves offered by the same or other manufacturers which are not intended for molten salt service. These valves could, in fact, be used after the appropriate materials selection process has been considered that requires a detailed customization. The necessity of needing to customize the valve excludes it from the list of entirely off-the-shelf solutions.

Company	Valve type	Size	Materials	Maximum
	or location			temp.
Guichon	Tank	DN* 20 –	Carbon steel,	750 °C
Valves	bottom	DN 500	stainless steel,	
[53] <i>,</i> now	outlet	(OD 26.7	nickel alloys,	
part of		mm –	titanium, tantalum,	
Valco		508.0	zirconium body	
Group [54]		mm)		
	In-line	DN 15 –		850 °C
	globe,	DN 915		
	piston			
	type Y			
	Gate and	DN 20 –		890 °C
	slide	DN 1400		
Emerson	Triple	DN 80 –	All-metal	450 °C
[55]	Offset,	DN 2800	construction,	
	emergency		braided graphite	
	shutoff,		bearing protectors,	
	switching		two-piece graphite	
			packing gland,	
			multi-layered	
			duplex and graphite	
			seal rings	
Samson	Single-	DN 15 –	Stainless steel	400 °C,
[56]	seated	DN 500	body,	580 °C
	globe		metal, carbide	with the
			metal, ceramic,	bellows
			PTFE, PEEK seat-	seal
			plug seal,	
			adjustable packing	
			with a zinc-	
			impregnated	
		D N 1 -	coating	
GAP	Y and T	DN 15 -	Stainless steel body	680 °C
Valves [57]	globe	DN 600	including alloy	
			316H	

Table 1. Characteristics of chosen off-the-shelf molten salt valves.

*DN stands for Nominal Diameter, a dimensionless number designating size for reference purposes, which is an indication of a diameter of a pipe [58]

The detailed design of the above molten salt valves is not available. Judging by available information, the vast majority are intended for CSP plants, and more specifically, for nitrate salt service. Only Guichon Valves seems to provide valves that could be used with fluoride and chloride salts proposed for MSRs, since the materials selection and the maximum temperature are more suitable. Graphite packings are chosen due to their very good performance, however, frequent maintenance due to corrosion thereof seems unavoidable.

The seemingly sparse choice of available valves is not surprising. Commercial MSRs are non-existent and the number of CSP plants utilizing molten salts is still quite limited, which translates into a lack of incentives for valve manufacturers to provide specialized molten salt valves due to low demand. In light of these observations, custom-made valves will be the only possibility for the coming years. Even now, customization of a non-stocked component might take up to 40 weeks, whereas establishment of a dedicated mass-production process would require more resources. However, mechanical valves for molten salt service exist in a wide range of dimensions. The agreeable material or design has not yet been found.

2.4. Materials lifetime

As valves have moving parts that interface with both the process fluid and the atmosphere outside of the associated piping system, the most sensitive part of a valve is its sealing system. It is predominantly the packing material that wears and corrodes first during a valve's lifetime. Usually, off-the-shelf valves used in nitrate salt service utilize long stems and graphite packing. Elongating the stem allows for lowering of the temperature and the addition of more packing material, thus prolonging the life of the valve; graphite is relatively temperature- and corrosion-resistant and is widely used in the nuclear industry. Polytetrafluoroethylene (PTFE) is another standard material with very good chemical resistance used in valve packings, however, it has an upper temperature limit of 315 °C [59] and cannot withstand radiation.

Incorporation of a bellows seal avoids the issue with leaking packings, but appears to be limited to smaller valves [36]. Bellows might work very well
with water or corrosive fluids; nevertheless, a phase change material (PCM) induces issues not characteristic to materials always being liquid during operation. The bellows cannot be moved once salt freezes in its folds, otherwise the stress concentration is too high and the bellows can rupture. Maintaining of a valve's temperature above the melting point is required.

To date, the most widely used molten salt in the industrial sector has been solar salt, which is a mixture of 60 wt% NaNO₃ and 40 wt% KNO₃. There are other nitrate-based salts used or proposed for use in CSP plants which are also sometimes referred to as solar salts, but these other salt mixtures have their own commercial names and different compositions. Solar salt is corrosive both to structural materials of piping that is being used and to graphite packing in valves. CSP plant owners have reported a need for maintenance of an entire molten salt circuit due to leakages [60]–[62]. Frequent maintenance lowers the capacity factor of a facility and is an unwanted situation. There is currently no solution to this issue.

Valves used with nitrate salts will not necessarily be compatible with halide salts. Nitrate salts decompose at temperatures higher than 550 °C [63], which limits their high-temperature applications and therefore allows for usage of less exotic valves. By comparison, halide salts could be operated at up to 1000 °C [64], which makes for a large difference in the behavior of valve materials. Besides, corrosivity of halide salts is much higher than of nitrate salts [65] and increases further with a temperature rise [66]. Internal parts of valves for the use in nitrate salt service are covered with a protective oxide layer which would be deteriorated by halide salts, leaving the metal surface subject to corrosion [17]. Special corrosion resistant materials are required to extend the lifetime of valves used with halide salts.

Since the 1970s, there have been many developments in graphite- and metal-based corrosion-resistant high-temperature seals [17]. However, no demonstration has been made for usage with molten salts based on fluorides or chlorides. In practice, valves are tested for leak-tightness with water or gas. The use of surrogate fluids is a known and widely accepted practice in industry, where high operating temperatures or corrosivity of process fluids requires another fluid with similar thermophysical characteristics to be used for tests, prior to building a prototypic device utilizing the fluid of interest. Non-dimensional analysis and scaling laws are used to translate results obtained with the surrogate fluids and scaled facilities. Such an approach yields accurate results in thermal hydraulics analyses, but it is chemistry of a system that plays a pivotal role in a material's behavior – and in an analysis of a performance and lifetime of a component, the use of a surrogate fluid makes little sense. As chemistry changes with temperature, it is erroneous to extrapolate results of the analysis from one temperature level to another without taking reaction kinetics and thermodynamics into account. Therefore, it is an imperative that a component is eventually tested under operational conditions with the process fluid that is intended for the operation. Additional co-design and industrial research is needed before a truly MSR-compatible mechanical valve can be commercialized, especially with taking into account how many different MSR designs and molten salts are being developed worldwide.

2.5. Historical developments: mechanical valves

2.5.1. ORNL in the 20th century

A considerable interest in molten salt technologies had existed at the ORNL since the 1950s. Developers of MSRs were fully aware that large-scale power plants would depend heavily on mechanical components like valves, pumps, and mechanical joints [67]. They recommended that their performance should be adequately demonstrated. As a result, an ORNL team developed a valve to be used with a fissile fuel salt [17].

From the beginning of the work on the high-temperature mechanical valves for MSRs, it was clear that it was not initially feasible to consider mechanical valves as being able to fulfil requirements of long-term leak-tightness and operability. A double bellows seal valve made of Inconel 600, developed at the ORNL, experienced fusion of the valve's seat and plug due to their long-duration contact at above 650 °C [17]. The majority of off-the-shelf isolation valves originally used the same or similar materials for the seat and the plug – and still continue to do so, leaving no possibility to avoid the issue of cold welding without extra customization of the seat and the plug.

A subsequent valve member and seat material testing program showed that molybdenum worked well, not experiencing fusion, with copper and tungsten in high-temperature molten salts. Composites of titanium and tungsten carbides mixed with nickel, belonging to the family of materials called cermets (ceramic-metal composites), also proved satisfactory. The testing campaign concluded with five valves having seats and plugs made of different materials being investigated with over 7000 h of accumulated experience. The valve's plug was a sphere that fit into a mating seat, while a stem penetrated a bellows seal on a gas side of the bellows. The researchers concluded that in such valves, cermet seats and poppets (assemblies of discs and stems) of valves are the ones yielding the lowest leakage (2 cm³/h) with a concurrent absence of high-temperature bonding. No further research has been conducted at the ORNL for a few decades.

2.5.2. John Hopkins University

The first official work on mechanical valves for nuclear molten salts after the closure of the ORNL's MSR program began in 2010 with the US Department of Energy's over 1.1 million dollar funding received by Johns Hopkins University [68]. The research intended to develop carbide coatings for nickel alloys, graphite, and carbon composites for use in fluoride salt valves [69]. Unfortunately, the project failed to yield satisfying results. It is noteworthy that there has been development in materials science research heavily focused on characterization of candidate materials for use in MSRs exposed to various molten salts [70]–[74]. The results of the research and work of many other scientists constitute the basis for the development of molten salt mechanical valves and deserve acknowledgment.

2.5.3. ORNL today

In 2019, the ORNL published their plans for testing a double bellows sealed Inconel 600 valve in their Liquid Salt Test Loop circulating FLiNaK salt [17]. The valve design was chosen as a result of a systematic assessment of various existing valves. This valve was not a standard component, however, it was relatively easy to produce through customization of an existing valve. The ORNL team commented that "with enough commercial interest, such a valve would eventually be available off the shelf" – which might be true but it is impossible to predict when the availability increase is observed.

2.5.4. Sandia National Labs

Sandia National Laboratories appear to be continually at the forefront of molten salt component testing for use in CSP plants. Bradshaw revealed in 1986 [75] that multiple packings and sealing materials for solar salt were investigated at 288 °C, 400 °C, and 565 °C and included PTFE, graphite, asbestos, aramid, glass and ceramic fibers, perfluoroelastomers, and boron nitride. Some of these materials were resistant to corrosion at the lowest temperature (especially PTFE and graphite), but none were able to resist higher temperatures. The author cites a previous work [76] suggesting the use of aluminum and nickel at 400 °C, but the metallic packings were not tested further and are not presently in common use, likely due to galvanic corrosion. The other packings deteriorated rapidly at 400 °C. The researchers underlined that it is not only chemical compatibility that is a deciding factor in whether a packing material is suitable for molten salt service; it is also preferable friction and wear properties, as well as physical properties which allow sealing stress to be retained long-term.

Drawing from materials selection research, Sandia tested two molten salt pumps and ten valves in two loops at 565 °C and 285 °C at the National Solar Thermal Test Facility between 1988 and 1990, with the accumulated experience of 6700 h and 2500 h respectively [35], and with the usage of solar salt. The valves were of standard design, with standard packing gland arrangements. One hot- and one cold-salt valve had a bellows seal with a secondary packing seal, and the packings were composed of alternating wire-reinforced graphite braid and glass-reinforced PTFE rings. Hot-salt valves utilized long stems to lower the packing's temperature. At the same time, all valves had their packing glands insulated and electrically heated above the salt's liquidus point. Valve tests investigated the operability of the valves and the lifetime of three different kinds of stem seals: a linear packing seal for pneumatically actuated valves, a rotary packing seal for manual handwheels, and a bellows seal.

The linear packing seals experienced several complete failures. Even the smallest amount of leakage into the packing gland was devastating, as the

oxidizing nature of the salt propagated the damage and quickly led to complete packing failure. This was deemed unacceptable in a power plant and a search for alternative materials was conducted. Aluminum, fiberglass, and polybenzimidazole fibers were investigated and the latter two proved promising when combined with PTFE rings. According to the researchers, small leaks that developed did not progress rapidly and were slowed down by tightening the packing gland. Despite this, leakages of an order of 10 cm³/h were unavoidable but could be effectively managed. Instrumentation, heaters, and insulation required protection to avoid damage by salt leaks. Such a solution does not seem reasonable by modern-day standards as process fluid must be constantly replenished and leaks collected and treated, which cannot be performed in a nuclear power plant in the same way as in solar plants.

The test of the rotary packing seal was successful, with the valve operating for 3300 h and the packing never requiring replacement. The valve that was equipped with such a seal was a butterfly control valve, which did leak, however, at its flanged connections to the piping. All other valves were welded in place instead. Therefore, the use of a relatively inexpensive waferstyle butterfly valve was discouraged due to a high potential for leaks resulting from thermal cycling. A more recent numerical study [77] performed for Sandia proved that valve packing lifetime increases when the packing stress is added by stem rotation rather than translation.

The bellows seal valve failed after 700 h of operation after the bellows broke and the secondary graphite packing was damaged. Reasons for the bellows' rupture were not known. Its temperature was monitored and maintained above the liquidus point, removing the expectation of freezing of salt in the folds. An inadvertent actuation of the valve was speculated to be the reason. Whatever the mode of failure, the bellows could not be as easily and cheaply replaced as the packing, and as such the packed valves were chosen to be the main R&D focus at Sandia.

The operational principle of an isolation valve differs from a throttling valve like the ones described above; it is either in a fully open or a fully closed position. This allows for a design feature called *backseating*. The Sandia team used backseated shut-off valves which had a second seat below the packing gland that isolated the valve packing from the molten salt when the

valve was open [35]. This allowed for reduction of the leakage risk in valves with packings.

The researchers identified another possible leakage location, namely at the bonnet flanges. In this case, a valve's feature of being made of multiple subcomponents increased the risk of failure. They noted that careful torquing of the bolts at the operating temperature stopped the leaks. This finding stresses the importance of not only an adequate choice of valve materials and their assembly, but also of the specific procedures a valve must be subjected to once it is placed in service.

Recently, Sandia has started testing two alternative valve designs: one using metal O-rings in the packing, and the other using a linear electric actuator immersed in salt which does not need external seals [59]. The latter seems promising, however, one can think of multiple novel issues that will need to be resolved, e.g. problems with internal leaks, actuator blockage, current induction in the salt, etc. Since the vast majority of valves are actuated from the outside and utilize external seals, much development is needed to commercialize such a product. Nonetheless, Sandia's scientific output provides valuable advice for valve producers.

2.5.5. Abengoa

Additional loops with mechanical valves have been built by Abengoa in Spain. Prieto et al. describe a molten salt solar thermal pilot facility that was brought into operation in 2009 [78]. Here, the solar salt loop was equipped with electrically actuated globe valves. Two issues were present, namely the electrical actuators inserted a voltage signal into the system, resulting in equipment damage, and valve gaskets leaked. Whereas the latter has already been described in this chapter, the former issue has not been encountered before in other tests. It is worth noting that molten salts are ionic liquids – a molten salt's compounds are ionically bound and the salt is electrically conductive (up to 10^6 times more than water [11], [79], [80]). This results in an increased potential for an electromagnetic influence of electrical components on a salt's behavior, and vice versa.

This influence can be either negative or positive if intended to be so. By 1983 it was proven that an electromagnetic field has a non-negligible effect on the molten salt flow [81]. Due to the molten salt's ionic nature, it might be viable to use electromagnetic valves for flow control, similar to valves proposed for molten metals in the casting process [82], [83]. Up to now, no major developments in this area have been observed.

2.5.6. CIEMAT

To date, valve manufacturers have focused primarily on developing bellowsfree valves for molten salt service, which require a new packing material. Rodríguez-García et al. [84] conducted packing life tests of various valves with solar salt in BES-I and BES-II facilities. They showed that bellows-free valves have a high failure rate due to packing damage.

The same group of researchers from CIEMAT [85] pointed out that heat tracing and its integration with piping and valves is one of the most important issues that should be taken into consideration in the design phase of a facility. A valve, whatever the type, cannot withstand multiple thermal cycles or being frozen for a prolonged time, therefore it must be kept above the melting point of the salt - ideally with a uniform temperature distribution. This can be achieved only with the use of heat tracing, e.g. external heaters wrapped around the component, which limits the possible geometrical and dimensional production configurations of a valve. Because of their greater thermal inertia, valves should be equipped with heaters that are controlled independently from their associated piping, with the use of separate temperature sensors. The sensor position should also be selected carefully. For small valves the sensor should be located where the lowest temperature is expected, and in large valves more sensors at the top and bottom parts of the valve should be installed. Such practical considerations are usually omitted in publications, yet they play a pivotal role in the proper operation of molten salt valves and in a test result analysis.

2.5.7. Bhabha Atomic Research Centre

In India, researchers from the Bhabha Atomic Research Centre in Mumbai have built the Molten Salt Natural Circulation Loop (MSNCL) and installed two bellows seal stainless steel 316 control valves in its drain lines [86]. The valves are made for 21.3 mm OD pipes and are rated for 500 °C. They have their own heating jackets, and the temperature of the surface of the valves is measured by thermocouples brazed on their outside walls. Solar salt is being used and the facility is expected to use different fluoride salts in the future. To date, no account of issues encountered with the valves has been provided and the facility appears to be working to satisfaction [87], corroborating bellows seal valves' superiority over valves based on packings.

2.5.8. University of Wisconsin-Madison

The University of Wisconsin-Madison (UW) has conducted an extensive experimental work on molten fluoride, chloride, and nitrate salts [36]. Their Nitrate Salt Large Heat Transfer Loop had a Vogt throttling valve, which was a stainless steel 316 forged globe valve sized for a 60.33 mm OD pipe socket welded to the loop piping. Its bonnet was elongated (see Figure 8) and gaskets were made of Thermiculite 835 (vermiculite reinforced with a stainless steel core). The stem packing was made of glass-filled PTFE, and its temperature was kept below the temperature limit for PTFE through the use of a separate heater. No issues with the valve have been reported. A Swagelok bellows sealed stainless steel valve with compression fittings for 12.7 mm OD tubing was also placed in a transfer line that was used sporadically. The valve was heat traced and no issues with it have been experienced either.



Figure 8. Molten salt valve installed in the Nitrate Salt Large Heat Transfer Loop [36].

A lack of encountered issues may derive from the fact that solar salt was used in the two loops described above and good practice was used in the valve assembly. However, the scientists agree that "the design of (...) valves (...) need to be studied in more depth for commercial scale systems" [36]. Few other research groups have inexplicitly provided a record of mechanical valve usage in molten salt loop facilities [88], [89]. Experimenters have not yet provided detailed reports of their work with salts other than nitrates in their molten salt loops or mechanical valve test rigs. As this kind of research is more applied and industrial than basic and academic, some level of secrecy is to be expected – which slows down, if not curbs, any potential collaborative development or improvement of new concepts.

2.6. Historical developments: freeze valves

Standard, mechanical valves were not used in one of the first molten salt reactors ever built, the Molten Salt Reactor Experiment (MSRE), due to wellknown but unsolved issues with leaks, corrosion, and valve alignment [17]. Instead, all twelve valves of the MSRE in contact with the molten salt were freeze valves of almost the same design [90]. Before the freeze valves were incorporated into the MSRE circuits, a design study had been completed that investigated three different heating technologies for the freeze valve [91]: a direct resistance heater (Figure 9), an induction heater (Figure 10), and a radiant heater (called a *clamp-on Calrod* heater, Figure 11). The valves were tested in a vertical rig (see Figure 12) where the salt level was controlled with the use of helium pressure. The salt could be drained to a sump tank and sent up to a head tank, and salt level was indicated with contact probes sending a signal to turn on an indicator light. The valves were tested with a uranium- and thorium-containing fluoride salt. The valves were cooled by a gas jet stream directed at the valve body, i.e. the flattened section in the middle of the pipe, and each valve underwent 100 cycles of freezing and melting with no failures recorded.

Eventually, the Calrod-heated valve was chosen for the MSRE due to its simplicity as it did not require cooling of an expensive high-frequency generator (like in the case of the induction-heated valve), and was less bulky than the resistance-heated valve. In the radiant heater valve, each flat side of the valve body was equipped with a 1 kW heater bent into a *W* shape that was clamped to the freeze valve using three sets of metal strips. Three thermocouples were welded to the external walls of the valve: in the center of the flat section, and $1\frac{1}{2}$ " (38.1 mm) higher and lower. The average melting time was 3 min with a 1.6 kW input, and an air flow of 8 scfm (12.8 Nm³/h, i.e. evaluated at 0 °C and at 101.325 kPa) was required to maintain the plug frozen.



Figure 9. Resistance-heated freeze valve tested at the ORNL [91]. Photo courtesy of the Oak Ridge National Laboratory.



Figure 10. Induction-heated freeze valve tested at the ORNL [91]. Photo courtesy of the Oak Ridge National Laboratory.



Figure 11. Calrod-heated freeze valve tested at the ORNL [91]. Photo courtesy of the Oak Ridge National Laboratory.



Figure 12. ORNL's freeze valve test rig [91]. Photo courtesy of the Oak Ridge National Laboratory.

After performing successfully in the test rig, the Calrod-heated valve was tested in the MSRE Engineering Test Loop built for testing prototypic components of the MSRE [92]. Two identical valves were mounted horizontally and equipped with surge pots for salt level control (see Figure 13 and Figure 14); these two characteristics ensured that there was always a sufficient quantity of salt in the freeze valve to create a leak tight plug when needed. Two 1 kW Calrod heaters were wound spirally on the flat valve sections (see Figure 15) to avoid small bend radii introduced in the original test valve and to provide better air flow [91]. The valve was operated with FLiBe salt (Li₂BeF₄) and went through 40 cycles. The air flow to maintain the plug was around 3.5 scfm (5.6 Nm³/h), and 6-7 scfm (9.6-11.2 Nm³/h) was needed to form it. The valve's operation was deemed successful and the valve was recommended for use in the MSRE.



Figure 13. Freeze valve design used in the MSRE Engineering Test Loop [91], [93]. Figure courtesy of the Oak Ridge National Laboratory.



Figure 14. Example of a horizontal freeze valve assembly [94]. Photo courtesy of the Oak Ridge National Laboratory.



Figure 15. Freeze valve used in the MSRE Engineering Test Loop [95]. Photo courtesy of the Oak Ridge National Laboratory.

Eleven of the twelve MSRE freeze valves were aligned horizontally, except for FV-103 in the fuel salt drain line that was tilted approximately 3° to facilitate reactor core draining. Also, not all of the valves had surge pots like described earlier. Each freeze valve differed slightly in design depending on its function and location in the system, and each temperature setpoint for the cooling gas and heater was different and required calibration in the field, which points to the freeze valve's design not being universal.

The freeze valves involved in the draining and filling system were located as indicated in Figure 17. The main drain valve, FV-103, would open within 9-11 min after an emergency drain signal, and the fuel salt loop would drain completely within another 9-11 min to both drain tanks through normally open FV-105 and FV-106 on an emergency drain [90]. This time could go up to 41 min, depending on which salt and gas valves were open, and that longer time was still considered acceptable.

The freeze valves had three modes of operation: deep-frozen, frozen, and thawed, with an increasing temperature setpoint controlled by the heaters. Either of the states could be achieved by a control action such as a hand switch. As easy as it seems, each valve had six control modules, resulting in 144 lamps indicating an "alarm" or a normal state. The light bulbs were frequently failing and the operators had difficulty in controlling the freeze valves manually [90] – which should have been predicted before the experiment started, given the multitude of controls and complexity of operation.

Furthermore, the name *freeze valve* can be misleading. Semantically, a valve is understood as a single component built of multiple smaller parts that all take part in executing a certain function. A freeze valve's function, on the other hand, is achieved with the help of a few separate components or even entire systems, whose functions can be either cooling or heating of the valve's surface, as well as of its internals. In some circles freeze valves are referred to as *freeze plugs*, but this name describes only the result of one of the freeze valve operations, i.e. a solid salt plug located within the freeze valve's body, and does not acknowledge the complexity of the device. The reader should be aware that the freeze valves, despite the ambition of the MSR designers to label them as inherently passive and simple safety



Figure 16. MSRE freeze valve with an air jacket before assembling heaters and cooling tubes [92]. Photo courtesy of the Oak Ridge National Laboratory.



Figure 17. Location of freeze valves in the MSRE systems [90]. FFT is the fuel flush tank used for cleaning of the MSRE fuel salt loop, and FD-1 and FD-2 are the fuel drain tanks. Figure courtesy of the Oak Ridge National Laboratory.

features, are highly engineered devices. Execution of nuclear safety functions through freeze valves depends on the proper operation of multiple systems. This means that the failure or spurious operation of the freeze valve is associated with a higher risk than if it was for a truly individual component [96]. In fact, shutdown safety procedures for the MSRE relied completely on the correct operation of the freeze valve systems, as the reactor's three control rods were not able to insert enough negative reactivity to scram (shut down) the reactor like in the case of other reactors. The control rods were used only to control the temperature of the fuel salt; the subcriticality of the reactor was achieved by draining the reactor core

through the freeze valve. This would be a significant safety concern today, as an accident where the fuel salt stays in the reactor core could jeopardize the integrity of the reactor [92].

Moreover, a freeze valve does not act with the dynamics of a mechanical valve; its response is very slow, which needs to be taken into account in the design of the entire system based on a freeze valve. Mechanical valves are able to close, open, or regulate the flow within a time of less than a second from the time they receive a signal initiating the movement [97]. This swiftness allows for more accurate control of the process and is heavily relied upon in industries requiring precision. On top of that, a freeze valve cannot be used for throttling the flow, as its state can only be open or closed. Mechanical valves can change the flow velocity in a certain part of a system with ease [98], whereas in systems not utilizing mechanical valves this could be done only for the entirety of the system by regulating the speed of a pump [99].

Another safety concern with respect to spurious operations of a freeze valve is an unanticipated thaw of a freeze valve in a drain line while, at the same time, drain tanks are not being cooled. This would result in an unacceptable temperature increase [92]. Additionally, operation-wise, refilling the fuel salt loop after a (spurious) draining is a long process that should be avoided [96], especially in commercial power plants.

Guymon, in the review of the MSRE systems and components performance [90], summed up the MSRE freeze valves as having "a good record of satisfactory performance". Chisholm, however, skeptically underlines that a detailed review of the ORNL documentation points out a couple of failures and incidents that do not indicate satisfactory operation [96]; e.g. the main freeze valve FV-103 underwent a complete failure briefly mentioned in the same report of Guymon. Moreover, FV-105 failed during the last day of operation of the MSRE [93] due to the stress introduced during thermal expansion of a material welded to the valve's external wall, which may raise suspicion that the termination of the MSRE had not initially been scheduled to take place on that day.

The expected lifetime of the MSRE freeze valves was limited by the stress produced in thermal cycling during the freeze-thaw operation. The ORNL

researchers emphasized that this issue must be studied, were the freeze valves to be used in a full-scale MSR power plant. With no other positive evidence, it is wise to take the overly optimistic ORNL final reports with a grain of salt, as more research in freeze valve technology is needed.

After the US MSR Program was stopped, work on freeze valves for MSRs was not continued until the early 2000s. The only other mentions of phase change utilizing valves from the last century were found in a patent search which revealed that in 1971, a company called Okano Valve submitted an application for a freeze seal sodium valve in the UK [100]. This design would not be interpreted as a freeze valve by modern standards because the principle of the invention was a frozen *seal* in a mechanical valve for molten sodium service; the seal being a mechanism preventing leakage rather than controlling the process fluid. Nonetheless, it is worth mentioning as a similar approach could be taken with present day mechanical valves, where issues with packing damage remain unsolved. In the patent, the lowermost packing ring was made of an intricate configuration of fibers that would make the sodium freeze in the ring and keep it plugged so that no further leakage was possible, while allowing for movement of the stem. The packing would be made of a metallic material such as nickel or aluminum.

Another worldwide patent from 1999 [101] – the only patent found for a *freeze valve*, talks about a tube or a plurality of conduits with the liquid inside cooled by a heat sink. The frozen liquid would be remelted with the use of either electric resistors or a laser beam. The volumes of the frozen plugs would be lower than 1 mm³, which makes the freezing and melting process incomparably faster than in the MSRE. That freeze valve was intended to be used in liquid analyzers in clinical chemistry, which is a notably different environment from a nuclear reactor, and is not relevant for further discussion.

2.7. Historical developments: hybrid valves

Before the MSR research program at the ORNL was shut down indefinitely, one of the program's goals was to revive studies on molten salt valves. Worth discussing is a concept developed at that time which involved a combination of a mechanical valve with a freeze valve where only a small volume between the valve seat and poppet (which were not in contact with each other) solidified, rather than the entire volume of the pipe. The avoidance of direct contact between the moveable sealant parts of the mechanical valve eradicated the problem of the valve becoming permanently stuck in a closed position.

The hybrid valve design proposed for use in the never-built Molten Salt Reactor Demonstration Plant was a bellows seal valve (see Figure 18). In order to close the valve, a poppet was lowered to nearly touch the seat, and a cooling fluid was circulated through the poppet, which resulted in the creation of a solid sealant ring of salt between the two parts [102]. To open the valve, the fluid inside the poppet was heated and the salt ring was melted, after which the poppet could be withdrawn. The cycling was controlled by an electrical actuator, and a smaller volume of frozen salt resulted in a shorter response time of the valve. The technology, however, has not been developed further since 1972 and research on the design remains inactive.



Figure 18. Hybrid drain valve intended for use in the Molten Salt Reactor Demonstration Plant [102]. Figure courtesy of the Oak Ridge National Laboratory.

2.8. Freeze valve research today

Today, with the renaissance of MSRs, freeze valves are investigated all over the world and face various problems related to design. To begin with, Shanghai Institute of Applied Physics (SINAP) of the Chinese Academy of Sciences has developed molten salt loops, some of which have been equipped with freeze valves. The "FLiNaK loop" had a valve that resembled the MSRE design in having a flattened section. The researchers encountered a problem with the freeze valve operation when, during the loop commissioning, the freeze valve's body cracked [103]. The salt was not melted and was not kept at a high enough temperature at both ends of the valve, which caused a pressure increase due to the salt expansion during thawing in the center of the valve. The solution to this problem was to install additional heaters on both ends of the freeze valve.

Li et al. [89], in order to improve on SINAP's MSRE-inspired freeze valve design, suggest adding a *passive mechanical device* to the freeze valve assembly which would activate upon a loss of power accident and aid with thawing of the salt plug. Since the freeze valve is normally not insulated and loses heat through free convection to the environment, this loss should be minimized in order to melt the freeze plug faster in an accident scenario. By using a sliding multilayer metal foil (which is an insulating material) that moves downwards to cover the non-insulated freeze valve section, the melting process can be accelerated. No consideration has been given to how this mechanism based on gravity should be designed or implemented.

TUD is known for popularizing and performing numerical and experimental research on freeze valves and phase change, especially within the framework of projects SAMOFAR [104] and SAMOSAFER [105] supported by the European Commission, focusing on the design of the Molten Salt Fast Reactor (MSFR). Over the past decade, numerous bachelor's and master's theses have been produced, and one PhD project has focused on modelling and experimentation with melting and solidification of water and salts.

The first work was done in 2016 by Koks [106] who investigated the melting behavior of a freeze plug in the MSFR. A simple, vertical, cylindrical freeze valve geometry was upgraded with a metallic holder so that melting of the plug could take place from both the top and the sides to decrease the reactor

draining time. An exploratory study was conducted with COMSOL and confirmed that the draining time would be lower than the maximal allowed drainage time of the MSFR. While the increase of the heat transfer rate towards the freeze valve can in principle be achieved with metallic inserts, the practical side of this solution requires more exploration.

Another COMSOL model of a melting problem was created by Swaroop later in 2016 [107], using the lid driven cavity geometry [108] to take forced convection into account. Designers of passive freeze valves usually wish for the heat of the fuel salt above the freeze plug to melt the plug open – also in scenarios where the fission reactions in the reactor core are brought to a halt with, for example, shutdown rods, and only a small portion of the initial power produced, known as decay heat, is present and decreasing. Swaroop concluded that the melting of the simple MSFR freeze plug using the decay heat of the fuel salt only is not feasible within a reasonable timeframe. A suggestion was made to utilize a thermal expansion based valve instead. Such a valve contains a metal cylinder made of a material with a high thermal expansion coefficient that pushes out a rod located inside the valve body while expanding, resulting in opening a passage through the valve. This idea is worth investigating further, and similar valves already exist and are used in automotive engine systems [109].

The simple freeze plug was upgraded to a *grate*, i.e. the freeze valve pipe was equipped with multiple plugs in place of one (see Figure 19), in Makkinje's study [110]. Results of COMSOL and Matlab calculations indicated that using multiple plugs sped up the melting process by decreasing the size of the plug and utilizing the thermal conductivity of the metal that forms the grate. A more detailed numerical research was undertook using this concept by Tiberga et al. [22], following a master's thesis work of Shafer [111].

Shafer evaluated the feasibility of the grate with multiple plugs *in situ*. COMSOL-based simulations showed that a simple, single plug would melt within the MSFR's 600 s limit only if it was placed 10 cm below the reactor core (due to the high enough heat transfer rate at that location). This is not viable because of temperature and velocity fluctuations that would affect the state of the freeze plug during normal operations. A heating ring design,



Figure 19. Cut of the model of the freeze plug grate with seven freeze plugs [110].



Figure 20. Decay heat design of the MSFR freeze valve studied by Shafer [111].

made of another metal conducting the heat faster than the material the drain pipe is made of (see Figure 20 to the right), was deemed less reliable due to a thin frozen layer located on top of the metal grate that prevented the heat transfer through the top of the plate, even though the sides of the

plugs melted. The single plug design (left in Figure 20) allowed for a minimum 35% faster draining time than the multiple plug design.

The idea of introducing a dissimilar material to the freeze valve assembly to enhance the heat transfer within the freeze valve was studied experimentally for the first time by Giraud et al. [34] in a facility called the Forced Fluoride Flow for Experimental Research (FFFER) and later in a facility called Salt at WAII: Thermal excHanges (SWATH). In the FFFER loop, approx. 50 I of the FLiNaK salt was pumped, and a system constituted by a ball valve and a horizontal freeze valve was used for the separation of the loop from its drain tank. The freeze valve was made of four cylindrical plugs and was cooled by gas tubes circulating the cold gas around the assembly. The freeze valve was not only equipped with a cooled copper ring for speeding up the heat conduction (see Figure 21); it also had a large steel mass to store the thermal energy that could be transferred to the frozen salt after the power loss. The equilibrium between heating and cooling required for maintaining the freeze valve in a closed position was found as a result of preliminary numerical simulations and through experimental trials. The experimental campaign resulted in the observation of discrepancies in operational characteristics of the freeze valve depending on the flow recirculation in the pipe connecting the freeze valve to the rest of the loop. The conclusion from this experiment was that the design of the freeze valve must always take the valve's location into account.



Figure 21. Freeze valve implemented in FFFER [34].

One of SWATH experiments consisted in building an improved MSFR freeze valve, utilizing the experience gained at FFFER. Here, the FLiNaK salt was used again, compressed air tubes were used for the cooling of the copper disk, and the valve was equipped with a steel mass and lower and upper heaters (see Figure 22). The novelty was the geometry of the plugs, which were triangular ("petal-shaped", see Figure 23), and the inclusion of the entire disk inside the steel mass to increase the heat transfer efficiency. The molten salt was moved between the drain tank and the vertical freeze valve with the use of argon gas pressure. The vertical arrangement was selected to make the control of the process and data acquisition easier. The salt level was measured using a metal rod inserted from the top.



Figure 22. Freeze valve tested in SWATH [34].



Figure 23. Petal-shaped freeze plugs in the SWATH freeze valve [34].

CFD simulations of the valve opening were performed using ANSYS, with no natural circulation in the liquid accounted for, and using an apparent heat capacity method for phase change. The valve was considered open when the salt near the copper walls melted and there was no solid salt layer above the disc, as this allowed for the molten salt above to flow downwards. The numerical model agreed well with the experimental data. The authors observed, however, that copper would not be suitable for the use in MSRs due to its weak mechanical properties at high temperature. Another highly conductive material should be found, should such a disc be used in a reactor.

An alternative, wedge-shaped freeze plug design was investigated by Shafer in his thesis [111], both experimentally and numerically using an enthalpyporosity approach. The geometry was chosen due to the fact that a cylindrical plug may be pushed down the draining pipe due to inadvertent melting, whereas the converging shape of the wedge requires the entire volume of the freeze plug to be molten to open the passage for the molten salt above the plug. Paraffin was used as a surrogate fluid for the molten salt because of a comparable thermal conductivity and Stefan number used for determining dynamics of phase change. The computational results were validated against the experimental data. There was much room for improvement of the experimental apparatus; however, the enthalpyporosity method yielded qualitatively similar results and was recommended for future studies of molten salt phase change.



Figure 24. Progression of melting of the paraffin-filled wedge-shaped freeze plug [111]. The original size of the plug is marked in red and the top surface of the molten paraffin is shown in green.

The bachelor's thesis of Deurvorst [112] investigated the addition of fins in various arrangements onto the multiple-plug design in order to improve heat transfer characteristics of melting. The addition of the closely staggered fins resulted in an up to 25% reduction in the melting time. While this idea seems innovative and promising, the influence of the fins on freezing or manufacturability of such a component, however, were not analyzed, and the input data was not representative of the MSFR.

An ongoing doctoral work of Kaaks at TUD focuses on the melting and solidification phenomena in an MSR and is part of the SAMOSAFER

project [113]. Kaaks is improving the phase change modelling capabilities using TUD's own CFD software called DGFlows that is based on the discontinuous Galerkin approach [114]. The phase change modelling is done with the enthalpy method. The use of the discontinuous Galerkin method is expected to yield higher accuracy than the popular finite volume methods. Experimental validation of this and other codes is possible with the use of TUD's own water freezing experimental facility ESPRESSO [115]. The novelty of the approach and especially the building of a new facility that can be used for phase change research are highly appreciated in the molten salt community where there is a scarcity of experimental validation data.

Another PhD work worth mentioning is the dissertation of Tano Retamales from Grenoble Alpes University dealing with the multiphysics modelling of molten salt reactors and with experimental validation [116]. Interestingly, the modelling part touched upon both macro- and mesoscopic phenomena related to molten salt phase change. The latter included phase segregation in multicompound salts to predict the microstructure formed during solidification, as the salt compounds undergo phase change at different temperatures. The resolidification of a well-mixed molten salt that underwent composition changes due to chemical and nuclear reactions can result in phase separation, which will eventually lead to differently behaving phases within the salt once the salt is to be remelted. Not taking this into account could result in erroneous calculations of the melting time required and could potentially result in circuit damage. In his models, Tano Retamales coupled phase growth with the flow equations and suggested that high precision models of molten salt phase change should be developed using multiscale approaches.

Tano Retamales' heat transfer and phase change experiments were performed in a dedicated solidification experiment (see Figure 25) in the SWATH facility at the French National Centre for Scientific Research in Grenoble in order to validate the numerical model developed earlier. The molten FLiNaK salt was cooled inside a graphite crucible via a cooling tube located in the center of the crucible, and the tube could be rotated to study the effect of the forced flow on the solidification. The temperature was measured on the crucible and on the central tube in a few locations, and the





solidification front could be inspected visually by extracting the tube from the crucible. The results were successfully compared with CFD model simulations and could be used to benchmark other codes.

Aji from the University of Electro-Communications in Tokyo conducted an investigation of basic parameters in developing freeze valves for MSRs [117], where two sets of experiments were performed to understand crucial features of simple freeze valves and used CFD models to learn what the most

optimal parameters are. The researcher found that in a vertical configuration of a cylindrical freeze valve, the presence of natural convection prolongs the valve's opening time. A novel analysis of an influence of an inclination angle on the operation of a freeze valve was performed and the conclusion was that the opening time decreases significantly for a horizontal orientation and even more for negative inclination angles, due to the natural convection playing a greater role. Nonetheless, the extent of the influence of natural convection depends on dimensions of a freeze valve and Aji's results can be generalized only for small-diameter freeze valves. However, the smaller the inclination angle, the more difficult it is to close (freeze) the valve; the most efficient configurations for the two opposite functions of the freeze valve are acting against each other and the optimal orientation has to be found including both states in the analysis.

Even though there has been much scientific research and experimentation on valves for molten salts, the "perfect" design has not been identified yet – neither for mechanical nor freeze valves. With a short-term outlook for the necessary growth needed in the feasibility of MSRs, it is difficult to feel assured that a suitable industrial solution will be found within the next decade so that first MSRs could be commercialized and made safe and lowmaintenance, unless a molten salt valve-free reactor is created. This lack of the solution to issues inherent in freeze valves, however, motivated the author's experimental research goals that are described in the next chapters. While the problem was being studied, the author came to a conclusion that there was a significant research gap in the modelling of phase change in molten salts, as well as in the understanding of the behavior of the CMSR's sodium hydroxide salt, that the author focused on in the second half of the project.

3. Phase change

3.1. Physical description

The occurrence of phase change processes can be justified by the destruction or formation of intermolecular bonds as a result of changes in intermolecular forces that depend on the internal energy of the system [118]. Each state of matter is characterized by its bond energy and molecular configuration. In a solid, the intermolecular forces are very strong and the molecules are held in a fixed pattern. In a liquid, the bonds are weaker, but still keep the unorganized molecules together. Melting happens due to an increase of the vibrational energy of the solid molecules which overcomes the intermolecular attractive force, thus allowing for the molecules to move. As such, phase change is a process of reordering the molecules.

Phase change of a single-component substance occurs at a single temperature. For substances that are a mixture of substances melting at different temperatures, phase change can spread over a range of temperatures; in such a case there forms a mixture of solid and liquid inbetween the completely solid (solidus point) and completely liquid (liquidus point) state, which is referred to as a mushy zone. The mushy zone is characterized by different thermophysical and transport properties of the material than the solid and liquid state and therefore requires a dedicated study if one were to describe phase change in full. There is a significant lack of data on materials having a mushy zone and on the behavior thereof.

To mathematically describe the phase change processes, the enthalpy *H*, being a thermodynamic state function used for quantifying changes in energy of a system, is introduced:

$$H = U + PV, \tag{1}$$

where *U* is the internal energy, *P* pressure, and *V* volume of the system. The total differential can be expressed as:

$$dH = (TdS - PdV) + (PdV + VdP),$$
(2)

with T being temperature and S entropy. Therefore, a change in enthalpy between states A and B can be expressed as a reversible process, assuming constant pressure, as:

$$\Delta H = \int_{A}^{B} T dS = \Delta Q. \tag{3}$$

The heat ΔQ delivered to the system is equal to the changes in the system's enthalpy, here at a constant temperature for simplicity, which for the melting process taking the substance from A being the solid state to B being the liquid state would be the melting point. While for other temperatures the total enthalpy of the system increases monotonically with increasing temperature (see Figure 26), the enthalpy change from liquid to solid is discontinuous for a pure substance [119]. This discontinuity in the H(T) function defines the heat of fusion H_{f_r} i.e. the latent heat of the solid-to-liquid phase change. A certain quantity of a substance can exist in a solid, liquid, or mixed state depending on its total enthalpy.



Figure 26. Enthalpy-temperature phase diagram for a pure substance, adapted from [119].

PCMs can be used for latent heat energy storage, where the thermal energy can be stored while the system is heated up, and released over a long period of time [120]. While heat is absorbed, the material is molten, whereas it solidifies when the system releases heat [118]. A latent heat thermal energy storage system is superior to a sensible energy storage system due to a larger amount of heat being stored, smaller dimensions, and isothermal conditions of heat absorption and release. Due to the nature of the system taking advantage of the phase change, phenomena of melting and freezing are studied in order to optimize storage systems. This includes development of analytical and numerical models which can be utilized by the energy industry as a whole, and especially in fields of CSP coupled with energy storage and MSRs.

3.2. Analytical methods

The primary focus of solid-liquid phase change modelling is tracking of the moving interface between different phases that are characterized by usually significantly different properties, giving rise to varying rates of mass, momentum, and energy transport. Such problems have been termed Stefan problems due to the work of Josef Stefan who studied the melting of a polar ice cap and found analytical solutions to the moving boundary problem [121], [122]. Analytical solutions are limited to ideal cases with constant material properties. The advent of computers allowed for a rapid development and implementation of numerical methods, increasing the set of tools available to a phase change researcher, and enabling research in three dimensions. Nowadays, CFD models are used to guide the design of systems where phase change occurs, and are validated against experimental data. Whereas a macroscopic description of a phase change process with convection is well developed, there is a lack of multiscale models involving microscopic phenomena that dictate the behavior of a PCM. Moreover, few experimental facilities are dedicated to phase change research - and there is still much to discover.

The original Stefan problem describes the freezing of a one-dimensional cavity, whose one side's (x = 0) temperature is lowered to a temperature T_1 below the melting point T_m at a time t = 0, with the rest of the material at

 $T_2 > T_m$. As a conduction-only problem, it can be described by the Fourier law for the solid [123]:

$$\frac{\partial}{\partial x} \left(k_s \frac{\partial T_s}{\partial x} \right) = \rho c_s \frac{\partial T_s}{\partial t}, \qquad 0 \le x \le s(t), \tag{4}$$

where k_s is the thermal conductivity of the solid, T_s temperature of the solid, ρ density, c_s heat capacity of the solid, and s(t) the position of the moving boundary between two phases. The other equation is for the liquid:

$$\frac{\partial}{\partial x} \left(k_l \frac{\partial T_l}{\partial x} \right) = \rho c_l \frac{\partial T_l}{\partial t}, \qquad s(t) \le x.$$
(5)

Constant density is assumed due to the constant volume of the domain. At the interface s(t) between the two phases:

$$T_s = T_l = T_m,\tag{6}$$

and the heat balance across the boundary, termed the Stefan condition, reads:

$$\rho H_f \frac{ds(t)}{dt} = k_s \frac{\partial T_s}{\partial x} \Big|_{x=s(t)} - k_l \frac{\partial T_l}{\partial x} \Big|_{x=s(t)}.$$
(7)

The analytical solution is given by:

$$s(t) = 2\lambda \sqrt{\alpha_s t},\tag{8}$$

where α_s is the thermal diffusivity of the solid and the constant λ can be found as a solution of:

$$\frac{\lambda H_f \sqrt{\pi}}{c_s [T_m - T(0, t)]} = \frac{\exp(-\lambda^2)}{\operatorname{erf}(\lambda)} - \frac{k_l}{k_s} \sqrt{\frac{\alpha_s}{\alpha_l} \frac{T(x, 0) - T_m}{T_m - T(0, t)}} \frac{\exp\left(-\frac{\alpha_s \lambda^2}{\alpha_l}\right)}{\operatorname{erfc}\left(\lambda \sqrt{\frac{\alpha_s}{\alpha_l}}\right)}, \quad (9)$$

where erf is the Gauss error function defined as:

$$\operatorname{erf}(\lambda) = \frac{2}{\sqrt{\pi}} \int_0^{\lambda} \exp(-t^2) \, dt \,, \tag{10}$$

and erfc is the complement of erf:
$$\operatorname{erfc}(\lambda) = 1 - \operatorname{erf}(\lambda).$$
 (11)

The temperature at any point can be evaluated then as:

$$T = \begin{cases} \frac{T_m - T(0, t)}{\operatorname{erf}(\lambda)} \operatorname{erf}\left(\frac{x}{2\sqrt{\alpha_s t}}\right) + T(0, t), & x < s(t) \\ T_m, & x = s(t) \\ T(x, 0) - \frac{T(x, 0) - T_m}{\operatorname{erfc}\left(\lambda\sqrt{\frac{\alpha_s}{\alpha_l}}\right)} \operatorname{erfc}\left(\frac{x}{2\sqrt{\alpha_l t}}\right), & x > s(t) \end{cases}$$
(12)

Even though Stefan's solution is valid only for a simple geometry, it is still used for validation of computer codes. It also shows that the rate of the phase change process depends on a dimensionless number called the Stefan number:

$$St = \frac{c\Delta T}{H_f},\tag{13}$$

where ΔT is the difference between the temperature of the surrounding and the melting point.

Neumann [124] extended Stefan's solution to a problem where the boundary conditions include subcooling or superheating. Paterson [125] derived a solution to the same problem in cylindrical coordinates, involving exponential integrals. Other researchers [126]–[128] have developed complex approximate solutions to problems with a constant heat flux boundary condition utilizing a heat balance integral method. Calculating a result of any of the abovementioned equations is not trivial, and all of them are based on idealized conditions that are hardly met in nature. However, they laid the foundations for an understanding of phase change and creation of relevant computer models.

3.3. Numerical methods

The first numerical methods developed for phase change problems utilized only the heat conduction equation and omitted convection in the melt due to the complexity of handling the Navier-Stokes equations and computational limitations. Several discernible methods have been created:

- Fixed grid methods are methods where the heat transport is approximated using a finite difference approach [129]–[131]. Temperature is solved for on a fixed grid in predominantly onedimensional space and time. The moving boundary is located between neighboring nodes and its location recalculated at each iteration. Time step and mesh size must be carefully chosen to obtain an accurate result, making this method computationally expensive.
- Variable grid methods are similar to the above, but utilize dynamic meshing and/or non-uniform time steps to speed up a simulation [132]–[134].
- Apparent heat capacity method and all methods mentioned afterwards do not explicitly track the moving boundary. They incorporate the Stefan condition in the equations that apply to the entire domain, while the condition was applied only to the moving boundary in the two previously mentioned methods. In this method [135], [136], the heat of fusion is accounted for in the heat capacity of the material, which is artificially increased in the temperature range of the phase change:

$$c_{app} = \frac{H_f + \int_{T_{sol}}^{T_{liq}} c(T) \, dT}{T_{liq} - T_{sol}},\tag{14}$$

where c_{app} is the apparent heat capacity, T_{liq} liquidus point, and T_{sol} solidus point. Very small time steps are required with this method; otherwise, the heat of fusion might be "skipped" in a time step where the temperature rises from below solidus to above liquidus points and vice versa. Additionally, for pure materials having the same liquidus and solidus points, an artificial difference between them must be imposed that cannot be too small.

 Heat integration method [137], [138] stops the temperature increase in cells that have reached the melting point and the amount of heat that the cell would otherwise receive is added up with each iteration until this heat equals the heat of fusion – and the temperature can increase again. This method is computationally inexpensive and can be applied to three dimensions, but does not solve momentum equations.

• *Source-based method* [139] allows for addition of any heat source *S*, including the heat of fusion, to the energy equation:

$$\rho c \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right) + S.$$
(15)

This method is computationally efficient, especially for phase change with the mushy zone, and can readily be incorporated in algorithms of existing codes.

• Enthalpy method [140]–[142] uses the enthalpy h in place of the heat capacity in heat transport equations, and utilizes relations between the enthalpy and temperature to solve for either:

$$\rho \frac{\partial h}{\partial t} = \frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right). \tag{16}$$

The method is reported to be costly but more accurate for nonisothermal PCMs than the previously mentioned methods [143].

Modern computers allowed for momentum equations to be solved alongside the heat conduction equation. The influence of the convection on the phase change process can be significant and is an object of experimental studies. Gau and Viskanta [144] studied melting and solidification experimentally and numerically as early as in the 1980s. The phase change experiments were performed in a rectangular cavity whose horizontal walls were the system's heat source and heat sink, and the vertical walls were insulated. A Lipowitz eutectic metal alloy with the melting point of 70 °C was used to study the process. Measurements of temperature fluctuations were used to indicate existence of natural convection. The moving interface was probed, and the liquid metal was poured out of the test cell to study the shape of the solid-liquid interface. Results indicated presence of natural convection, however due to a composition stratification of the material, suppression of the natural convection and therefore of the melting rate was observed.

Dantzig [145] studied melting and solidification with convection in the melt using a finite element method and the enthalpy method with an enhanced viscosity in the mushy region. The model was used to study melting of gallium investigated earlier by Gau and Viskanta [146], as well as other researchers' work. Dantzig identified a problem pertaining to the use of numerical methods, namely discrepancies coming from the fact that the natural circulation within the melt may be governed either by one large vortex (referred to as a cell) or multiple small ones. A dynamic nature of the melting including natural convection was stressed. Later, Noureddine et al. [147] proved that previous works did not use sufficiently converged numerical grids, and that a multicellular flow pattern was the correct one. The discrepancies between the experiments yielding a single convection cell and the numerical solutions might result, as Noureddine implies, either from an inadequate mathematical model, or the experiment not meeting assumptions of the mathematical model.

A more applied research has been conducted by Anggara et al. [148] who studied melting of a PCM called RT 52 in a concentric tube heat exchanger. A CFD model was validated with an experiment (see Figure 27), where hot water was circulated in an outer tube and the PCM was stored in the inner tube. The model was calibrated with experimental results so that the parameters describing the behavior of the mushy zone and the mesh refinement were representative of the experimentally obtained data. The temperature, as well as the liquid fraction computed by ANSYS Fluent using the enthalpy-porosity approach agreed with the experiment to a good extent.

Vogel and Thess [149] performed a benchmark experiment to validate numerical models of melting governed by natural circulation. For this purpose, n-octadecane was melted from both sides of a rectangular box and shadowgraph imaging and particle image velocimetry techniques were utilized for observations of the moving boundary and measurement of velocities in the melt. Two different modelling methods were compared with



Figure 27. The melting contour obtained at different time steps in the experiment and in the simulation of Anggara et al. [148].

the experimental data, a detailed 2D model utilizing the volume of fluid method with variable thermophysical properties and an extra volume of air allowing for salt expansion, and simplified 2D and 3D models based on the Boussinesq approximation and constant properties. The two methods were qualitatively comparable in terms of predicting the liquid fraction, but differed significantly in predicting velocities (see Figure 28). The Boussinesq method was compared with the measurements and agreed with the liquid fraction and temperature, but overestimated the velocity (see Figure 29). Even though free convection was added to the models, the way the different numerical schemes approached the problem yielded results which were not comparable quantitatively. However, overall phenomena of phase change and natural convection were captured to a reasonable extent, which validated the use of simple models for general phase change studies.

Another interesting study was performed by Marušić and Lončar [150] who directly measured the melting front propagation in NaNO₃ and modelled the melting process using the enthalpy-porosity approach. The experimental apparatus was constructed as a rectangular cavity heated from one side and cooled from the other. The front of the cavity was transparent for melting front measurements using visual techniques (see Figure 30) and the



Figure 28. Phase state and velocity fields for the 2D volume of fluid model (V-2D) and the 2D Boussinesq model (B-2D) at two different time steps [149]. The solid state is shown in black.

influence of natural convection was clearly visible. Various inclination angles were used to study the influence thereof on the melting process. A numerical model was created in OpenFOAM and utilized the Boussinesq approximation. The authors reported that the mushy zone constant they used, which yielded results agreeing with the experimental data, was much larger than most values found in literature. The study provided valuable data



Figure 29. Phase state and velocity fields obtained with the 3D Boussinesq model and in the experiment [149].

that could be used for validation of other computer codes. As the authors mention, even if temperature profiles in the real scenario and in the simulated one are comparable, oftentimes the front propagation is not modelled accurately, which can lead to false validation of the models, if only the temperature measurements are looked at. This underlines the importance of code validation using more sophisticated techniques, and the need for more validation facilities dedicated to salt phase change which would broaden the scope of possible analyses.



120min

150min

210min

Figure 30. Photos of the melting front propagation in NaNO $_3$ [150]. The left wall is heated.

4. Numerical benchmark

Introduction

Due to the scarcity of experimental facilities and benchmark-quality data that could be used for code validation of salt melting and solidification models, the results of computer simulations of salt phase change cannot be considered as a final confirmation of an MSR design's safety. Without experiments substantiating the correctness of software's numerical approach, licensing of nuclear reactors based on simulations is not possible. While new experimental facilities are being built and empirical data collected, work on reactor designs does not stop. CFD and other modelling techniques are still supporting design decisions despite not necessarily being certified for non-conventional nuclear reactor designs. To guide reactor designers in choosing models and codes which have the lowest error and properly model physics, a numerical benchmark can be created which compares capabilities of various codes and quantifies discrepancies between them. Such a project was taken up by the author with collaborators from TUD, under the umbrella of the SAMOSAFER consortium, with a focus on the melting of a freeze plug.

The following section contains an original manuscript describing the benchmark and results for comparison with other codes, submitted for publication.

A numerical benchmark for modelling phase change in molten salt reactors

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Abstract

The design of a molten salt reactor is largely based on CFD simulations. Phase change plays an important role in the safety of the reactor, but numerical modelling of phase change is particularly challenging. Therefore, the knowledge of the margin of error of CFD simulations involving phase change is very important. Relevant experimental validation data is lacking. For this reason, a numerical benchmark designed after the freeze valve is proposed. The benchmark consists of five stages, where with each step more complexity is added. The step-wise addition of complexity allows for pinpointing potential sources of discrepancy. Results were obtained with three different codes: STAR-CCM+, OpenFOAM, and DGFlows. The results were found to be largely consistent between the codes, however the addition of conjugate heat transfer introduced some discrepancies. These results indicate that careful consideration is needed when coupling conjugate heat transfer solvers with solidliquid phase change models.

Keywords:

phase change, melting, molten salt reactor, benchmark, freeze valve

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1. Introduction

Solid-liquid phase change plays an important role in many applications, such as latent heat storage (see Faden et al. (2019b)), metallurgy (see Ben-David et al. (2013)), and the design of the Molten Salt Fast Reactor (MSFR) (see Cartland Glover et al. (2019), Tiberga et al. (2020), and Voulgaropoulos et al. (2020)). Due to the mathematical complexity of solid-liquid phase change as a moving boundary problem, extensive research has been conducted on its analytical and numerical solution since the end of the 19th century. Stefan (1889) formulated a simple onedimensional melting problem, to which an analytical solution can be found. Subsequent efforts were devoted to solving Stefan problems in multiple dimensions (see Friedman (1968) and Wilson et al. (1978)), coupled with fluid flow (e.g. by Dantzig (1989) and Voller and Swaminathan (1991)), and using different properties for the solid and the liquid phases (see for instance Belhamadia et al. (2012)). Most phase change problems of industrial relevance require numerical solutions, and recent advancements in computing power allowed an increase in the accuracy and complexity of the different models.

The present work was performed in the context of the development of the MSFR under the framework of the SAMOFAR (2014) and SAMOSAFER (2018) projects. A key and unique safety component of the MSFR is the freeze valve, which is designed to melt in case of an accident scenario (see for instance Chisholm et al. (2020) for a recent and comprehensive overview of the freeze valve design and development). A sufficiently short opening time of the valve is required to drain the reactor quick enough to prevent the temperature from exceeding dangerously high values, as stated by Tiberga et al. (2020). Apart from experimental investigations such as those performed by Giraud et al. (2019), the design of the freeze valve relies heavily on numerical simulations to obtain predictions of its melting time. Experimental studies suitable for numerical validation have mainly focused on the melting of pure metals or paraffin wax in rectangular or cylindrical enclosures, such as those performed by Gau and Viskanta (1986), Jones et al. (2006), and Faden et al. (2019a) and do not include the full complexity of the MSFR freeze valve design. For this reason, it is of paramount importance that sufficient knowledge is obtained regarding the accuracy of currently used numerical modelling approaches and their possible limitations in predicting the melting behaviour of the MSFR and any other similar freeze valve design. Recently, a multiphysics numerical benchmark for codes dedicated to MSRs was proposed (Tiberga et al. (2020a)), and results were compared for four different codes (Tiberga et al. (2020c), Blanco et al. (2020), Cervi et al. (2019), Fiorina et al. (2015)). The simplicity of the benchmark and its stepby-step approach made it a suitable tool for testing the performance of various codes and detecting possible discrepancies. In a similar fashion, we propose a two-dimensional numerical benchmark based on one of the MSFR freeze valve designs (Giraud et al. (2019)), to compare the solid-liquid phase change modelling capabilities and their coupling with fluid flow and conjugate heat transfer models of different numerical codes. The benchmark consists of five different stages and with each stage, complexity is added as the model evolves towards a more realistic representation of the MSFR freeze valve. The first stage consists of a variation on the classical Stefan problem, however featuring a time-dependent temperature boundary condition that is representative of shut-down conditions in the MSFR. In the second stage, volumetric heating is added to model the influence of radiation and heat deposition from the fuel salt on the melting of the freeze plug. In the third stage, solid walls are added to the freeze valve geometry and conjugate heat transfer modelling is required in addition to solving the melting problem. In the fourth stage, the role of natural convection on the melting behaviour is investigated, and in the fifth and final stage, forced convection is added, mimicking the recirculation of the fuel salt above the freeze valve. In this work, three different numerical codes are used to compare the results for the five benchmark stages: an in-house code DGFlows developed at Delft University of Technology (Hennink et al. (2021), Tiberga et al. (2020), Kaaks et al. (2023)), the commercial code STAR-CCM+ (Siemens Digital Industries Software), and the open-source code OpenFOAM (Weller et al. (1998)). The step-wise addition of complexity allowed for identifying at which steps discrepancies between the results provided by the codes would arise.

The remainder of this work is organized as follows. In section 2, a brief introduction is given to the numerical challenge of solving solid-liquid phase change problems. Subsequently, in section 3, the various modelling approaches of the three codes are presented. In section 4, the five benchmark stages are introduced, and the results of the codes are discussed and compared. Finally, section 5 summarizes the most important results of this MSFR freeze valve numerical benchmark study and presents the conclusions.

2. Challenge of Modelling Solid-Liquid Phase Change

Standard notation is used throughout the document unless otherwise specified. The enthalpy transport equation in conservative form is written as:

$$\frac{\partial H}{\partial t} + \nabla \cdot (\boldsymbol{u}H) = \nabla \cdot (\lambda \nabla T), \tag{1}$$

where *H* is enthalpy, *t* is time, *u* is velocity, λ is heat conductivity, and *T* is temperature. For most heat transfer problems, the enthalpy-temperature relationship is smooth and the temperature gradient in the diffusion term may be expressed in terms of the enthalpy ($\nabla T = \frac{1}{\rho c_p} \nabla H$), hereby eliminating the temperature as the unknown and resulting in a linear energy transport equation that can be solved with standard solution methods. In contrast, solid-liquid phase change is characterized by a jump in enthalpy at the melting point, leading to a non-smooth enthalpy-temperature relationship (see Figure 1).



Figure 1: Enthalpy-temperature relationship for an isothermal solid-liquid phase change. The slope of the solid region depends on the density ρ_s and heat capacity $c_{p,s}$ of the solid phase, whereas the slope of the liquid region depends on the density ρ_l and heat capacity $c_{p,l}$ of the liquid phase. The magnitude of the enthalpy jump depends on the liquid density and the latent heat *L*.

Assuming constant thermophysical properties in each phase, the temperatureenthalpy relationship reads:

$$T(H) = \begin{cases} \frac{H}{\rho_{s}c_{p,s}}, & H \le \rho_{s}c_{p,s}T_{m} \\ T_{m}, & \rho_{s}c_{p,s}T_{m} \le H \le \rho_{s}c_{p,s}T_{m} + \rho_{l}L \\ T_{m} + \frac{H - (\rho_{s}c_{p,s}T_{m} + \rho_{l}L)}{\rho_{l}c_{p,l}}, & H \ge \rho_{s}c_{p,s}T_{m} + \rho_{l}L \end{cases}$$
(2)

where ρ_s is the density of the solid and ρ_l of the liquid phase, $c_{p,s}$ is the heat capacity of the solid and $c_{p,l}$ of the liquid phase, T_m is the melting point, and L is the latent heat of the solid-liquid phase change. With this temperatureenthalpy relationship, the energy equation becomes highly non-linear. Therefore, the challenge in modelling solid-liquid phase change problems is to solve the energy equation with the non-smooth enthalpy-temperature coupling and to accurately track the displacement of the solid-liquid interface.

3. Characteristics of the Codes Used

A short description of each code used in this benchmark is presented below.

3.1. STAR-CCM+

The following description of STAR-CCM+ version 2020.2 used in this benchmark is based on the User Guide (Siemens Digital Industries Software). CFD modules of STAR-CCM+ utilize the finite volume method and solve the Navier-Stokes equations in each computational cell. The software is able to model multiphase flow using Eulerian and Lagrangian approaches.

3.1.1. Volume of Fluid

A phase change problem is a multiphase problem, as more than one thermodynamic state of the matter – in our case, solid and liquid – are present and interact with each other within the same system. In order to model phase change in STAR-CCM+, the Volume of Fluid approach, traditionally used for tracking interfaces between gases and liquids (Hirt and Nichols (1981)), is used by the software. Volume of Fluid is a simple model based on the Eulerian formulation of a multiphase fluid, where two or more immiscible phases share an interface. Mass, momentum, and energy are treated as mixture quantities rather than phase quantities. The dynamic viscosity and thermal conductivity

are volume-weighted, and the specific heat is mass-weighted. Conservation equations are solved for the mixture in a computational cell. The mesh must be fine enough to resolve the interface between the phases.

Phases are described by the phase volume fraction α_i :

$$\alpha_i = \frac{V_i}{V},\tag{3}$$

where V_i is the volume of phase *i* in the cell of volume *V*. The phase mass conservation equation is:

$$\frac{\partial}{\partial t} \int_{V} \alpha_{i} dV + \oint_{A} \alpha_{i} \boldsymbol{v} \cdot d\boldsymbol{a} = \\ = \int_{V} \left(S_{\alpha_{i}} - \frac{\alpha_{i}}{\rho_{i}} \frac{D\rho_{i}}{Dt} \right) dV - \int_{V} \frac{1}{\rho_{i}} \nabla \cdot \left(\alpha_{i} \rho_{i} \boldsymbol{v}_{d,i} \right) dV,$$
(4)

where *a* is the surface area vector, v is the mixture velocity, $v_{d,i}$ is the diffusion velocity, $S_{\alpha i}$ is a source term of phase *i*, and $D\rho_i/Dt$ is the Lagrangian derivative of the phase densities ρ_i .

A Segregated Multiphase Temperature model is activated in STAR-CCM+ in order to solve the total energy equation. The temperature is the solved variable and the enthalpy is computed from the temperature according to the multiphase equation of state. In our STAR-CCM+ model, the convective flux in the Volume of Fluid transport equation is discretized using a second-order scheme. The second-order convection scheme is used to solve the energy equation as well.

3.1.2. Melting-Solidification

The solid-liquid interface is not tracked directly by the software; instead, an enthalpy formulation is used to determine the relative fraction of the solid and liquid phases:

$$H_{ls}^* = H_{ls} + (1 - \alpha_s^*)L, \tag{5}$$

where H_{ls} is the enthalpy of the liquid-solid phase, H_{ls} is the sensible enthalpy, L is the latent heat and α is the relative solid volume fraction. For linearized

melting, the liquid fraction corresponds to the fraction of the latent heat of fusion that has been absorbed by the system. In STAR-CCM+, each mesh cell is characterized by an individual value of the relative solid volume fraction. If the material's solidus and liquidus points are the same, a difference of 0.002 K is introduced automatically between them so that it is possible for the software to take the latent heat into account in a phase change problem. This way, the relative solid volume fraction between fully solid and fully liquid states is calculated as:

$$\alpha_s^* = \frac{T_{liquidus} - T}{T_{liquidus} - T_{solidus}}.$$
(6)

One of the optional models for phase change in STAR-CCM+ is a Melting-Solidification Flow Stop model. With the help of this functionality, the flow is stopped in a cell when a specified solid fraction is exceeded. To avoid assigning velocities to the cells undergoing melting and to resemble the way in which DGFlows and OpenFOAM treat phase change, the default solid fraction value of 1 has been changed to 0.01. This way, the momentum equations are solved only in the cells that have (almost) fully undergone phase change to the liquid state.

3.1.3. Conjugate Heat Transfer

Coupled heat transfer between a liquid and an adjoining solid, i.e. conjugate heat transfer, is modelled with the use of an interface between the two materials. Each material has its own thermal boundary conditions, and the interface can have an additional heat source *S*. The energy conservation equation at the interface:

$$\dot{q}_{fluid} + \dot{q}_{solid} = -S,\tag{7}$$

where q_{fluid} is the heat flux from the fluid through the boundary and q_{solid} is the heat flux leaving through the boundary into the solid, is solved for each side of the interface with the use of linearized heat flux coefficients:

$$\dot{q} = A + BT_c + CT_w + DT_w^4, \tag{8}$$

where T_c and T_w are the cell and wall temperatures, respectively, and A, B, C, and D are the net wall heat flux coefficients, which in case of this paper are:

$$A = \lambda [\nabla T_c - (\nabla T_c \cdot ds)\vec{a}]$$
(9a)

- $B = -\lambda \vec{a} \tag{9b}$
- $C = \lambda \vec{a} \tag{9c}$
- $D = 0. \tag{9d}$

3.2. OpenFOAM

OpenFOAM (Weller et al. (1998)) is the leading open-source CFD software. In this work, a phase-change model based on the 'linearized enthalpy approach' (Kaaks et al. (2022), Kaaks et al. (2023)) has been implemented in OpenFOAM v8, distributed by the OpenFOAM foundation. The 'linearized enthalpy approach' is based on the conservative form of the enthalpy transport equation (see Equation 1) and builds on the work of Faden et al. (2019a), Nedjar (2002), and Swaminathan and Voller (1993). Using the 'linearized enthalpy approach', the volumetric enthalpy is linearized around the latest known temperature value:

$$H^{n+1,i+1} = H^{n+1,i} + \frac{dH}{dT} \left(H^{n+1,i+\frac{1}{2}} - H^{n+1,i} \right), \tag{10}$$

where n+1 refers to the latest time-step, i+1 refers to the newest iteration, i indicates the previous iteration, and $i+\frac{1}{2}$ denotes the use of an intermediate value. Here, the following approximation for the enthalpy-temperature derivative is used:

$$\frac{dH}{dT} \approx \frac{1}{2} \left(\rho_s c_{p,s} + \rho_l c_{p,l} \right). \tag{11}$$

Performing the second order accurate BDF2 time integration and replacing the unknown enthalpy with the linearized enthalpy yields the 'linearized enthalpy equation':

$$\frac{dH}{dT} \left(\frac{3T^{n+1,i+\frac{1}{2}}}{2\Delta t} + \nabla \cdot \left(\mathbf{u}T^{n+1,i+\frac{1}{2}} \right) \right) - \nabla \cdot \left(\lambda \nabla T^{n+1,i+\frac{1}{2}} \right) = \frac{dH}{dT} \left(\frac{3T^{n+1,i}}{2\Delta t} \right) - \frac{3H^{n+1,i} - 4H^n + H^{n-1}}{2\Delta t}.$$
(12)

Here we use the 'sensible enthalpy only' formulation for the heat convection term (König-Haagen et al. (2020))."

The 'linearized enthalpy equation' is linear in the unknown temperature and is iterated until convergence. At each iteration, the volumetric enthalpy at the cell centers is updated and the temperature is recalculated according to the enthalpy-temperature relationship (see Equation 2):

$$H^{n+1,i+1} = H^{n+1,i} + \frac{dH}{dT} \left(T^{n+1,i+\frac{1}{2}} - T^{n+1,i} \right)$$
(13a)

$$T^{n+1,i+1} = T(H^{n+1,i+1})$$
(13b)

The non-linear enthalpy-temperature iterations are terminated when the following convergence criterion is reached:

$$max\left[res, \sum_{n_{elem}=0}^{n_{elem}=N_{elem}} (T^{n+1,i+1} - T^{n+1,i})\right] < tol.$$
(14)

In this work, $tol = 10^{-6}$. Here, *res* is the initial residual of the iterative matrix solver and *N* is the total number of cells. Upon convergence, the difference between the old and the new temperature values approaches zero and the solution to the 'linearized enthalpy equation' approaches the solution to the original enthalpy transport equation in conservative form.

A no-slip condition at the solid-liquid interface is enforced using the 'Darcy source term' approach (Brent et al. (1988), König-Haagen et al. (2017)) and natural convection is treated through the Boussinesq approximation. As such, the momentum equation reads:

$$\frac{\partial(\rho_{l}\boldsymbol{u})}{\partial t} + \nabla \cdot \left(\boldsymbol{u} \otimes (\rho_{l}\boldsymbol{u})\right) = = \nabla \cdot \left[\mu \left(\nabla \boldsymbol{u} + (\nabla \boldsymbol{u})^{T}\right)\right] - \nabla p + \rho_{l}\boldsymbol{g}\beta(T - T_{m}) - C\frac{(1 - \alpha)^{2}}{\alpha^{3} + b}\boldsymbol{u}.$$
 (15)

Here, *C* is a large parameter (10^{10} in this work) and *b* is a small parameter to avoid division by zero (10^{-3} in this work); μ is the dynamic viscosity, *p* is the pressure, *g* is the gravitational acceleration, and β is the thermal expansion coefficient.

To model the conjugate heat transfer, the total mesh is separated into a metal and a salt part. Separate matrix equations are solved for each part, and the temperature at the interface between the metal and the salt is calculated through harmonic averaging:

$$T_{IF,metal} = \frac{T_{nearest,metal} \frac{\lambda_{metal}}{\delta_{metal}} + T_{nearest,salt} \frac{\lambda_{salt}}{\delta_{salt}}}{\frac{\lambda_{metal}}{\delta_{metal}} + \frac{\lambda_{salt}}{\delta_{salt}}}$$
(16)

Here, $T_{nearest}$ is the temperature at the nearest cell-center of the metal and salt domain respectively, and δ is the distance from the cell center to the interface.

The full solution algorithm is as follows:

- 1. Solve the momentum equation in the salt part.
- 2. Solve the energy equation in the salt part through a series of non-linear enthalpy-temperature iterations.
- 3. Perform the pressure correction in the salt part (in this work, 3 corrector steps are used).
- 4. Solve the energy equation in the metal part.
- 5. Repeat steps 1–4 until the total number of outer iterations has been reached.

3.3 DGFlows

DGFlows is an in-house CFD code based on the discontinuous Galerkin Finite Element Method (DG-FEM), developed at the Radiation Science and Technology Department of Delft University of Technology (Hennink et al. (2021), Tiberga et al. (2020)). DG-FEM combines attractive features of the finite element and finite volume methods, such as an arbitrarily high order of accuracy, high geometric flexibility, local conservation of vector and scalar fields, possibility for upwinding and a compact numerical stencil facilitating efficient parallelization of the solution procedure (Tiberga et al. (2020), Hennink et al. (2021)). To model phase change, the 'linearized enthalpy approach' has been implemented in DGFlows. The DG-FEM variational formulation of the coupled system of energy, momentum, and non-linear enthalpy-temperature coupling equations reads (Kaaks et al. (2023)):

Find
$$m_h \in V_{h,m}^d$$
 and $p_h \in V_{h,p,H,T}$ and $H_h \in V_{h,p,H,T}$ and $T_h \in V_{h,p,H,T}$
such that $\forall v_h \in V_{h,m}^d$ and $\forall q_h, \forall w_h \in V_{h,p,H,T}$,

$$\sum_{T \in T_h} \int_T v_h \cdot \frac{\partial m_h}{\partial t} + a^{conv}(u_h, m_h, v_h) + a^{diff}(m_h, v_h) + a^{diff}(v_h, v_h) + a^{lource}(v_h, m_h, v_h) + a^{lource}(v_$$

$$\sum_{\mathbf{T}\in\mathbf{T}_{h}} \int_{\mathbf{T}} w_{h} \cdot \frac{\partial H_{h}}{\partial t} + a^{conv}(\boldsymbol{m}_{h}, T_{h}, w_{h}) + a^{diff}(T_{h}, w_{h}) =$$

$$= l^{conv}(\boldsymbol{u}_{h}, w_{h}) + l^{diff}(w_{h}) \qquad (17c)$$

$$T_{h} = T(H_{h}) \qquad (17d)$$

Here, m is the mass flux, u is the velocity, *H* is the enthalpy, *T* is the temperature and *p* is the pressure. *a* and *l* correspond to the bilinear and the linear forms respectively, with the superscripts '*conv*', '*diff*', '*div*', and '*source*' referring to the contributions from the convection, diffusion, divergence and source terms respectively. Finally, T defines the local element and the subscript '*h*' defines the finite element approximation. A hierarchical set of orthogonal basis and test functions (normalized Legendre polynomials) are used to approximate each variable within the elements. A mixed order formulation is used, that is $P_{p,H,T} = P_m - 1$, where 'P' is the polynomial order of the finite element approximation. The symmetric interior penalty (SIP) method is used to discretize the diffusion term, and the Lax-Friedrichs numerical flux is used to discretize the convection terms.

The non-linear enthalpy-temperature iterations are performed in a similar manner as the implementation of the 'linearized enthalpy approach' in OpenFOAM. For more detailed information on the implementation and validation of the DG-FEM formulation of the 'linearized enthalpy approach', please refer to Kaaks et al. (2023). To model the conjugate heat transfer, a material identifier is used to distinguish the metal and the salt parts of the domain. The momentum equation is only solved within the salt, where the noslip boundary condition is applied at the metal-salt interface. The enthalpy transport equation is solved for the full domain. Here, continuity at the solid-liquid interface is already imposed through the penalty terms in the SIP discretization of the heat diffusion, and therefore no additional treatment is

required.

Time-stepping is performed using the second order BDF2 method. All integrals are evaluated through Gaussian quadrature with a polynomial accuracy of $3P_m$ -1. Meshes are generated with the open-source software tool Gmsh by Geuzaine and Remacle (2009) and METIS by Karypis and Kumar (1998) is used to partition the mesh. The resulting matrix equations are solved with iterative Krylov methods using the PETSc library (Balay et al. (1997)).

4. Results and Discussion of the Numerical Benchmark Study

A numerical benchmark is proposed based on the MSFR freeze valve design described by Giraud et al. (2019). The freeze valve is a key passive safety feature unique to the MSFR, and is designed to melt in the case of a reactor anomaly, draining the fuel salt into an emergency drainage system. The goal of the benchmark study is to provide a first indication of the consistency between different solid-liquid phase-change modelling approaches, and to identify possible sources of discrepancies between the codes. The benchmark consists of five stages, where with each new stage an additional level of complexity is introduced, as the model converges towards a more realistic design of the MSFR freeze valve. At each stage, the calculated temperatures, position of the melting front, and velocities are compared amongst the three different codes.

In the first stage of the benchmark, the fuel salt undergoes melting inside a two-dimensional cavity encompassing the salt domain. The heat source, modelled after the decay heat of the MSFR, is located at the top boundary of the model. The heat is conducted towards the bottom part of the domain, where phase change takes place. In the second stage, a volumetric heat source is added to the entire salt volume to mimic the heat deposition due to neutrons and photons arriving at the freeze valve's location, originating from the reactor core above. This heat source follows a similar time-dependent function as the decay heat. In the third stage, a solid wall is added to the side of the freeze valve geometry. Conjugate heat transfer is modelled to investigate the effect of heat conduction in the metal and subsequent heat exchange between the salt domain and the metal wall resulting in the melting of salt next to the wall. In the fourth stage, momentum equations are implemented with the use of a Boussinesq approximation, and the natural circulation takes place in the salt volume, making the melting process more realistic. In the last, fifth stage of the benchmark, movement of the top boundary is added to impose forced convection that is present in the reactor, where the molten fuel salt above the freeze valve is recirculated.

4.1. Stage 14.1.1. Description

To accommodate as many different software suites as possible and to keep the computational cost affordable, a two-dimensional Cartesian geometry was chosen for the benchmark. Due to the symmetric nature of the modelled freeze valve, the geometry is cut in half at the symmetry axis to save computational resources.

The model geometry is a 200 mm high and 100 mm wide rectangle (see Figure 2). The bottom and right boundaries are adiabatic, no-slip walls. The left boundary is the symmetry axis. The symmetry axis is characterized by the normal components and gradients of all variables being set to zero, and zero fluxes across the axis. The top boundary is a no-slip wall with a variable-temperature boundary condition.

The decay heat of the MSFR expressed as power P is characterized by the following formula derived by Tano Retamales et al. (2018):

$$P(t) = 6.45908 \cdot 10^6 - 6.92 \cdot 10^5 \cdot \ln(t) \quad (W \, \text{m}^{-3}), \tag{18}$$

with *t* measured in seconds. From the decay heat, Tiberga et al. (2019) derived an equation for the average temperature of the shut-down reactor:

$$T(t) = -0.0001t^2 + 0.5244t + 923(K),$$
(19)

which is used as the time-dependent boundary condition at the upper wall that controls the melting process. The bottom 90% of the freeze valve geometry is initially at 831 K (frozen salt), i.e. there is 10 K of subcooling, and the top 10% is just above the melting point, at 841.001 K.



Figure 2: Geometry with boundary (marked as "BC") and initial conditions (marked as T_0) of stage 1. The dark blue color indicates the molten salt, and the light blue color indicates the solid salt.

Since the essence of the benchmark is the phase change modelling and associated fluid flow and conjugate heat transfer, we use the same constant density for the solid and for the liquid phase. The thermophysical properties of the salt, taken from Tiberga et al. (2019), are listed in Table 1.

The computational grid is uniform and made up from 200×100 squares. The time step is 0.5 s. A set of different time steps and mesh refinements were investigated in a sensitivity analysis. The time steps analyzed on the 200×100 mesh were the following: 2.0, 1.0, 0.5, and 0.1 s. The mesh refinements with the 0.5 s time step were: 50×25 , 100×50 , 200×100 , and 400×200 . Stage 1 is in principle a one-dimensional heat conduction problem. Temperatures and the melting front at the centerline after 2500 s obtained by

the three codes are directly compared.

Property	Value	Unit
T_m	841	K
L	159	kJ kg ⁻¹
$\rho_s = \rho_l$	4390	kg m ⁻³
$\lambda_s = \lambda_l$	1.5	$W m^{-1} K^{-1}$
$C_{p,s}$	815	$J kg^{-1} K^{-1}$
$C_{p,l}$	1000	$J kg^{-1} K^{-1}$
β	$2.5 \cdot 10^{-4}$	K^{-1}
μ	$7.5 \cdot 10^{-3}$	Pa s

Table 1: Thermophysical properties of the salt used in the benchmark.

4.1.2. Implementation

In both OpenFOAM and STAR-CCM+, the diffusion terms were discretized using a central differencing scheme and a second order upwind scheme was used for the convection terms. Therefore, both the velocity and the temperature are second order accurate in space. In DGFlows, linear elements were used for the temperature, enthalpy, and pressure, and quadratic elements were used for the velocity (recall the use of a mixed order formulation), leading to a second order accurate discretization of the temperature, enthalpy, and pressure, and a third order accurate discretization of the velocity. In all three codes, a second order implicit time-stepping scheme was used (i.e. BDF2).

In STAR-CCM+, in stages 1–3, a maximum number of 30 inner iterations were used as a stopping criterion for the implicit unsteady solver. The segregated flow solver was frozen at the beginning of the simulation, which in STAR-CCM+ jargon means that no momentum equations were solved and the velocities were zero for stages 1–3. For both OpenFOAM and DGFlows, non-linear enthalpy-temperature coupling iterations were performed until the desired error tolerance of $tol < 10^{-6}$ was reached. No option was available to avoid solving the momentum equation, however the specified boundary and initial conditions and omission of the Boussinesq source term correctly led to zero velocities throughout the domain.

4.1.3. Results

After the simulated time reached 2500 s, the temperature distribution (Figure 3) and melting front position (Table 2) were derived. The three codes yielded very similar results. The melting front positions differed by less than 1 mm, which implies that the methods used for calculating one-dimensional heat conduction and resulting phase change are equivalent.



Figure 3: Temperature vs. *y* coordinates for the three codes obtained in stage 1 of the benchmark.

Table 2: Final melting front position in stages 1 and 2 of the benchmark (in mm) obtained by the three codes.

Code	DGFlows	STAR-CCM+	OpenFOAM
Stage 1	147.312	147.426	147.048
Stage 2	146.393	146.180	146.000

4.1.4. Results of the Sensitivity Analysis

Figure 4 shows the temperature and Table 3 compares the position of the melting front at the symmetry axis at the end of the simulation for all time step sensitivity analysis cases. In the same fashion, results of the mesh sensitivity analysis are shown in Figure 5 (temperature) and Table 4 (melting front).

			DODI
Δt (s)	STAR-CCM+	OpenFOAM	DGFlows
2.0	147.415	147.048	147.312
1.0	147.423	147.048	147.312
0.5	147.426	147.048	147.312
0.1	147.428	147.048	147.312

Table 3: Time sensitivity analysis on the solid-liquid interface position for the three codes obtained in stage 1, with the position given in mm.

Table 4: Mesh sensitivity analysis on the solid-liquid interface position for the three codes obtained in stage 1, with the position given in mm.

mesh size	STAR-CCM+	OpenFOAM	DGFlows
50×25	147.536	144.271	146.771
100×50	147.484	146.109	147.370
200×100	147.426	147.048	147.312
400×200	147.425	147.031	147.335

The time step sensitivity analysis suggests that for stage 1, i.e. with no natural circulation, the model is time-step independent for the 200×100 mesh. STAR-CCM+ is the only code with very small changes to the melting front position with an increasing time step, whereas the results obtained by OpenFOAM and DGFlows are exactly the same for each time step studied. The mesh refinement sensitivity analysis suggests that the 200×100 mesh yields an accurate result while taking a lower amount of computing time than the more refined case. Surprisingly, even the coarsest mesh of 50×25 elements produced good results, whereas Stefan problems are known to be sensitive to the resolution of the mesh (Lacroix and Voller (1990), Hannoun et al. (2003)). Possibly, this is because the large temperature differences over

the entire domain lead to a relatively small contribution of the latent heat peak to the total energy balance.



82



Figure 4 (a, b, c): Temperature vs. *y* coordinates for the three codes obtained in the time step sensitivity analysis of stage 1.





Figure 5 (a, b, c): Temperature vs. *y* coordinates for the three codes obtained in the mesh refinement sensitivity analysis of stage 1.

4.2. Stage 24.2.1. Description

In a nuclear reactor, radiation is emitted from within the fuel. Energetic neutrons and photons travel within the reactor vessel and heat up the reactor structures. In a molten salt reactor, this heat can also be transferred to the salt that has not undergone fission, such as the solid plug located in the freeze valve. By approximating this heat source to 1% of the decay heat of the reactor, a time-dependent volumetric heat source H_s is added to the energy equation in the entire salt region of our model (Tano Retamales et al. (2018)):

$$H_{\rm S}(t) = 6.45908 \cdot 10^4 - 6.92 \cdot 10^3 \cdot \ln(t) ({\rm W m^{-3}}).$$
(20)

4.2.2. Results

After the simulated time of 2500 s, the temperature distribution (Figure 6) and melting front position (cf. Table 2) were derived. As in stage 1, the three codes yielded similar results. The temperatures are slightly higher than in stage 1 due to the additional heat source, and the melting front shifted by approximately 1 mm towards the bottom.



Figure 6: Temperature vs. *y* coordinates for the three codes obtained in stage 2 of the benchmark.

4.3. Stage 3 4.3.1. Description

As the next step approaching the design of the MSFR freeze valve, a 10 mm thick pipe wall, meshed in the same way as the salt volume, is added to the right side of the model (see Figure 7). The pipe is made of Hastelloy N with properties taken from Tiberga et al. (2019) and listed in Table 5.



Figure 7: Geometry with boundary (marked as "BC") and initial conditions (marked as T_0) of stage 3. The dark blue color indicates the molten salt, the light blue color indicates the solid salt, and the pink color represents the metal wall.

Conjugate heat transfer relations are applied on the interface between the salt and the metallic wall. All other boundaries of the pipe wall are adiabatic, including the top boundary. The initial wall temperature is 831 K. In stage 3, gravity is discarded to analyze how heat conduction from the wall in itself affects the melting process.

Property	Value	Unit
ρ	8860	kg m ⁻³
λ	23.6	$W m^{-1} K^{-1}$
c_p	578	$J kg^{-1} K^{-1}$

Table 5: Thermophysical properties of Hastelloy N used in the benchmark.

Since significant complexity is added to the third benchmark stage, an additional mesh and time step convergence study was performed. The mesh refinements with the 0.5 s time step were: 100×55 , 200×110 , 400×220 , and 800×440 . Based on the results of the mesh refinement, the 800×440 mesh was selected for the final result. Therefore, compared to the mesh-converged solution of stages 1 and 2, the meshing in the third stage is refined by a factor of four. The time steps analyzed on the 800×440 mesh were 0.5 s and 0.1 s and very little change was observed, suggesting that at these conditions our models are fully converged with respect to the time step.

4.3.2. Implementation

In STAR-CCM+, the wall is a separate solid region with its own properties. A contact interface was created between the wall and the salt and a conjugate heat transfer relation was added (see section 3.1).

In OpenFOAM, the mesh was decomposed into a solid part (for the Hastelloy) and a liquid part (for both the molten and the frozen salt), each with their own set of thermophysical properties and their own set of initial and boundary conditions. The temperature at the metal-salt interface was calculated based on a harmonic averaging of the heat fluxes (see section 3.2).

In DGFlows, a material tag was added to the solid and the liquid region, where for each tag a set of thermophysical properties wasassigned. At the metal-salt interface, the no-slip condition was imposed, however no explicit treatment was needed for the energy equation as the temperature continuity condition at the interface follows naturally from the penalty terms included in the SIP-DG formulation (see section 3.3).

4.3.3. Results

Figure 8 shows the temperature obtained in the third stage with the OpenFOAM model. Whereas the models for stages 1 and 2 yielded quasi onedimensional results, this was no longer the case for stage 3, since the addition of the metal wall produced a variation of the temperature in the x-direction. Because all boundaries of the metal wall were adiabatic (see Figure 7), no heat was conducted into the metal wall from the top and therefore the highest temperature values can be found within the salt. Due to the better thermal conductive properties of Hastellov N compared to the salt, below a height of approximately y = 0.17 m, higher temperatures and an enhanced melting rate were observed in the vicinity of the wall. The melting fronts for the meshconverged solution of 800×440 cells obtained by the three codes are plotted in Figure 9. Whereas a near-perfect agreement between the three codes was observed for the previous two stages, a discrepancy can now be seen between the melt front positions of DGFlows on the one hand, and OpenFOAM and STAR-CCM+ on the other. The discrepancy appears to be larger in the region close to the Hastelloy wall.

To further shed light on this matter, three locations of interest were chosen, for which results are probed along a vertical line, at: x = 0 mm, x = 75 mm, and x = 95 mm. Temperature profiles for all three probes at t = 2500 s are plotted in Figure 10. From the temperature probes, one can observe that far away from the Hastelloy wall, at x = 0, the agreement between the three codes is excellent, however as one moves closer to the wall, DGFlows produces different results from the other codes.



Figure 8: Temperature contour plot for the entire geometry of stage 3; results taken from OpenFOAM. The 800×440 mesh was used with a time step of $\Delta t = 0.5$ s.

Figure 9: Melting front positions obtained by the three codes in stage 3. The 800×440 mesh was used with a time step of $\Delta t = 0.5$ s.





Figure 10 (a, b, c): Temperature vs. y coordinates for the three codes obtained in stage 3 of the benchmark. Results taken at three different x locations.

The results for benchmark stage 3 show that the conjugate heat transfer between the solid wall and the melting salt appears to introduce a discrepancy in the modelling behaviour of the three codes. A separate validation was performed for the conjugate heat transfer without phase change with the use of a different model, where virtually identical results were observed between DGFlows and STAR-CCM+. Based on these observations, we believe the coupling between the conjugate heat transfer and the non-linear phase change phenomena are the source of disagreement between DGFlows on the one hand, and STAR-CCM+ and OpenFOAM on the other.

Note that the three codes adopt different modelling strategies for the conjugate heat transfer. OpenFOAM solves the heat equation in the salt and metal domains sequentially (i.e. first the heat equation in the salt is solved, then the heat equation in the metal), whereas in DGFlows the heat equation is solved for the full domain and no distinction is made between the solid and the liquid regions. In STAR-CCM+, a segregated solver was used, which is a method similar to the one used by OpenFOAM.

It is possible that the simultaneous solution of the heat transport equation leads to a faster melting in the vicinity of the Hastelloy wall with respect to a sequential solution of the heat transport equations, since the salt immediately experiences the presence of the enhanced heat transfer through the metal wall, instead of the solution of the heat transfer through the metal wall lagging behind that of the salt. However, we would expect that the discrepancy between the codes would become smaller for smaller time steps, which does not seem to be the case, see section 4.3.4. Due to a lack of a suitable analytical or experimental reference solution, we cannot say which of the three codes produces the most correct results. For now, we identify the coupling of the conjugate heat transfer and solid-liquid phase change modelling as a potential source of discrepancy between numerical software and we recommend to take this matter into consideration when modelling the MSFR freeze valve.

4.3.4. Results of the Sensitivity Analysis

Figure 11 shows the results of the mesh refinement sensitivity study. With every refinement step, the difference between the results from the previous coarser mesh and the new finer mesh becomes smaller. STAR-CCM+ showed the largest sensitivity to the mesh size, whereas DGFlows' results did not vary significantly between the different mesh refinement cases. Possibly, this is due to the high accuracy of the discontinuous Galerkin method in calculating
the discontinuity in the temperature gradient at the interface between the solid and the liquid salt, thus preserving the overall accuracy of the numerical scheme at the metal wall. It was decided that the 800×440 mesh should be used for this and next benchmark stages. Figure 12 shows the sensitivity of the temperature results to the time step. For all three codes, very little difference could be observed between a time step of $\Delta t = 0.5$ s and $\Delta t = 0.1$ s, and therefore $\Delta t = 0.5$ s was used for the rest of the analysis of stage 3.







(c) DGFlows

Figure 11 (a, b, c): Temperature vs. *y* coordinates for the three codes obtained in the mesh refinement sensitivity analysis of stage 3. Results shown for x = 90 mm. Here, a time step of $\Delta t = 0.5$ s was used.





Figure 12 (a, b, c): Temperature vs. *y* coordinates for the three codes obtained in the time step sensitivity analysis of stage 3. Results shown for x = 90 mm. Here, a mesh of 800×440 elements was used.

4.4. Stage 4 4.4.1. Description

In stage 4, we allow for natural circulation. Salt closest to the heated wall will have a lower density and will start flowing upwards. To model the free convection of the salt, we use the Boussinesq approximation:

$$M_S = -\rho g \beta \cdot \left(T_{ref} - T \right)$$
 (N m⁻³), (21)

where the salt's thermal expansion factor is $\beta = 2.5 \cdot 10^{-4} \text{ K}^{-1}$, based on the density data in Beneš and Konings (2009), the gravitational acceleration $g = 9.81 \text{ m s}^{-2}$, and the reference temperature $T_{ref} = 831 \text{ K}$. The dynamic viscosity of the salt is approximated to $\mu = 7.5 \cdot 10^{-3} \text{ Pa} \cdot \text{s}$ (Beneš and Konings (2009)) and a fully laminar and incompressible flow is assumed.

4.4.2. Implementation

The time step was lowered to 0.1 s for stages 4 and 5 to account for the increased convergence requirements (i.e. Courant number below 1) when changing the model from conduction only to convective phase change. In STAR-CCM+, in stages 4 and 5, the maximum number of inner iterations was changed from 30 to 90 to achieve better convergence. In both OpenFOAM and DGFlows, three outer iterations were added to better resolve the velocitytemperature coupling. Computational requirements increase significantly from stage 3 to stage 4, as a set of new equations is added to the model in addition to reducing the time step and increasing the number of iterations.

4.4.3. Results

Figure 13 shows the absolute flow velocity for the fourth benchmark stage, also showing the streamlines. A maximum velocity of around $u = 4 \text{ mm s}^{-1}$ is reached, corresponding to a Reynolds number of $Re \approx 468$. Therefore, our assumption of laminar flow is justified. Two recirculation zones can be observed, one near the top of the domain where the salt is being heated and one near the melting front. One may observe the salt flow up along the warmer Hastelloy wall and down along the melting front.

Figure 14 shows a comparison of the melting front positions for all three codes. The addition of natural convection, as opposed to heat conduction

dominated phase change, results in an increase of the melting rate and compared to stage 3, more of the salt has melted. However, similarly to what has been observed by Aji (2020), the effect of natural convection slows down the melting of the freeze plug at the sides, thus prolonging its opening time. Instead, the heat transfer is shifted towards the top side of the plug.

In addition, a significantly better agreement was observed between the three codes. We believe this is because the higher heat transfer within the bulk of the salt, induced by the natural convection, reduces the local effect that the solid wall has on the overall melting rate. The better agreement in stage 4, as opposed to stage 3, further supports our hypothesis that the coupling of the heat transfer within the salt and the metal domains was the source of discrepancy between STAR-CCM+, OpenFOAM, and DGFlows.



Figure 13: Contour plot of the flow field with streamlines for stage 4. Results obtained with OpenFOAM, with a 800 × 440 mesh and a time step of $\Delta t = 0.1$ s. A cut-off velocity of $4 \cdot 10^{-5}$ m s⁻¹ (i.e. approximately 1% of the maximum velocity) was used for the streamlines.

Figure 14: Melting front positions obtained by the three codes in stage 4. The 800×440 mesh was used with a time step of $\Delta t = 0.1$ s.

Figure 15 depicts the absolute velocity profiles for all three codes, evaluated at the same *x*-locations selected for stage 3 (i.e. x = 0 mm, x = 75 mm, and x = 90 mm). Figure 16 shows the temperature profiles at these locations. Similar results are obtained for the absolute velocity profiles for all three codes, although small differences are still visible. Interestingly, for y = 90 mm, the velocity results for OpenFOAM appear to deviate from those obtained by STAR-CCM+ and DGFlows; the code predicts a lower peak value of the velocity around y = 0.12 m. Regarding the temperature profiles, an excellent agreement between the three codes was obtained, with the results hardly distinguishable from each other.





Figure 15 (a, b, c): Absolute velocity profiles obtained by the three codes in stage 4. Results taken at three different *x* locations.



(b) x = 75 mm



(c) x = 90 mm

Figure 16 (a, b, c): Temperature vs. y coordinates for the three codes obtained in stage 4. Results taken at three different x locations.

4.5. Stage 54.5.1. Description

In a molten salt reactor, the fuel salt above the top of the freeze valve is not stagnant, but is assumed to be in motion, both during normal operation and emergency drainage of the fuel salt into the dump tanks. The movement of the salt at the freeze valve's top boundary might influence the dynamics of the phase change. In our model, circulation is enforced by moving the top lid in the positive *x* direction with a tangential velocity of 0.01 m s⁻¹. This value was sufficiently high to influence the melting behaviour of the freeze valve, but sufficiently low such that our assumption of laminar flow is still valid.

4.5.2. Results

Figure 17 shows the absolute velocity and Figure 18 shows the melting front positions for stage 5. Compared to stage 4, higher velocities are observed in the recirculation zone near the top of the domain, as a consequence of the velocity boundary condition now imposed at the top wall. However, this boundary condition does not seem to significantly impact the flow in the rest of the domain. Whilst the differences between the fourth and the fifth

benchmark stage are small, the higher degree of mixing at the top leads to a small increase of the melting rate, as can be seen from the overall position of the melting front. Similarly to stage 4, a very good agreement was observed between the three codes.



Figure 17: Contour plot of the flow field with streamlines for stage 5. Results obtained with OpenFOAM, with a 800 × 440 mesh and a time step of $\Delta t = 0.01$ s. A cut-off velocity of $4 \cdot 10^{-5}$ m s⁻¹ was used for the streamlines.

Figure 18: Melting front positions obtained by the three codes in stage 5. The 800×440 mesh was used with a time step of $\Delta t = 0.01$ s.

Finally, one can now have a look at the development of the melting front from the simpler to the more detailed model, depicted in Figure 19. The changes in the shape of the melting front between stages 2 and 3, and 3 and 4 are substantial and show the importance of conjugate heat transfer and natural convection. An important figure of merit in the MSFR freeze valve design is the opening time, which is one of the factors that determine whether the proposed design meets the safety requirements. Omitting the Hastelloy wall from the simulations would result in a considerable under-prediction of the freeze valve opening time. On the other hand, neglecting the role of natural convection would lead to an over-prediction of the valve opening time.



Figure 19: Melting front positions obtained in all stages of the benchmark by STAR-CCM+.

5. Conclusions

Due to the lack of suitable experimental benchmark data, experimental validation of MSFR freeze valve models is very difficult. In order to help overcome this challenge, this work proposes a numerical benchmark for the MSFR freeze valve consisting of five different stages. A principal feature of this benchmark is a step-wise addition of complexity with every stage of the benchmark. This allows for pinpointing which parts of the model introduce discrepancies between different software suites. Additionally, this benchmark can easily be replicated in other CFD codes. In the present work, results of the benchmark were obtained using solid-liquid phase change models and flow and conjugate heat transfer solvers implemented in STAR-CCM+, OpenFOAM and DGFlows. For all three codes, the melting front position, temperature profiles, and absolute velocity profiles were compared. The

results from the benchmark demonstrate a consistent performance of the three codes' phase change models and flow solvers. However, a discrepancy between the results of DGFlows on the one hand, and STAR-CCM+ and OpenFOAM on the other, was observed when adding conjugate heat transfer to the benchmark. This may indicate a different performance of segregated conjugate heat transfer approaches as opposed to fully coupled ones for modelling solid-liquid phase change. For this reason, we recommend carefully considering the conjugate heat transfer modelling approach when simulating the MSFR freeze valve or any other problem where a coupling between conjugate heat transfer and solid-liquid phase change phenomena plays a role. The results from all three codes have been placed in an online repository, and interested users of CFD codes are invited to carry out the benchmark exercise and compare their results and findings with ours, which can help further develop numerical tools dedicated to phase change and molten salt reactors.

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Data Availability

Data presented in the figures, to be used for comparison with more codes, can be found under the associated link: <u>https://doi.org/10.5281/zenodo.7821693</u>.

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107

Closing remarks

With a good amount of codes being compared with the use of this benchmark in the future, the author's hope is to contribute to the expediting of licensing of MSRs through the choice of codes having the highest probability of granting success. At the same time, methods that seem to yield erroneous results can be pinpointed and updated, which would increase the quality of future research on salt phase change. Through a detailed analysis of the methods utilized by a CFD code, it is possible to design dedicated experiments whose focus would be on measuring parameters in the regions that are prone to generate discrepancies in the results. This way, both the models and the physics of the problem itself could be understood better.

5. Research on molten salt loops

MSR systems, just like with any other facilities requiring cooling of the process fluid, base their architecture on circuits or loops. The coolant, a molten salt in the case of the MSRs, is circulated around a loop, predominantly with the use of a pump. The flow of the molten salt allows for heat from the reactor core to be transported to and extracted in a heat exchanger and further used for steam production.

Loops can also be built in a lab as devices serving several research purposes; they can be used as test rigs for flow, heat transfer, and corrosion measurements, and component testing, among others. Integrating a freeze valve into a molten salt loop allows for its testing at conditions resembling the ones of an MSR, where the freeze valve is not fully isolated from the rest of the circuit and is under the influence of the salt circulating in its vicinity. It is important to conduct experiments at realistic conditions in order to understand how a sum of various effects influences the freeze valve's behavior. Besides, using freeze valves to isolate one part of the experimental loop from the other significantly lowers the complexity and price of the setup, as the usage of custom-made exotic-alloy mechanical valves for isolation purposes is avoided.

In an MSR, apart from transporting the heat, the molten salt flowing in a loop undergoes or contributes to many other processes that can be studied in laboratory loops. It can be chemically and physically processed in a continuous manner, which increases its purity (and thus the lifetime of the reactor) and allows for separation of unwanted fission products. Delayed neutron precursors (nuclei of fission products that do not release neutrons immediately after the fission) are transported with the fuel salt to further places in the primary circuit, which increases materials irradiation away from the core and changes neutronics characteristics of the fission process. Thermal gradient across the loop enhances corrosion; products of the corrosion reactions are transported with the flowing salt and can precipitate in locations prone to clogging. During accidents, the flow of the salt lowers the temperature of the reactor, keeping it in a safe state. Understanding these phenomena is crucial to the safe and efficient design, construction, operation, maintenance, and decommissioning of MSRs. To be able to model the behavior of power plants using numerical techniques and to obtain an operational license, experimental molten salt loop facilities are built. Separate and integral effect tests can be executed at these facilities to validate computer models and confirm that the reactor will work as expected. Apart from thermal-hydraulic effect studies and component testing, salt processing and corrosion phenomena can be investigated with the loops as well. This chapter discusses the past and ongoing research on molten salt loops, including the author's own.

5.1. Historical ORNL loops

Prior to the operation of the MSRE, thermal convection loops were the main type of research facility that was used for dynamic studies of molten salts (in contrast to static studies where salts do not flow). Since the major issue with molten salts is their compatibility with the structural materials they interact with, the loops were used primarily for corrosion and mass transfer studies. By building the loops from materials to be screened, filling them with chosen molten salts, and inducing the natural circulation, it is possible to investigate which combination is the most efficient economically and safety-wise to be used in a full-scale plant. Tens of such loops were built at the ORNL to pick the material for the MSRE and gain operational experience working with molten fluoride salts.

The majority of the loops were of the same design referred to as a *harp configuration*. The exemplary loop NCL-20 [151] was fabricated from $\frac{3}{4}$ " (19.1 mm) OD and 1.83 mm thick Hastelloy N tubing. It was equipped with surge tanks to allow salt expansion and sampling, as well as a flush and a dump tank for filling and draining the loop (see Figure 31). Between the bottom tanks and the harp (the circulation zone), horizontal freeze valves were used to isolate the systems from one another, as mechanical valves couldn't be used. With the use of clamshell heaters on the hot leg, and coolers on the cold leg if needed, a desired temperature distribution was



Figure 31. Natural circulation loop in a harp configuration used in the Molten Salt Reactor Program [151]. Photo courtesy of the Oak Ridge National Laboratory. achieved. By heating up the molten salt at the bottom and side legs, a temperature gradient resulting in the density gradient was established, which caused the salt to flow.

Wetted surfaces of the loops were made entirely from the same structural material so that dissimilar materials do not influence the corrosion results. In some of the loops, e.g. loop NCL-16 [152] shown in Figure 32, there was a 1/8'' (3.18 mm) OD rod immersed in each vertical leg, on which there were corrosion specimens (coupons) that could be extracted from the loop. They were made of materials which had a particular influence on the corrosion, and their dimensions were 19.05 x 9.65 x 0.76 mm. The molten salt could be sampled for analysis as well, thanks to a sampling system atop each vertical leg.

Among others, the fluoride salts LiF-BeF₂-UF₄ [152] and NaBF₄-NaF [151] were tested in Hastelloy N loops with the temperatures between approximately 430 °C and 700 °C. Specimens were analyzed after some thousand hours of exposure (e.g. 19,300 h for NCL-20) and conclusions were drawn regarding which material worked best and what conditions specifically affected the corrosion rate. The next step of the materials selection involved testing the candidate materials' behavior in the forced convection regime.

However, in an MSR, the chemical attack is not the only issue. Radiation is another factor in the equation that was studied at the ORNL. The Oak Ridge Research Reactor (ORR) was a pool, water-based reactor built in the late 1950s which was used for irradiation experiments [153]. It had a power output of 30 MW and an average thermal neutron flux of $1.6 \cdot 10^{14}$ n/cm²s. Its horizontal beam hole was used to host and operate two uranium-fluoridecontaining thermal convection loops made of Hastelloy N and having graphite channels, shown in Figure 33 [154], therefore resembling the MSRE's reactor core with the graphite moderator. Material compatibility with the salt, the stability of the fuel salt under radiation, and the fission product chemistry were investigated. The salt used was ⁷LiF-BeF₂-ZrF₄-UF₄ and the enrichment of the uranium went up to 2.1 mole %.



Figure 32. Thermal convection loops NCL-15 and NCL-16 prior to operation [152]. Photo courtesy of the Oak Ridge National Laboratory.



Figure 33. In-Pile Molten-Salt Loop No. 1 in the ORR [154]. Photo courtesy of the Oak Ridge National Laboratory.

The first loop of that set was irradiated at full reactor power for more than 1300 h, with 289 h of operation including being filled with fuel salt. The second, improved loop (see Figure 34) was irradiated at full reactor power for more than 1700 h, with 1369 h of operation including fuel salt in it. Although the successful operation of the loop components was demonstrated as a result of the experiments, the loops developed fission product and fuel salt leaks and the tests needed to be stopped prematurely when the intention had been to run them both for more than 8000 h. Initiating events of the failures turned out to be stresses due to thermal cycling and thermal expansion of different elements of the loops. The initial calculations suggested that the expected stress should be within material limits, however, the experiments indicated that the ductility of Hastelloy N is reduced at high temperature and under irradiation. Improving the structural properties of the alloy was suggested for future experiments by increasing titanium concentration to 2%.



Figure 34. In-Pile Molten Salt Loop No. 2 in the ORR [154]. Photo courtesy of the Oak Ridge National Laboratory.

The ORNL team conducted tests not only with molten salts, but also with molten lead, which was proposed as a coolant for molten salt breeder reactors [155]. According to them, lead could be in direct contact with the molten salt, thus removing the need for heat exchangers, which made it even more attractive. Several thermal convection loops were built of Croloy (steel with 2.25% Cr and 0.5-1% Mo), carbon steel, stainless steel 410, and Nb-1%Zr alloys, to test the compatibility of the materials with liquid lead. No nickel materials could be used because of the high solubility of nickel in lead. All steel loops tended to plug in the cold region due to the formation of dendritic crystals of iron and chromium, and the niobium-zirconium alloy showed the best results.

After the materials and salts were tested in the thermal convection loops, the promising candidates were used to build loop facilities equipped with pumps that would emulate the reactor operating conditions, with the exception of radiation. A total of 25 forced convection loops for molten fluoride salt corrosion testing were built at the ORNL in the early 1960s [156], with the compatibility of various structural materials (mainly Hastelloy N and Inconel) under differing conditions of temperature and flow rate being investigated. Just like the natural circulation loops, the forced convection loops were standardized so that experimental results could be reliably compared with each other, as well as to reduce the cost of construction. Each loop consisted of a pump, two heated and a singular cooled section, a freeze valve, and a drain tank (see Figure 35). A centrifugal sump pump with an overhung vertical shaft designed at the ORNL was used in the loop, where in total over 40 such pumps were made in four different materials for various test rigs.



Figure 35. Forced convection loop designed by the ORNL [156]. Figure courtesy of the Oak Ridge National Laboratory.

Most of the loops' tubing was of ½" (12.7 mm) OD and 18 m long, and the entirety of the wetted surface was made of the same material. The maximum wall temperature was between 648 and 815 °C, the maximum temperature difference between the cold and hot leg was 93 °C, and the salt flow rate could go up to 3 gpm (0.68 m³/h). Thermocouples were spot

welded to the tubing and used for temperature measurements that allowed for control of the electrical resistance tube heaters and of the air blower that cooled the coiled cold leg.

The salts that were studied were fluorides of sodium, lithium, beryllium, zirconium, thorium, and uranium in various proportions. Samples of the salt were removed periodically with a sampling device attached to the pump, and analyzed to indicate corrosion rates. To accurately extrapolate corrosion rates to a reactor case, very long duration tests had to be run. Some of the loops operated for more than two years, and the total accumulated operating time summed to 290,000 h.

To start the loop operation, after initial equipment checks, the chosen molten salt was poured into the drain tank at a very high temperature to avoid solidification. Inert gas pressure was applied and the salt was moved up to the circulation zone. The freeze valve was closed and the pump speed was then increased. The first load of salt was circulated for 2 h to clean the system, and then removed and replaced with the salt used for the corrosion test. When the tested salt was circulating, the desired temperature and flow conditions were established by manipulation of heater and cooler power and pump speed.

As a result of these corrosion tests, Hastelloy N was chosen as a material for the MSRE to be used with the LiF-BeF₂-ZrF₄-UF₄ salt [92], with the corrosion rate expected to be less than 25 μ m/yr. [156]. The corrosion analysis indicated that the primary corrosion product was chromium which reached an equilibrium concentration after 5000 h of operation, so decreasing its amount in the alloy was advised.

The loops were also used for heat transfer measurements (see Figure 36) and calculations of local heat transfer coefficients, salt velocity, and Reynolds, Prandtl, and Nusselt numbers. Experimental data agreed well with the empirical Sieder-Tate correlation in the fully turbulent region and with the modified Hausen equation in the transitional region, which proved that molten salts behave like other Newtonian fluids [157] and indicated that they have an extended transition region from the laminar to the turbulent flow. With this knowledge, the scientists were able to model the behavior of molten salts in the same way that other conventional fluids were modelled.



Figure 36. Forced convection loop FCL-2b used for heat transfer coefficient measurements [157]. Photo courtesy of the Oak Ridge National Laboratory.

Later on in the 1980s after the MSR Program was terminated, the ORNL team, to benchmark experiments that Sandia National Lab had performed, investigated the solar salt in Incoloy and stainless steel 304L and 316 natural circulation loops using the same principles as in the previous fluoride loops [158]. They concluded that 600 °C was the temperature limit for use of solar salt in these alloys, as the initially low corrosion rates of less than 13 μ m/yr. increased rapidly when the temperature of 600 °C was exceeded. The main corrosion processes were the growth of thin oxide scales and chromium dissolution in the salt. Like before, the same natural convection loop design proved a reliable tool for corrosion and mass transfer measurements. However, no further historical reports of the ORNL's work on molten salt loops have been found by the author. Sandia's historical loop experiments focused on nitrate salts [159] and are not considered relevant for further study in this overview.

5.2. Research loops today

There are a plethora of currently existing molten salt loop research facilities worth mentioning. Even though publicly available experimental data obtained with them is still rather scarce, an analysis of concepts being studied, materials and configurations used, and instrumentation techniques implemented allows for deduction of the most favorable solutions and designs. Table 2 compares some of the characteristics of all the loops described later in this section.

5.2.1. ORNL

The ORNL has recently begun to study molten salts – although much less extensively than 60 years ago. The Liquid Salt Test Loop has been built to demonstrate the technology for use with molten fluoride salts (see Figure 37), as the ORNL's ambition is to develop a fluoride salt-cooled high temperature reactor (HTR). The loop is equipped with heat tracing and an induction heater for tests of a pebble bed contained in a SiC tube and filled with 3 cm diameter graphite spheres. The facility can have additional valves, sensors, and other components installed to be tested at high temperature. So far no research data has been made public, to the best of the author's knowledge, even though the loop is already around 10 years old.

Another facility being built at ORNL, Facility to Alleviate Salt Technology Risks, aims to enable extensive testing of CSP technologies based on chloride salts [160]. It will have its own salt preparation system capable of supplying 200 kg batches of salt and once operating, it will be the largest hightemperature molten salt facility in the US, with 120 l of salt in circulation.

Facility /	Construction	Liquids	Operational	Notes
Institution /	materials /	used	temperature	
Source	dimensions			
Liquid Salt	Inconel 600	FLiNaK	max. 700 °C	Equipped with
Test Loop /	pipes; SiC test			a centrifugal
ORNL / [17],	section / 162.7			sump pump and
[161]	mm OD, 6.35			a salt-to-air heat
	mm thick			exchanger
Thermal	Stainless steel	FLiNaK	min. 540 °C	Natural
convection	316H pipes /		max. 650 °C	convection;
loop / ORNL /	26.7 mm OD,			corrosion
[162]	2.79 mm thick			samples hanging
				in the loop
Facility to	Hastelloy C-276	mixture	max. 725 °C	Forced
Alleviate Salt	and Inconel 600	of NaCl,		convection, loop
Technology	/ 60.3 mm OD,	KCI,		connected to
Risks / ORNL	3.91 mm thick	MgCl2,		a 200 kg salt
/ [160]	pipes	and		preparation
		CaCl2		system
Molten Salt	Inconel 625	solar	max. 565 °C	Four heater-
Natural	pipes / 21.3	salt;		cooler
Circulation	mm OD, 3.65	fluoride		configurations
Loop /	mm thick;	salts in		available
Bhabha	Stainless steel	the		
Atomic	316 expansion	future		
Research	and melt tanks			
Centre / [86]				
DYNASTY /	Stainless steel	water;	N/A	Can be used for
Polytechnic	316 pipes / 42	glycol		both natural and
University of	mm OD, 2 mm	and		forced
Milan / [88],	thick	Hitec in		convection
[163]		the		experiments
		future		
Heat Transfer	Inconel 600	Hitec	min. 200 °C	Forced
Salt loop /			max. 400 °C	convection
SINAP / [103]				
FLiNaK loop /	Hastelloy C-276	FLiNaK	min. 500 °C	Forced
SINAP / [103]			max. 600 °C	convection,
				induction heating
				of a pebble bed
				test zone

Table 2. Characteristics of chosen molten salt loops recently used in research.

Nitrate Natural Circulation Loop / SINAP / [103]	Stainless steel 316	Hitec	min. 200 °C max. 400 °C	Natural circulation
High- temperature molten salt loop / UW / [36]	Stainless steel 316 tubes / 25.4 mm OD, 3.05 mm thick	MgCl₂- KCl, FLiNaK	min. 500 °C	Equipped with a thermal mass flow meter, a laser manometer, and a centrifugal pump; custom- made instrumentation
Nitrate Salt Large Heat Transfer Loop / UW / [36]	Stainless steel 316L pipes / 60.33 mm OD, 3.91 mm thick	nitrate salt	N/A	Forced convection
Nitrate Salt Materials Loop / UW / [36]	Stainless steel 316	KNO₃- NaNO₃	N/A	Forced convection; seven immersion heaters inside the piping
Natural Convection FLiBe Loop / UW / [164]	Stainless steel 316 tubes / 25.4 mm OD, 3 mm thick	FLiBe	min. 500 °C max. 800 °C temperature gradient up to 120 °C	Natural convection; copy of the ORNL's design; fiber optics and electrochemical probes used
Various microloops / TerraPower / [165]	Stainless steel 316, stainless steel 316H, Inconel 600, Inconel 625, Hastelloy N, Hastelloy C- 276, Incoloy 800H, Nickel- 201 / 6.35 mm OD, 0.89 mm thick	NaCl- MgCl ₂ ; MgCl ₂ - NaCl- KCl	min. 453 °C max. 760 °C most loops max. 620 °C	Natural circulation loops of the same design used for material screening



Figure 37. ORNL's Liquid Salt Test Loop [166]. Photo courtesy of the Oak Ridge National Laboratory.

The ORNL also uses natural convection loops [162] – here, a thermal convection loop has been made for corrosion measurements. An overflow tank was located above the hot leg ("top pot" in Figure 38), and a fill tank above the overflow tank; there was also a drain tank below the cold leg. The entire loop was wrapped with heating tapes and thermocouples were positioned in thermowells around the loop. Stainless steel 316H coupons hanging on wires made from the same material were exposed to the FLiNaK salt for 1000 h. The samples from the hot leg lost their mass and the samples from the cold leg gained mass, which is a typical mass transfer phenomenon due to the thermal gradient.



Figure 38. ORNL's thermal convection loop [162].

5.2.2. Bhabha Atomic Research Centre

Bhabha Atomic Research Centre of India has built the MSNCL loop to support the development of their 600 MWth pebble bed HTR using a molten fluoride salt as a coolant, and their 2 MWe solar power tower system using the solar salt [86]. The loop facility utilizes the solar salt and is used for thermal hydraulic and material compatibility studies, as well as development of instrumentation and plant components. In the second phase of the experimental studies, different fluoride salts will fill the loop.

The loop has a drain/melt tank at the bottom and an expansion tank at the top (see Figure 39 and Figure 40), both equipped with band heaters for keeping the salt molten. 25 kg of the salt are melted in the melt tank and pressurized by argon gas to fill the loop. A pipe-in-pipe air cooler is used as the heat sink and external heaters are the loop's heat source. Four different heater-cooler configurations are available through an exchange of the loop's flanged elements. Temperature is measured by K-type thermocouples both on the outside walls and inserted into the salt through Inconel 625 thermocouple fittings.



Figure 39. Model of the MSNCL [86].

Srivastava et al. [86] managed to validate an in-house developed code LeBENC against all steady state and transient experimental results from MSNCL. They also proved that a correlation developed by Vijayan et al. [167] for thermal convection molten salts loops, relating Reynolds number to Grashof number (see Equation below, with the derivation to be found in [168]), is correct, which was a notable advancement of the understanding of molten salt's thermal hydraulics.

$$Re_{ss} = C \left(\frac{Gr_m}{N_G}\right)^r \tag{17}$$

where Re_{ss} is a steady state Reynolds number, C and r are constants that take different values for a laminar and a turbulent flow, Gr_m is a modified Grashof number, and N_G a geometric parameter depending on the loop's design.



Figure 40. Photo of the MSNCL [86].

5.2.3. Polytechnic University of Milan

In Italy, the DYNASTY loop is being developed at the Polytechnic University of Milan (see Figure 41). Its goal is to study internally heated fluids in a natural circulation regime and validate semi-analytical and numerical models. The internal heat source, due to the non-triviality of its is substituted with an "All-External Heat Flux" implementation, homogeneously distributed along the hot sections of the loop, which is in essence heat tracing, akin to the typical arrangements in other loops. Cammi et al. [88] argue that for a very high length-to-diameter ratio of a loop, the external heating can be a good approximation of the internal heating. It is not only the dimensions, but also the structural material and process fluid's heat transfer characteristics that play a role here, which should not be forgotten when comparing results from heat transfer experiments from different loops. A confirmation of validity of this approach is expected to come once more experimental data from the loop is collected.



Figure 41. Photo of the DYNASTY facility [163].

DYNASTY has a fill tank at the top of the loop and a drain tank at the bottom (see Figure 42). The top leg is finned and coupled with an axial fan to provide a powerful heat sink. The bottom part of the loop has two branches that can be isolated from each other; one is used for natural circulation experiments and the other is equipped with an in-line centrifugal pump for forced circulation studies. The natural circulation branch has a Coriolis mass flow meter, which isn't suited for small loops, but might yield reasonable results with a relatively large loop like DYNASTY. Four J-type thermocouples measure the fluid temperature in the center of the pipe. The pipes are wrapped with separately regulated heating tapes, which allows for testing of the heating transients with different configurations of the heaters.

Up until now, the facility has been used with gas and water and without insulation to study heat transfer characteristics of the entire system. Future experimental campaigns are going to work with glycol as a surrogate fluid for the molten salt. The Hitec nitrate salt (NaNO₃ 7 wt%, NaNO₂ 40 wt%, and KNO₃ 53 wt%) will be investigated in the last research campaign [88]. The first experimental results of heating and cooling transients with water presented by Benzoni et al. in 2022 [163] can be used for validation of natural circulation models. Among others, the authors confirmed the oscillating nature of the "Horizontal Heating Horizontal Cooling" and "Distributed Heating" configurations, in which the symmetry of the loop does not allow for the flow to be established in one direction and reach a steady state.

5.2.4. SINAP

Since 2011, SINAP in China has developed three molten salt loops called the Heat Transfer Salt loop, FLiNaK loop, and Nitrate Natural Cirulation Loop, all benefitting Chinese research into a thorium MSR [103]. The Heat Transfer Salt loop was filled with Hitec salt at a maximum temperature of 400 °C and pumped at a flow rate below 2 m³/h. Lessons learned from building and experimenting on the loop for 15,000 h allowed SINAP to better the system design for more demanding future experiments. The FLiNaK loop has operated for "thousands of hours" with the inductively heated FLiNaK salt at


Figure 42. Model of the DYNASTY loop [163].

up to 600 °C with a flow rate of 15 m³/h. The more advanced, higher temperature facility validated the loop layout and sealing technologies. Prototypes of high temperature molten salt pumps, valves, heat exchangers, and instrumentation were successfully developed, and more tests with pebble bed heat transfer are scheduled.

The latest Nitrate Natural Cirulation Loop has worked for a few thousand hours in a natural circulation regime. Its objective is to gather experience on design and validation of a passive decay heat removal system for an HTR. The loop has suffered two failures: both the storage tank cracked due to the lack of heat treatment after machining of the vessel head, and the freeze valve's body (described in the previous chapter). Nonetheless, according to Fu [103], the feasibility of the passive heat removal system was demonstrated.

5.2.5. University of Wisconsin-Madison

UW has used 1500 h towards the dynamic exposure of materials to molten salts, and has built a high-temperature forced convection loop (see Figure 43). Type-K thermocouples are welded to the walls of the tubing or inserted into the loop to measure temperature [36]. Two different, narrower heat transfer test sections have been used for various experiments, increasing usefulness of the facility.

Since the minimum operational temperature of the loop is around 500 °C, off-the-shelf instrumentation and components available for the loop are limited, and in-house developed devices are used to reduce costs and increase accuracy. Differential pressure measurements are carried out with the use of laser level indicators, by using a laser to penetrate the loop through quartz windows in "pressure cans" filled with an inert gas. The flow rate is measured with a custom thermal flow meter utilizing the energy balance equation to solve for the mass flow rate, knowing exactly how much energy has been transferred to the fluid and what temperature gradient has been created through heating. A conventional pump was modified to allow it to operate at higher temperatures; its graphite seal is flushed with an inert gas to keep its temperature below the 500 °C oxidation limit. All the above modifications are required for safe and long-term operation of the loop yielding high-quality and conclusive research data.



Figure 43. UW's high-temperature forced convection loop [36].

Another loop of UW is the Nitrate Salt Large Heat Transfer Loop (see Figure 44). The loop is also pumped and equipped with an ultrasonic flow meter that can work at lower operational temperatures of nitrate salts. Three internal cartridge heaters and six external heating tapes are used for temperature control. Both the internal and external temperature of the fluid and the walls, respectively, are measured with type-K thermocouples. The test section is cooled with chilled water pumped through cooling tubes.

The third loop of UW is called the Nitrate Salt Materials Loop (see Figure 45), similar in construction to the previous two, but equipped with internal heaters unlike any other loop described before. The cooling is done with the use of copper cooling coils wrapped around the piping, in which the cooling water is circulated. Additionally, an ultrasonic flow meter is used.



Figure 44. Nitrate Salt Large Heat Transfer Loop at UW [36].



Figure 45. Nitrate Salt Materials Loop at UW [36].

The newest loop at UW is the Natural Convection FLiBe Loop [164] reaching flow rates of LiF-BeF₂ in 66-34 mol% around 5 cm/s, whose design is a copy of the ORNL's thermal convection loops. Four sets of radiant clamshell ceramic heaters are used and a tube-in-tube heat exchanger cools the salt in the top leg. A total of 49 K-type thermocouples and 8 fiber-optic distributed strain sensors are used to measure the temperature in a very detailed manner.

What is novel in this loop is chemistry monitors; a three-electrode electrochemical probe allows for a qualitative analysis of impurity concentrations. Since the small tube dimensions, low flow rate, and very high temperature do not allow for use of any flow meters, a thermal (cold) pulse method is used to estimate the salt velocity, knowing the distance between two thermocouples and the time it takes for the heat pulse to travel between them. A method of increasing the cooling air flow rate for a few seconds and then turning off the blower for a similar duration before going back to previous conditions produced the most conclusive results. Nonetheless, the uncertainty of these estimates is very hard to determine, and such methods can be used only to confirm whether the salt is flowing in a given direction.

The loops of UW have been used for corrosion and heat transfer studies. Results from several experiments have been published; for example, Apurba et al. [169] showed that the widely accepted Gnielinski correlation [170] relating the Nusselt number with Reynolds and Prandtl numbers does not hold for molten salts at very high Reynolds numbers which have not been studied before. A new correlation was developed, and valuable data is available for code validation purposes. Relating to materials, researchers have reported possible issues with heat-affected zones of the welded areas of tubes which should be studied from the perspective of corrosion effects. Additionally, the necessity of development of high-temperature and corrosion-resistant instrumentation was underlined.

5.2.6. TerraPower

An advanced nuclear reactor developer, TerraPower, has an extensive track record of more than nine years of circulation time accumulated by 49 thermal convection loops made in nine different alloys [165]. All loops are of the same, miniature design called a *microloop* design, made from $\frac{1}{4}$ " (6.35 mm OD) tubes, and are used for screening of materials for a molten chloride salt reactor. During TerraPower's experimental campaign, corrosion of the structural material was quantified with the use of a maximum corrosion depth and a linearly extrapolated corrosion rate, and only three of the alloys tested had corrosion rates lower than 100 µm/yr.: Inconel 600, Hastelloy C-276, and Hastelloy N. Corrosion induced by chloride salts proved to be much more aggressive than one induced by fluoride salts due to different mechanisms of attack.

The researchers at TerraPower stressed the importance of salt purity which is necessary for establishing unbiased and reproducible corrosion experiments, not to mention increased corrosion due to, among others, humidity [165]. Purchased salts were deemed "of suboptimal quality" and a dedicated salt purification process was developed.



Figure 46. TerraPower's microloop design, adapted from [165].

Figure 46 depicts the design of TerraPower's microloops, being a classical parallelogram heated with resistance wire trace heating. The loop is equipped with a surge tank at the top which allows for salt expansion and contraction with temperature. Noteworthy is the application of two simple freeze valves to separate the circulating salt from the loop's two drain tanks. The valves are cooled with a cooling gas and thawed with ceramic clamshell heaters.

Control of the microloops' temperature profile proved difficult. Removing insulation to change the temperature gradient seemed impractical and cumbersome, and increasing the cold leg heaters' power eventually led to stopping the flow. Since the salt circulates in the loop, any alteration to the temperature spreads along the loop's length and affects the temperature in further locations. The loops were allowed to reach their steady state temperature distribution themselves, with only the maximum temperature being controllable, which created variance between different loops. A strict observation of the temperature distribution across the loop enabled prediction of when the loop would fail due to corrosion product buildup, as the flow was gradually slowed down by the growing debris, which resulted in a decreasing lowest temperature of the system. As can be inferred from Table 2, most of the research institutions tend to use widely available stainless steel 316 as a construction material for their loop facilities. It is compatible with both nitrate and fluoride salts (given proper treatment and conditions) – which are both the most actively used salt families in molten salt loop research. Many loops are based on the same, simple design – a small collection of pipes put together with an occasional addition of a different-sized test section. Addition of freeze valves allows for avoidance of costly mechanical valves prone to failure. The simplicity of a loop as a research tool allows for great flexibility in what can be researched, ranging from heat transfer coefficients to corrosion measurements, the loops utilizing different heating and cooling methods and flow regimes.

To summarize the modern molten salt loop research, two areas of interest are common to the abovementioned loops: reliable high-temperature component development and numerical code validation. Molten salts are gaining popularity, but the vast majority of high-temperature material compatibility issues have not yet been resolved – especially not for fluoride salts. An understanding of molten salt's thermal hydraulic phenomena has increased since the MSRE era and the capability for numerical modelling is much greater now, but still more, high-quality experimental facilities are needed to validate the various models. The licensing process of an MSR – even though non-existent as of now – will require both an experimental and a numerical proof that a reactor is safe throughout its entire lifetime. This is where flow loops can come in handy, as they provide a suitable test bed for studying the behavior of molten salts and operational procedures in relevant environments.

5.3. Loops at Seaborg Technologies

To bring their CMSR from the lab to the market, Seaborg Technologies is carrying out an extensive research program investigating the behavior of various molten salts. Just like at the ORNL in the past, Seaborg is testing the compatibility of structural materials with molten salts by first conducting static immersion tests, and then utilizing natural circulation loops to eventually transfer to forced convection systems. The author's industrial PhD project was the initial activity contributing to the company's dynamic test program with its first Nitrate Salt Loop 1 (NS1) and later the Moderator Salt Loop 1 (MS1) facility that was designed, built, and also operated by the author. Each of these loops was equipped with freeze valves, which allowed for studies of their performance alongside serving the essential isolating function. The company's ongoing and planned loop campaigns benefit from experience gained from two loop projects that are described in the following chapters.

136

6. Loop design process

Even though the two loops made during the PhD project were significantly different from each other in the design and experimental objectives, a process of designing them followed similar steps. The design process was based on lessons learned from historical and more recent loop research, Seaborg's quality assurance standards, the ISO 21500:2012 project management standard [171], and sound engineering practices. The following sections attempt to document the author's approach to the loop design.

6.1. Rationale for building the loops

With the core of this PhD work being development of freeze valves and improvement of the understanding of related phenomena, the experimental part of the project could be executed in either of two ways. One of them would be component design and testing in separation from environmental factors influencing the freeze valve operation, i.e. with dedicated freeze valve test rigs. The other would be integrating of the component in a system that would test the freeze valve's functions and overall behavior under relevant conditions, i.e. with flow loops. The author decided to choose the latter approach. With this approach, the research results could be directly used to scale up the technology, and the freeze valves enabled performing of multiple experiments within one loop facility. Integration of the freeze valves with the loops contributed to the increased effectiveness of the experimental campaigns and allowed for a reduction of raw materials used to carry them out. However, choosing this approach enlarged the scope of the experimental part of the PhD project. In addition to designing a freeze valve, designing a loop and the infrastructure around it was necessary. Also, salt property and salt flow studies needed to be carried out to increase the understanding of the loop's behavior.

Apart from its research goals described in the next chapter, NS1, being the first "out-of-the-fume-hood" experiment at Seaborg, had the commercial goal of demonstrating that the company was able to handle molten salts at

a larger scale than in a small laboratory crucible. Design choices were left to the author's discretion (subject to Seaborg's internal quality assurance processes), since no reactor-related research questions were required to be answered with the first loop. NS1 was intended to directly pave the way for more advanced molten salt loop experiments whose objectives were eventually going to be related to the CMSR design verification. A less corrosive, lower-temperature salt and cheaper structural materials were used to gain experience.

After a successful experimental campaign of NS1, a strategic decision was made to focus R&D efforts of the company on maturing the hydroxide salt corrosion control technology. Hence the idea of building a loop circulating NaOH was born. This time the loop was expected to provide research results proving that Seaborg's patented method of corrosion control [172]–[174] works in a dynamic system. As the loop was supposed to be a corrosion test bed, this imposed a number of limitations and requirements with respect to the design. For example, the loop had to be made of the same material in all wetted areas and kept at specified conditions at all times, and not be used for any tests that would disturb the steady state thermal gradient, this being one of the main variables influencing corrosion. As the company's product development is dependent on experimental data, the loop construction had to be conducted rapidly and within a limited budget. This implied that the use of custom-made components (e.g. valves) with long production lead times had to be decreased as much as possible, even though the use thereof would have been deemed greatly beneficial. Freeze valves were ideal for this reason and contributed to the success of the underlying experimental campaign.

6.2. Design decisions based on the literature study

Prior to designing NS1, a literature research was performed on past and existing loops. Most popular dimensions, materials, safety features, equipment, and operational procedures were studied. Additionally, consultations with fellow researchers who have built or worked with molten salt loops took place to discuss nuanced technical matters which are usually

not covered by scientific publications, such as a kind of insulation material needed or minimum dimensions of tubing that prevent clogging.

As a result of the study, it was concluded that nitrate salts are easiest to handle due to their low melting point, compatibility with inexpensive materials like stainless steel, lack of specific purification processes required, and relatively low toxicity, among others. With respect to dimensions, loops small enough that they do not contain more than 500 ml of molten salt, made the most sense to build. An assembly of small tubing that could potentially fit inside a fume hood was chosen. As a result of choosing metricunit dimensions for the tubing, a local manufacturer could be picked to provide the raw material to the lab, which was a more sustainable solution than procuring materials from overseas providers.

Regarding safety measures, a drip tray that could collect hypothetical leaks was placed below the loop, as advised by other researchers. Cover gas outlets (off-gas) were directed to a ventilation system so that possible salt decomposition gases were not a threat to operators, as nitrate salts disintegrate at high temperatures. The loop was heavily insulated to prevent the outer temperature of the insulation from exceeding 50 °C and to lower the energy usage.

Type-K thermocouples were chosen and attached to the outside walls of the loop as these appeared to be the most popular temperature measuring device (see section Research loops today). Synthetic air was used as a cover gas due to its low price and compatibility with the molten salt. No salt flow meters were installed on the loop, as this was not a common practice among microloop researchers. Heating tapes were chosen over other types of heaters due to their popularity and flexibility of assembly.

One of the issues that other researchers have encountered was burst piping and salt splashing due to the improper melting of salt. A safe procedure to melt solid salt is to start heating it from above and progress downwards with the heating while the salt melts, as it expands significantly during phase change. Having two heaters on the melt tank of NS1 allowed for even diversification of the heat load, following the preferred procedure.

After the NS1 experimental campaign finished and the MS1 project was about to start, another, more extensive and accurate literature and market

study was performed. Corrosion of NaOH needed to be understood better, as well as availability of components made from exotic materials to be potentially used in the loop. Nickel-201 needed to be sourced from the US, and imperial-unit dimensions of the tubing were chosen as they were more readily available. Procedures required for the corrosion control system were created. Safety of the installation was enhanced by encapsulating the loop completely in a ventilated box. Some of MS1's features were first-of-a-kind and not tested before, such as the usage of new freeze valve shapes, and engineering judgment needed to be exercised due to the lack of previous experience.

6.3. Project management

To coordinate multiple assignments, procurements, and collaboration with colleagues in the multidisciplinary and extensive loop projects, the author followed best project management practices that streamlined the process.

Each project was divided into several phases, with Phases O-B presented graphically through flow charts on the following pages:

- 1. *Pre-ject* (Phase 0), in which the scope of the project was developed and a project plan created.
- Preparatory work (Phase A), in which a conceptual design, detailed budget, preliminary analysis report (mechanical strength calculations and first CFD studies), operational sequence of the experiment (operating procedures), and chemical and project risk assessments were made.
- 3. Detailed work (Phase B), in which the design was finalized, procurement started, and the facility and its operations described in full.
- 4. Manufacturing and assembly.
- 5. Commissioning (including shakedown tests) and operation (experiment).
- 6. Sample characterization and result analysis.
- 7. Decommissioning.



Figure 47. Flow chart for Phase 0 of a loop build project.



Figure 48. Flow chart for Phase A of a loop build project.



Figure 49. Flow chart for Phase B of a loop build project.

By assigning functions that an experimental facility shall perform to reach the objectives of a project, it is possible to create the requirements necessary for the facility to be able to perform these functions. For example, the function "Drain molten NaOH" can be executed only when there is a requirement imposing that "The loop shall have an opening that allows for draining molten NaOH". Consequently, the requirements inform the design. Each requirement was given a *base*, i.e. an explanation why this specific requirement was made, for reference purposes. Beside requirements having their root in the system's functions, there were requirements that were included after performing a *compliance due diligence*; relevant national and international regulations were studied in order to establish whether what was being designed did not violate national laws or create hazards that the author had not been aware of. As a result, the loops and their automation system conformed to or were inspired by the following regulations:

- Directive 2006/42/EC on machinery [175].
- Directive 2014/68/EU on pressure equipment [176].
- Directive 2009/125/EC on ecodesign requirements for energy-related products [177].
- Executive order BEK nr 1082 af 12/07/2016 (Elinstallationsbekendtgørelsen) on safety for the construction and operation of electrical installations [178].
- Act LBK nr 26 af 10/01/2019 (Elsikkerhedsloven) on electricity safety [179].

The critical elements of the loop design were decided on in the early stages to begin procurement of long lead-time items while the rest of the design was being finalized. As an example, nickel tubes and heating elements were ordered at the beginning of the project, thereby establishing the dimensions of the loop. This solution limits possible changes to the project, but at the same time significantly reduces the time required for the project to finish. It is also easier to design a system according to what components are available, instead of making a perfectly optimized design that is not feasible to be manufactured. This is why a market analysis and budget creation are one of the first things needed after settling on the scope of a project, and establishing contacts with suppliers early on is crucial to the success of a loop construction project. The projects required detailed schedules so that their execution could be tracked. A list of expected deliverables is necessary for creating a project schedule with activities revolving around the creation of deliverables. Having a list of all activities and reasonable estimates of their duration allows for placing the activities in order and assigning the dependencies of one on another. Not all activities follow a waterfall order (one directly following the other); many project-related activities can be done in parallel – if there are enough resources to do these tasks. Once a sequence of all activities is created in a graphical form of a Gantt chart (see Figure 50 for an example), a critical path can be found, i.e. the longest in duration path consisting of activities that lead to completing the project. Any delay to the activities in the critical path would result in the entire project being delayed, so these activities must be controlled strictly. In the case of the loop construction projects, the critical activities have always been related to the procurement of certain electronic components and of nickel tubing. Any deviation from the original plan was acted upon and resulting changes communicated.

A stakeholder management plan is a crucial and often neglected part of project management. In the course of project execution, the importance of effective communication between the suppliers, manufacturers, and the project team became apparent multiple times. Verbal, in-person, or communication via phone proved superior over asynchronous exchange of written messages. At the same time, however, changes to the design or procurement of a component were not always documented in writing, which led to some mistakes and misunderstandings. This is why a clear plan about how often to communicate with the stakeholders and using which means should be prepared at the beginning of the project, and each change should be clearly stated with relevant documents updated.

Communication issues could have been highlighted as a high risk earlier in the planning phase of the NS1 project if a thorough project risk assessment and a risk management strategy had been created, which was done later for the MS1 project. A risk register with 79 risks was created, and the risks were assigned ranks according to their consequence and likelihood. They were

			 												_
Budgeting and procurement			-												4
Budgeting															в
Major quotation collection	ľ	t								Ma	jor q	u ot at	ion co	llection	5
Budget draft															в
Writing										Wri	itingi				T
Review										t		F	Reviev	N	T
Post-review update												+	ς Po	st-revie	40
Approval													+		A
Procurement															
Procurement of long lead time components initiated															t
Supplier database update										÷	Sup	plier	datab	ase up	dat
Numerical validation of the concept	Į.														N
Analytical calculations				Anal	dical	alcul	atipr	15							Т
Overall concept				, Overal	l conce	ept									T
Detailed solutions			p	Deta	iled so	lution	15								T
Pressure considerations			ľ	Pres	sure co	nside	racio	ns							T
Heat transfer considerations			Ļ	Heat	tran sfe	er con	sidle	ration:	s						T
Computational Fluid Dynamics											ا 🖣	Comp	utatio	nal Flu	id I
Overall concept			_	t				Overa	all co	ncep	et				T
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Figure 50. Fragment of a Gantt chart for MS1 Phase A showing dependencies of tasks. Elements lying on the critical path are marked in red.

subsequently placed in an ARTA grid (Accept, Reduce, Transfer, Avoid, see Figure 51) which helped deciding which risk response should be taken to reduce the risk understood as a multiplication of the consequence and likelihood. Most of the risks were categorized as "to be avoided", having a high likelihood and high consequence. The least number of them could be accepted, having a low risk to the success of the project. The risks were prioritized and grouped in nine categories for easier tracking: economy, design, chemical, operational, organizational, environmental, people, project management, and communication. Each risk was assigned to a person responsible for reducing it using a suggested risk response, with a deadline for doing so. All the tasks had an automatic notification system sending an email to an assigned person a certain amount of time before the deadline.



Figure 51. ARTA grid used for guidance in risk management, adapted from [180].

It needs to be stressed that a project risk assessment is not understood here as an experimental risk assessment, which is a separate document of utmost importance in any laboratory. An experimental risk assessment lists all specific chemical and physical risks associated with an experimental procedure and chemicals used in the experiment, and takes into account the material's safety data sheets provided by the suppliers, safety practices of the industry, location of the experiment, the experimental apparatus, personnel involved, and many others.

6.4. Good engineering practice

The term "good engineering practice" covers many areas of engineering and can be loosely defined as a prerequisite to compliance with rules and regulations dealing with safety, product quality, project management, and similar concepts [181]. The design and operation of Seaborg's molten salt loops are based on good engineering practices as there are not strict regulations and requirements applicable to this kind of research facilities – but, they still should be as safe and efficient as possible. Chosen aspects pertaining to NS1 and MS1 loops are described below.

The design of the loops should be based on the existing supply chain's offer and not require costly customization when it is not needed. In NS1 and MS1

loops there was no customization of any component, with the manufacturing of the loops excluded from the definition. All components and instrumentation were off-the-shelf, and the design and operation were adjusted to take this into account – hence the use of freeze valves in MS1, which allowed for avoidance of procuring a costly mechanical valve compatible with the experiment's requirements.

Regarding the project infrastructure, procedures for change control and design reviews should be established. The author created a design logbook where design decisions and their rationale were recorded. Whenever there was a suggestion to change the design of the loop, it had to be supported by evidence showing that the change is needed and that it makes the design better. After each major iteration of the design phase, a design review was completed, in which the design was evaluated with respect to fulfilling the set requirements and functions of the facility. In case the requirements were not met, an action was taken to fix it.

Commissioning procedures should be established in order to verify whether the manufactured and assembled apparatus fulfils the criteria and operates as intended. For the loops, the following tests were performed at least once:

- Visual inspection to check the dimensions of the received loop, weld appearance, angles, whether there are cracks and other defects, if all fittings are placed correctly and gas lines directed where they should be, valves are able to be fully closed and open, etc.
- Leak tightness test at the design pressure of the gas to check whether there are any leaks that need tending to. A leak detection spray was applied on all fittings and leaking connections were tightened or wrapped with a PTFE tape. Pressure relief valves were checked for opening at their setpoint pressure.
- 3. Operability of flow meters, pressure indicators, and the off-gas scrubbing system.
- 4. Control program tests to check whether the automation system performs the operations as they should be performed, e.g. if the operational sequence follows the given temperature settings in time and if the temperatures are recorded. These tests also allow for verifying whether the equipment such as heaters and coolers work properly and if all the electrical connections were made correctly.

Data from both the commissioning tests and the experiment itself was stored on an external server. Whenever there was a change made to an operational procedure or a deviation was observed, it was noted down in an electronic laboratory notebook, as it could have an influence on the final result. Analysis of corrosion measurements was performed with operational procedures in mind so that conclusions were not biased. A technical specification and an operation manual were created so that it was clear how the loop was to be operated, and so that the experiment could be analyzed properly and repeated in the same fashion if needed.

6.5. Design calculations

Overall, it is good practice to perform analytical calculations and numerical studies to guide the design of both a facility and an experimental procedure. This allows for an inexpensive analysis of the operational conditions without having to actually build the experimental apparatus that might be erroneously designed. Moreover, phenomena that a designer was not aware of initially may transpire while performing an analysis of simulation results.

To inform the dimensions of the loop necessary to establish the free convection flow, withstand corrosion for the duration of the experiment, and ensure safety of the installation, a set of calculations was made. First, the minimum required thicknesses of the chosen tubing and tanks to withstand pressures inside the setup were calculated with the use of the relevant ASME standards [182], [183]. A safety margin was added taking into account loss of material due to corrosion.

Second, the minimum height of the loop's circulation zone was found; Rayleigh number Ra was calculated, defined in this case as the ratio of buoyant and viscous forces times the ratio of momentum and thermal diffusivities (α):

$$Ra = \frac{H^2/\alpha}{\mu/(\Delta\rho Hg)} = \frac{\Delta\rho H^3 g\rho c_p}{\mu k},$$
(18)

where *H* is the height of the circulation zone, $\Delta \rho$ is the difference in densities of the cold and hot legs, and μ is dynamic viscosity. Ra is a determinant of the free convection flow, highly dependent on the height of the loop. Natural

convection is possible for $Ra > 10^5$ [184]. The width of the loop is of much less importance and was chosen arbitrarily.

Third, minimum insulation thickness was estimated using the standard heat transfer equations for cylindrical coordinates, with the requirement that the outer side of the insulation did not exceed 50 °C. The size of the insulation is important in designing distances between the equipment and size of the safety enclosure. Additional informative calculations could be performed to estimate the expected pressure drops and velocity of the salt, heat transfer characteristics (e.g. differences in diffusivities of the salt and the structural material), or heating requirements.

The operating conditions of natural circulation loops can be characterized using stability maps that show which combination of parameters described by dimensionless numbers yields a design that results in either of three forms of flow in a loop: a stable, oscillating, or no flow. The characterization is performed by linearizing the balance equations around a steady-state solution (see Vijayan [168] for a detailed explanation). The maps are created using modified Stanton and Grashof, Stanton and Reynolds, or Prandtl and Reynolds numbers [88]. Numerical simulations can be used to take nonlinearity of the equations into account. The design of a loop and temperature conditions to be applied and required to establish a natural circulation flow can be deduced from the stability map, thus lowering a risk of building an experimental facility that does not work.

In the case of NS1 and MS1 loops, a preliminary numerical analysis was performed for each loop, checking whether the first arbitrarily chosen temperature conditions to be imposed on the loop's tubing would result in a flow. CFD models for this purpose can be simplified. Preliminary calculations were done for the liquid salt only, not taking the tubing into account in the model (see an example in Figure 52). After establishing that the conditions applied would result in a stable flow, a more refined model was created where conjugate heat transfer relations were added between the salt and the tubes (see an example in Figure 53). Additionally, an analytical expression derived by Juarsa et al. [185] was used to predict the bulk velocity of the salt, since no measurements of the flow rate could be taken.



Figure 52. One of the first CFD models of the molten solar salt circulating in NS1. Velocity field in the middle plane.

These calculations helped design the experiment, as a range of operational conditions was tested in a modelled system and the most optimal configuration could be chosen for the steady-state operation of the loops. For both loops, a configuration where both the bottom and one horizontal leg were actively heated with the top leg being cooled yielded the best results. By changing the temperature of one heater, it was possible to control the temperature distribution across the loop and reach the desired temperature gradient. The temperature settings used in the simulations were used directly in the programs used for control of the loops' heaters. Besides, the simulations provided insight into what happens with the salt in the loop; the coldest and warmest spots could be identified for subsequent

corrosion specimen analysis. CFD proved to be an important, reliable, and inexpensive tool in designing the experiments.



Figure 53. One of the first CFD models of molten NaOH circulating in MS1. Temperature distribution in the middle plane with the temperature shown above 390 °C and below 460 °C.

6.6. The role of procurement and manufacturing

While scientific value is seldom attributed to procurement activities and the use of established manufacturing technologies, production of a research apparatus – whether in an industrial setting or strictly for academia purposes – could not be executed without these activities. The procurement, including market research, requesting quotations, equipment selection, budgeting and accountancy, establishing and maintaining relationships with suppliers, and waiting for the orders to be delivered amongst many others, easily can (and did in the author's case) constitute the lion's share of time spent on projects such as building loops. Sole equipment selection requires an extensive literature research (including both scientific articles and commercial equipment brochures), a trade-off study, and adjustment of the design of the loop and experimental procedures, which all take a significant amount of time. A sustainable design should take advantage of off-the-shelf components and avoid customization as much as possible to lower the cost and use of resources.

Similarly, finding a manufacturer that is able to provide machining, milling, and joining of (exotic) materials to specification requires resources and knowledge of the manufacturing processes. The loop projects presented in this thesis were performed holistically, with no prior experience, and the author would like to acknowledge the effort put into building experimental facilities from scratch, at the same time appreciating researchers that have gone through a similar path.

7. NS1 loop facility

Introduction

To investigate the operational feasibility of a simple freeze valve being a straight section of a cylindrical tube cooled and heated from the outside, a thermal convection loop called NS1 was designed and assembled by the author. A fully integrated circuit was built that would benefit research on molten salt thermal hydraulics, component compatibility, and process optimization at the same time. Solar salt was used, and the loop was made from stainless steel.

The following section contains an original conference paper characterizing NS1 and describing the research that was done with the use of the loop, presented at the 19th International Topical Meeting on Nuclear Reactor Thermal Hydraulics (ISBN 9789076971261) on March 11, 2022.

NS1 – A NATURAL CIRCULATION LOOP FACILITY FOR MSR RESEARCH

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ABSTRACT

A new natural circulation molten salt loop, NS1, is built at Seaborg Technologies (Denmark) to investigate the dynamics of molten solar salts, intended for application in the molten salt reactor (MSR) design. This includes the verification and validation of Computational Fluid Dynamics (CFD) modeling of the facility. Major aspects of the NS1 experimental campaign are successful salt handling at high temperature and nearatmospheric pressure, and the investigation of freeze valve operation. In the MSR concept, the freeze valve, made of a frozen fuel salt plug, constitutes a key safety component; it is designed to melt and drain the reactor core under the influence of gravity in case of an unexpected temperature increase. To investigate this concept, NS1 is equipped with a freeze valve that isolates the circulating salt from the loop's drain tank. In this paper, we describe the NS1 facility including its monitoring equipment, operating procedures, and salt loading and draining. The thermal hydraulics of the loop including the freeze plug is modeled through simulations using the CFD software STAR-CCM+, and compared to the experimental data, validating the results. The freeze valve is analyzed under prescribed operating conditions of the loop to investigate the performance of this safety component. Although performing satisfactorily when actively heated and cooled, the freeze valve in its current implementation could not be relied on as a passive safety component.

1. INTRODUCTION

Molten salt reactor designs include several passive safety systems rather than complex engineered features of conventional nuclear reactors. The freeze valve is a pivotal passive safety component of MSRs. Its principle of operation lies in solidification and melting of the fuel salt inside the valve to isolate the reactor core during operation and to allow draining of the core in case of an accident. An actively cooled, frozen plug of salt keeps the freeze valve closed. Under faulty reactor conditions, the freeze plug should have the capability to melt and drain the fuel from the reactor core fast enough to prevent any structural damage to the reactor. A substantial increase of the fuel salt's temperature in the reactor core or a loss of power to the freeze valve causes the plug to thaw, which leads to opening the freeze valve and draining the core under the influence of gravity to a dedicated tank placed below the reactor vessel, thus ensuring subcriticality while removing decay heat.

The concept of the freeze valve in an MSR was first tested in the Molten Salt Reactor Experiment at the Oak Ridge National Laboratory in the 1960s [1]. Only recently the MSR research has seen a renaissance and multiple research institutions and companies are investigating molten salt properties, flow characteristics, and phase change phenomena [2]. Studying molten salts through experiments and validation of thermohydraulics and CFD codes is required for proper modelling of MSRs. Such modelling is critical for demonstrating safety of MSR designs, eventually paving the way to licensing of new nuclear technologies [3]. Therefore, we have constructed a new molten salt loop, NS1, at Seaborg Technologies to perform research on molten salt dynamics in reactor-like conditions and modelling thereof.

2. NS1 FACILITY

NS1 is an experimental molten salt loop facility investigating natural circulation of a molten solar salt (Fig. 1). NS1's main research objectives are to test molten salt equipment such as a dual-use drain tank and a passive freeze valve, demonstrate hydrostatic loading and salt draining, and validate CFD models.



Figure 1. NS1 with its insulation and auxiliary connections.

2.1. Design Description

Distinguishing features of the NS1 facility are the freeze valve, drain tank used for filling the loop, and the use of cover gas flowing over the surface of the salt. NS1 can melt the solid salt in the drain tank, push it towards the circulation part, maintain a temperature gradient driving the natural circulation, and eventually drain the salt. Cover gas flow and pressure can be adjusted, and the temperature distribution can be changed. NS1 can be tilted between -10° and 10° with respect to the horizontal in order to study the influence of the inclination angle on the operations.

The loop consists of the following parts: the circulation part (including the molten salt tubes and the overflow tank), drain tank, mechanical valve, freeze valve, gas tubes, and auxiliary connections (Fig. 2). The loop is equipped with heating tapes wrapped around the walls of the tanks and tubes and with an air blower which both are coupled to the instrumentation and control system. The salt bearing tanks and tubes are insulated with a few layers of mineral wool and fiberglass.

The loop itself is made of stainless steel 316. The molten salt bearing tubes are of 12 mm outer diameter and 1.5 mm thick. The gas tubes are of 10 mm outer diameter and 1.0 mm thick. The approximate overall dimensions of the loop without the insulation are 95 cm in height and 90 cm in width. Fig. 3 shows the dimensions of the circulation part.

The primary heat source of NS1 is the hot leg's heating tape (HT-3, cf. Fig. 2), while heating tapes HT-1, HT-2, and HT-4 to HT-6 constitute secondary heat sources. The primary heat sink is the cover gas flowing through the overflow tank. The maximum temperature difference of the solar salt circulating inside the loop is approx. 60 °C. The loop operates under atmospheric pressure and with a maximum temperature of 450 °C. In Fig. 2, the salt's flow is counterclockwise and the cover gas flows from the left to the right.

The molten salt investigated in NS1 is a solar salt which is a mixture of 60% wt. sodium nitrate (NaNO₃) and 40% wt. potassium nitrate (KNO₃), with the relatively low solidus temperature of 494 K and the liquidus temperature of 511 K [4]. The solar salt is used in concentrated solar power plants as an energy storage and conversion medium [5]. The total mass of the salt loaded into NS1 is 0.48 kg, yielding a volume of roughly 266 cm³ at 450 °C.

The overflow tank accommodates salt expansion and houses an interface between the molten salt and cover gas. It has a cover gas inlet and an outlet, enabling the gas flow. Synthetic air is used as the cover gas due to its high corrosion resistance rather than atmospheric air that contains moisture [6]. Countercurrent flow of the cover gas removes heat from the loop.

The drain tank is of dual use; it is used for both draining the loop and loading it with the salt. It acts as a reservoir for the salt when the salt is not in circulation and allows for melting and solidification of the salt. The drain tank is equipped with an inner tube ending at 5 mm above the bottom wall, connecting the drain tank to the circulation part of the loop. The tank also has a gas inlet and an outlet. Such a design allows for loading of the molten salt from the drain tank up to the circulation part, as NS1 does not use a pump.

Above the drain tank there is a mechanical needle valve used for isolation of the drain tank from the circulation part of the loop if such a need occurs. A non-insulated section of the tube between the mechanical valve and the circulation part is referred to as the freeze valve. The outside wall of the freeze valve is cooled by the air blower which causes the salt to solidify in that section of the tube, forming a freeze plug. Thawing the plug, either passively or actively with a heater, opens the freeze valve.

2.2. Instrumentation and Control System

NS1's instrumentation system comprises a set of non-wetted thermocouples, gas flow meters, and gas pressure gauges. The heating tapes and the air blower are controlled by a Programmable Logic Controller (PLC) taking inputs from the thermocouples. There are seven K-type thermocouples installed on the external walls of the loop in locations shown in Fig. 2. There are six heating tapes coupled to one or more thermocouples, depending on the operational procedure. For example, the hot leg of the loop is heated by HT-3 and controlled by TC-4, whereas the freeze valve's air blower is coupled to HT-6 and TC-5. Each operational procedure is executed by the PLC controlling the heating tapes and the air blower so that the temperatures detected by the thermocouples are not below the setpoints defined for each procedure. All measurements are logged for plotting and postprocessing.

3. EXPERIMENTAL RESULTS

During the experimental campaign, we melted the solar salt inside the drain tank, loaded it into the circulation part, and formed the freeze plug. Afterwards, NS1 was allowed to reach steady state conditions. To finish the experiment, we initiated the draining procedure. This section describes the temperature results obtained during the aforementioned steps.



Figure 2. Left: NS1 with its main components. Right: Positions of heating tapes (HT) and thermocouples (TC).



Figure 3. Dimensions of the NS1 model and exact locations of the thermocouples' tips (in mm).

3.1. Molten Salt Loading and Freeze Plug Formation

Once the solar salt in the drain tank is molten and kept at 450 °C, it can be lifted to the circulation part of the loop with the use of the synthetic air's pressure. Before the loading, HT-3 is set to 350 °C (measured by TC-4) and the rest of the circulation part of the loop is kept below 300 °C. Pronounced spikes in the temperature plots appear when the much warmer salt passes TC-5 and the higher placed thermocouples (Fig. 4). Once the salt has reached the TC-1 and TC-2 thermocouples, the first air bubble appears as a sudden pulse in the outlet gas flow rate, the experimenter closes the gas outlet, and begins cooling down the freeze valve (at 300 s in Fig. 4).

The freezing is seen as a temperature stabilisation lasting approx. 230 s (cf. Fig. 4). Afterwards, the temperature decreases with a rate determined by the heat capacity of the solid solar salt and the cooling power. In the meantime, the temperature of the molten solar salt above the freeze valve plateaus at 300 °C in the cold leg. Some mild temperature oscillations are observed at the end of the procedure, distinctly visible in TC-2, which appears to be connected to bubbles of hot air mixing with and transporting droplets of the molten salt around the loop's upper part. The rapid oscillations of TC-4 are caused by the heating tape being activated by the control system to maintain the stable temperature of 350 °C.

The performance of the freeze valve is tested by increasing the loading gas pressure and opening the cover gas outlet valve. A gauge pressure of 100 kPa is easily withstood by the freeze valve and no movement up- or downwards is observed; hence the isolating function of the valve is achieved.

3.2. Steady State Operation

After the closure of the freeze valve has been confirmed, the design temperature conditions are applied with the hot leg reaching 450 °C, whereas HT-4 and HT-5's setpoints are 300 °C. This prevents freezing of the salt in the colder tubes of the circulation part and allows for the observation of the heated salt flowing through the loop. The drain tank's temperature is also kept above the melting point of the solar salt. With the air blower, the temperature of the freeze valve is maintained at 150 °C (measured by TC-5). The cover gas flow rate through the overflow tank is kept at 2.5 cm³/s. It takes roughly one hour for NS1 to reach its steady state conditions (cf. Fig. 5). Oscillations of TC-5 are caused by the control system's operation.



Loading procedure t=[0,1000]s

Figure 4. Temperatures recorded during the loading procedure.


Normal operation t=[0,4000]s

Figure 5. Temperatures recorded when approaching steady state conditions; note that TC-5 is shown with a different scale.

3.3. Molten Salt Draining

When the loop is to be drained, the air blower is switched off and heating tape HT-6 switched on to reach a temperature of 300 °C, which allows for an investigation of the active heating of the freeze valve. The drain tank is kept at 350 °C so that the salt puddle at the bottom does not block the flow of salt. All other heater setpoints are 300 °C except the one assigned to HT-3 which remains at 450 °C. This allows for observations of the draining process through the other thermocouple measurements.

The draining sets in after 665s, opening the passageway through the freeze valve to the drain tank. In Fig. 6 the temperature measured by TC-1 and TC-2 decreases once the salt exits the overflow tank. At the same time there is an increase in the temperature recorded by TC-3, as the warmer salt from the right leg of the loop flows towards the lower part of the loop. Also, at TC-5, the temperature increases, as the salt inside the freeze valve and below melts and is pushed into the drain tank by the warmer salt from above. A second, smaller temperature spike around 820 s is due to the manual tilting of the loop to remove the salt from cavities of the overflow tank and horizontal sections of the loop. Oscillations seen in other thermocouples are due to the control system's operation.

3.3.1. Performance of the passive freeze valve

During another NS1 experimental campaign, the draining procedure was executed in a different way, with the intention of investigating whether the freeze valve can open passively, without the heater melting the plug. The thermal energy stored in the molten salt after deactivating all heaters and the air blower turned out not to be sufficient for melting the freeze plug and opening the valve. Low temperature of the salt puddle in the drain tank and of the freeze plug in conjunction with a very small surface of the plug in contact with the liquid solar salt, and maintaining a flow of cold cover gas in the drain tank (for safety reasons), translated into low performance of the freeze valve in terms of it being a passive safety component. By varying the temperature setpoints and gas flow rates during the draining procedure a better performance can be achieved, however, that goes against emulating conditions of a total loss of power that might occur in a nuclear power plant.



Draining procedure t=[0,1100]s

Figure 6. Temperatures recorded during the draining procedure.

4. MODELLING AND SIMULATION

A CFD model of NS1 and its steady state conditions has been developed with the commercial software STAR-CCM+ (version 2020.2) [7]. Models representing physical phenomena taking place inside the loop were carefully chosen from the models available in the software. Geometry of the circulation part of the loop was drawn, boundary and initial conditions applied, and an appropriate meshing procedure was applied to the model.

4.1. Physics Models

The fluids used in the NS1 facility are modelled as incompressible, turbulent, multiphase flow. A k- ε turbulence model is used, following the study of the internal flow of molten nitrate salts by Bin et al. [8]. This turbulence model is improved by using a second-order realizable two-layer approach suggested by Rodi [9] and Shih et al. [10]. The model's two-layer all y^+ wall treatment of Wolfshtein type [11] is chosen due to better convergence compared to other variants of the two-layer formulation. A segregated flow model with a second-order convection scheme and flow boundary diffusion is applied, and the solver chosen is implicit unsteady, with the Gauss-Seidel relaxation scheme for the turbulence [7]. Adaptive Time Step is used, controlled by the Courant number weighted by the rate of change of volume fraction and limited to the software's default value of 0.4. The minimum time step is set to 1.0 ms.

Table I. Physical properties of the solar salt used in the CFD model. *T* is the temperature in °C [4]

Salt property	Formula
Density [kg m ⁻³]	$2090 - 0.636 \cdot T$
Thermal conductivity [W m ⁻¹ K ⁻¹]	$0.443 + 1.9 \cdot 10^{-4} \cdot T$
Heat capacity [J kg ⁻¹ K ⁻¹]	$1443 + 0.172 \cdot T$
Absolute viscosity [10 ⁻³ Pa s ⁻¹]	$22.714 - 0.120 \cdot T + 2.281 \cdot 10^{-4} \cdot T^{2}$

The fluids are modeled using a Volume of Fluid model with High Resolution Interface Capturing [12], which allows for describing multiphase fluids and interactions between immiscible phases. The solar salt is modeled as a homogenous liquid with the characteristic properties approximates as being polynomial functions of the temperature, cf. Table I. The cover gas is modeled as a non-reacting, multi-component ideal gas, composed of nitrogen and oxygen with respective mass fractions of 79.1% and 20.9%. The surface tension between the solar salt and the cover gas is approximated as 0.11 N/m [13] and the contact angle is set to 90° . A no-slip velocity condition at the wall, characteristic of all viscous fluids [14], is applied.

The structural material is modeled as a constant-density solid, using STAR-CCM+ built-in property data for stainless steel. Additionally, the Conjugate Heat Transfer through the interface between the fluid and the walls is incorporated in the model, with zero contact resistance.

4.2. NS1 Geometry

A full three dimensional model of the circulation part of the loop was created in the software's design tool (Fig. 7; dimensions in Fig. 3). The model is divided into six major boundaries: the gas inlet and outlet tubes (green, top left and right), overflow tank (gray), hot leg (green, right and bottom), cold leg (violet, left), and freeze leg (beige). Each boundary has its separate boundary conditions, associated with the region it belongs to. There are two regions: solid (the tubes) and fluid (inside the tubes). While the molten salt tubes were modeled as realistically as possible, the gas tubes were simplified as extruded volumes based on the surfaces of the holes in the overflow tank to aid convergence of the transient simulation, as the focus of the analysis is on the temperature distribution within the molten salt tubes.

4.2.1. Boundary and initial conditions

To represent the experimental conditions accurately without unnecessarily complicating the model, the following boundary conditions are applied:

- At the gas inlet a constant mass flow of 3.5 mg/s at 25 °C is imposed, which corresponds to the volumetric flow rate measured during the experiment.
- At the gas outlet a pressure outlet condition is applied, with zero average static pressure of the environment above the reference pressure. For both the inlet and outlet the turbulence intensity is set to 1% and turbulent viscosity ratio to 10, as advised for low-to-medium turbulent flows [7].
- At the walls of the cold leg and the overflow tank, convective heat flux to the environment is applied, with the ambient temperature of 35 °C and the heat transfer coefficient of 20 W m⁻²K⁻¹.

- At the walls of the freeze leg, convective heat flux to the environment is applied, with the ambient temperature of 27 °C and the heat transfer coefficient of 7.9 W m⁻²K⁻¹.
- The walls of the hot leg are always kept at the design temperature of $450 \ ^{\circ}\text{C}$.
- The top of the freeze valve is approximated to be at 240 °C (near solidus temperature).
- All other boundaries are modeled as impermeable non-slip walls where the fluid temperature and total enthalpy at the wall are extrapolated from the wall (no heat transfer coefficients available).



Figure 7. NS1 geometry model. Different colours represent elements with different boundary conditions.

The initial conditions are:

- Pressure of 0 Pa above the reference pressure (atmospheric).
- Temperature of the gas 25 °C, temperature of the salt 350 °C, temperature of the steel 300 °C.
- Level of the salt 314 mm above the centerline of the bottom leg, resulting in the overflow tank being filled up to the top of the salt inlet and outlet.
- Salt is stagnant, the air is flowing above it in the positive x direction with the velocity of 0.05 m/s.

4.2.2. CFD mesh

The volume of the loop was discretised using four kinds of built-in meshers, applied automatically by the software to specific regions of the model. In Fig. 8, examples of the meshers are shown: Tetrahedral Mesher (structural material, gray, and salt region, blue), Prism Layer Mesher (at all boundary layers), Generalized Cylinder Mesher (top left gas tube), and Triangle Surface Remesher (on the material's surface, not visible). The base mesh size was set to 1.0 mm, minimum surface size to 4.0% of the base, and maximum element size to 5.0 mm. Ten prism layers with the total thickness of 35% of the base were made with prism layer stretching of 1.4. Surface and volume growth rates (ratios of increasing cell sizes) were set to 1.2. These settings resulted in the volume represented by the total of 8.39 million cells.

Free Surface Adaptive Mesh Refinement with two refinement levels was added to the model to track the interfaces between the solar salt and the cover gas, which is required for proper modelling of phase interactions and bettering convergence. The mesh was updated automatically by the software to get the best possible results. The mesh around these interfaces was updated every tenth time step, which added up to 0.9 million extra cells. Fig. 8 shows an example of such a refined mesh.

4.2.3. Convergence

The convergence of the simulation was controlled by the adaptive time step and adaptive mesh refinement settings. Low Courant numbers and residual levels well below 10^{-3} (cf. Fig. 9) yielded a transient solution whose characteristics were considered accurate enough to be compared with experimental results.



Solution Time 171.3 (s)

Figure 8. Close-up of the left side of the overflow tank showing the mesh on the middle plane with visible refinements at the interfaces between the molten salt and the cover gas.



Figure 9. Plot of residuals of the simulation as a function of the iteration step.

5. CFD MODEL VALIDATION

The experimental results were used to validate the CFD model of the molten solar salt circulating in the NS1 loop. The simulation was carried out with the use of the Niflheim supercomputer at the Technical University of Denmark, using 120 tasks on Intel Xeon40 processors over the course of ten days. The CFD results are presented below.

5.1. Steady State Conditions

To compare the simulation with the experiment, a temperature field was analysed using the four thermocouples placed on the outside walls of the circulation part of the loop (cf. Figs. 3 and 10). Table II summarises the results, with the uncertainty of ± 1 °C. The simulation results are taken from a readout of temperature.

Table II. Comparison of the experimental and simulation results for temperature.

	Temperature [°C]			
Thermocouple	TC-1	TC-2	TC-3	TC-4
Experiment	376	361	376	450
CFD	400	361	376	450

For the thermocouples TC-2, TC-3, and TC-4 the simulations provide a good match between the experimental and calculated values. The cold salt entering the hot leg in the bottom left corner is heated and flows counterclockwise in the loop. The temperature at TC-1 should be greater than the one at TC-2 because of the cover gas cooling, and TC-3 should see a much lower temperature than TC-4 since the heating only begins near where TC-3 is located and where the cold salt enters the hot leg. TC-3's measurement is, however, influenced by conduction of heat through steel due to its location close to the heater. The difference between the experimental result from TC-1 and the simulation is significant.



Figure 10. Temperature field at the middle plane. The minimum temperature is set to 360 °C. A gray line shows the salt-gas interface. The locations of the four thermocouples are indicated.

Three possible reasons for TC-1 not giving the same results in the simulation were identified. First, the thermocouple is likely to have been mislocated from its original position or even detached from the metal tube while upgrading the installation and applying insulation. This could result in the temperature being lower by some tens of degrees due to measuring the temperature of the insulation or a cavity instead of the wall. Second, there is a large vertical temperature gradient on the flat wall of the overflow tank, which can prove challenging to resolve numerically. Third, the CFD model assumes that the entire surface of the hot leg is kept at 450 °C, whereas the heating tape does not cover the whole surface, especially not near ends of the tubes; the boundary condition applied on the hot leg, therefore, adds more heat to the system than is added by the heater. The temperature readings of the other thermocouples, however, suggest that the model is resolved properly.

5.2. Salt Droplet Entrainment and Freezing

The Volume of Fluid model enriched with the interface tracking, multiphase interactions, and adaptive mesh refinement represents particle transfer very well. Initial CFD models created for NS1 stressed the importance of air bubbles and salt droplets that appeared where they were not expected to be. Depending on the level of the salt in the overflow tank, the cover gas flow rate, and the temperature, a particular behaviour of the multiphase fluid was observed. When the salt level is too low or too high, air bubbles enter the salt bearing tubes and can travel with the flowing salt throughout the entire volume of the loop. The air bubbles could also block the flow and/or change the temperature distribution of the molten salt, but this hasn't been observed in the experiment.

More importantly, the simulations show that salt droplets can be entrained in the cover gas and appear in both the gas outlet and inlet. Once the solar salt enters the gas bearing tubes, it collects on the bottom of them (cf. Fig. 11) and then solidifies. This is confirmed by the experiment. NS1's gas tubes were disconnected from the loop and their insides inspected. Small volumes of the solidified solar salt were found. These solid volumes resulted in limiting the maximum cover gas flow rate. The CFD simulations proved to be an important tool for facility diagnostics, even though it was not the intention of the project.



Figure 11. Volume fraction of synthetic air inside the overflow tank. A long droplet of the salt is present in the inlet gas tube.

6. CONCLUSIONS

The NS1 loop facility has provided the means for investigating characteristics of molten salts and operational procedures for use in molten salt reactors. The facility offers operational experience in solar salt handling, including melting, loading, freezing, circulating, and draining the salt.

In this paper the design and operation of the NS1 facility are described, including first experimental results and CFD simulations using the STAR-CCM+ code. The experimental data provided support to the CFD simulations, thus validating the use of the code for modelling natural convection of molten salts in an open system with a flowing cover gas. Findings from the validation of the simulations against the experimental data stress the importance of high accuracy in the assembly of the instrumentation.

Although the cylindrical freeze valve cooled with an air blower and heated with a heating tape achieved the goal of isolating the circulation part of the loop from the drain tank, the present design was found not to function as a passive safety component under the prescribed operating conditions. Further research on the passive freeze valve technology should be performed in a different setup, focusing on enhancing heat transfer into the frozen plug.

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Closing remarks

The success of a freeze valve is dependent on its design, as well as on the design of the neighboring systems, which was confirmed by the operations of NS1 and experiments of Giraud et al. [34], and concluded by Tiberga et al. [22]. It seems infeasible to design a generic freeze valve, since the valve must be sized to fulfil its functions in full integration with the rest of the installation. The passive operation of a freeze valve adds more requirements to the design and is difficult to achieve, especially if instabilities of the systems around the valve are present, such as temperature fluctuations and presence of flow.

8. MS1 loop facility

Introduction

The NS1 freeze valve proved that a freeze valve is an efficient tool for system isolation and works very well with molten salt loops, allowing for separating different parts of a circuit from each other. Having this in mind, a new loop, MS1, was designed and assembled by the author. MS1 was filled with molten NaOH and the circulation of the salt was intended to take place in a closed system, i.e. without an interface with a gaseous atmosphere, to study dynamic effects of corrosion in the loop. Three freeze valves of a distinct shape were placed in the loop to achieve this purpose, allowing for isolating the circulating salt from the rest of the system. An alternative to the freeze valves was considerably costly, as a small number of custom-made exoticalloy ball valves would have to be specially manufactured. The freeze valves were believed to perform their function satisfactorily, and the experiment was to confirm whether they could be used as a replacement for mechanical valves in other similar facilities in the future.

The following pages contain the author's original manuscript submitted for publication and describing the MS1 facility and research done on a novel, C-shaped sodium hydroxide freeze valve.

--- Original article as submitted ---

Computational fluid dynamics model for a C-shaped sodium hydroxide freeze valve

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Abstract

Freeze valves are safety components implemented in molten salt reactor (MSR) designs that utilize a salt's phase change to isolate two parts of a system from each other. The correct prediction of the behavior of a freeze valve is crucial to the safe operation of MSRs.

A freeze valve made from a nickel (Ni-201) tube bent into a C-shape and filled with sodium hydroxide (NaOH) is studied experimentally at the MS1 loop facility at Seaborg Technologies. The molten salt initially fills the freeze valve and is cooled by means of an external air blower and solidifies to close the valve. A computational fluid dynamics code STAR-CCM+ is applied to model the thermodynamic and flow properties of the freeze valve. The model accounts for both conjugate and radiative heat transfer, utilizing a volume-of-fluid method with an enthalpy-porosity-based phase change numerical method. The influence of impurity content on the salt's melting point is modelled. Experimental temperature measurements are used to determine the model parameters, and the simulation results show a good agreement

with the experimental data. Correlation coefficients between the experimental and simulation data are above 0.996, with the average absolute value of their difference being approximately 5 °C. Our sensitivity analysis shows that the performance of the freeze valve is strongly dependent on the latent heat and the flowability threshold of the salt used by the software to model salt dynamics in the mushy zone.

Keywords

sodium hydroxide, molten salt reactor, freeze valve, solidification, passive safety, computational fluid dynamics

1. Introduction

Molten salts are used in concentrated solar power plants as heat storage and heat transfer fluids [1, 2]. Due to their low vapor pressure, molten salts may be operated at near-atmospheric pressures [3], thus removing the need to pressurize the heat transfer systems. Moreover, the low pressure operating regime of molten salts is one of the key safety claims of the nuclear molten salt reactor (MSR) design [4]. The MSR technology employs passive safety systems such as freeze valves. A freeze valve is filled with molten salt while in an open position and closes when the salt inside the valve solidifies. During power operation of an MSR, the freeze valve is actively cooled and isolates the reactor core from the drain tank system placed below the core. If the reactor overheats or loses electrical power due to a malfunction, the solid salt plug in the freeze valve should melt without the need for external power. This allows the reactor core to drain, leaving it in a safe shut-down condition.

The freeze valve technology originates from the Molten Salt Reactor Experiment [5] conducted in the 1960s, where freeze valves consisted of flattened sections of pipes that sealed off circuits of the reactor from their drain tanks by means of external cooling. That technology has, however, never been commercialized. MSRs are undergoing a revival under the framework of fourth-generation nuclear reactors [6]. Freeze valves for MSRs have been investigated experimentally by the Oak Ridge National Laboratory [7] which tested three different heating solutions for the flat-section valve design: a direct resistance heater, an induction heater, and a radiant heater. The radiant heater was the most optimal configuration in terms of simplicity, freeze and melting times, and electrical power consumption.

Wang et al. analyzed the influence of a partially melted freeze valve on the draining time analytically [8] in order to assess the passive draining properties of an MSR. The presence of a solid plug in a drain tube increased the draining time significantly. More recently, Giraud et al. have built an experimental facility called FFFER to study molten salt flow that incorporated a horizontal freeze valve equipped with a copper disk and a steel block to enhance heat transfer characteristics [9]. The valve had four small holes instead of one large hole to study the influence of multiple plugs on the melting time in an attempt to avoid issues with a partially melted plug. The valve performed satisfactorily, however, upon connecting it to a molten salt loop, its behavior was affected by the presence of a circulating salt. The authors have also stressed the importance of validation of computational fluid dynamics (CFD) models of freeze valves. The same group of researchers have built another facility, SWATH, which utilized an optimized FFFER freeze valve. A comparison of experimental data along with results of their CFD simulation of melting time showed good agreement, even though the model was very simplified.

A more advanced CFD model of the multiple-plug freeze valve has been developed by Tiberga et al. [10] and focused on simulating a loss of power accident of an MSR. The dependence of the melting characteristics on the number of plugs, subcooling, and distance from the reactor core was studied. The researchers concluded that the single-plug design was more favorable and that the distance from the reactor core needed to be as short as possible, in order for the freeze valve to operate passively.

The development of a freeze valve for the Thorium Molten Salt Reactor has been centered around the experimentation and modelling of flattened section valve designs [11]. A finite element model was created and calculation results agreed well with experimental data. An updated version of the design included heat fins which enhanced the cooling rate of the valve but resulted in a decreased melting rate [12]. Temperature results obtained by a CFD model incorporating the enthalpy-porosity method [13] agreed with experimental data to a reasonable extent.

Overall, experimental data to be used for validation of freeze valve models is scarce and a clear need exists for more facilities devoted to freeze valve research. Other applications of freeze valves include liquid chromatography and multi-step synthesis processes [14], however these technologies are considerably different from MSRs.

At Seaborg Technologies, a new molten salt loop facility, MS1, has been built to carry out research on various aspects of molten salt handling, including freeze valve operation. The MS1 facility investigates the behavior of sodium hydroxide (NaOH) due to its potential application in MSRs [15] and for thermal energy storage [16]. In this paper, we establish a CFD model for a C-shaped freeze valve filled with the NaOH salt which is mounted onto the MS1 loop. The novelty of our research lies in:

- The validation of the model with experimental data from a new facility;
- Utilization of a distinct shape of the freeze valve optimized for increased pressure resistance;

- Application of STAR-CCM+ to modelling of NaOH phase change with multiple heat transfer modes;
- The implementation of a temperature range of melting to simulate impurity contents in molten NaOH.

The model accounts for both conjugate heat transfer and radiative heat transfer, utilizing a volume-of-fluid method applied innately to phase change processes by STAR-CCM+, with an enthalpy-porosity-based phase change numerical method. To determine the model parameters, temperature measurements are performed during operation and draining of the loop. Overall, the simulation results are in good agreement with the experimental data. Our sensitivity analysis shows that the simulation results are mostly sensitive to the flowability threshold and the latent heat of the salt. These parameters are often not well determined as they depend on the impurity contents of the salt [16–18], the influence of which is modelled through adjustment of the melting point of NaOH.

2. The MS1 facility

MS1 is an experimental facility that enables natural circulation of molten NaOH. The objectives of the MS1 facility are to demonstrate successful handling of molten NaOH under dynamic conditions in a flow loop, investigate dynamic corrosion behavior of nickel exposed to molten NaOH, test a novel design of a freeze valve and its performance, and validate numerical models of NaOH phase change.

MS1 is composed of the following major parts (see Fig. 1): the top vessel, a rhombus-shaped salt circuit, and three C-shape freeze valves – two above and one below the salt circuit. The loop is built from 1/2'' (12.90 mm) outside diameter and 0.065'' (1.65 mm) thick seamless tubes made of Ni-201 material

and welded together. Ni-201 is defined as unalloyed nickel with the maximum carbon concentration of 0.02% and having a minimum nickel concentration of 99.2% [20]. High nickel content is crucial for ensuring low corrosion rates of the material exposed to molten alkali hydroxides [21].



Figure 1. Schematics of the metal parts constituting MS1.

The approximate height of the loop is 1.5 m and the width is 0.6 m. The internal volume of the salt circuit is 232.5 cm3. During the steady-state operations, molten NaOH flows clockwise in a closed loop (cf. Fig. 1), i.e. with all three freeze valves closed by solid NaOH plugs under active cooling. The flow is achieved by heating the external walls of the loop with electrical heating tapes, with the bottom leg being the main heat source and the top leg, thinly insulated and equipped with an air blower, being the main heat sink (cf. Fig. 2). Natural convection of molten NaOH is established by setting the temperatures at the top and bottom legs of the loop to 370 °C and 460 °C, respectively, recorded by 14 type K thermocouples with a 1.5 °C rated accuracy [22].

With the MS1 loop filled with liquid NaOH, the flow is expected to be laminar. The Prandtl number of the salt is between 5 and 11. Due to the harshness of the NaOH environment, i.e. the high temperature and high corrosivity, and the small scale of the tubing, accurate measurements of the flow velocity were not feasible. For the same reason, only external thermocouples were installed on the loop, as neither inserting thermocouples into molten NaOH nor the use of nickel thermowells were possible for this experiment.

To operate the system, MS1 was loaded with solid pellets of NaOH with the purity of above 98%. The loop filled with the salt was heated up and flushed with an inert gas to remove any moisture. Subsequently, the salt was melted, and after establishing steady-state conditions in the loop required for natural circulation, the freeze valves were closed through cooling and solidification of NaOH.



Figure 2. Photograph of the fully assembled MS1 loop. The freeze valve studied in this paper is marked and locations of relevant thermocouples indicated.

2.1. Freeze valve design and operation

The three MS1 freeze valves all share the same design. Each freeze valve is made of a 1/2'' (12.90 mm) outside diameter and 0.065'' (1.65 mm) thick Ni-201 tube which has been bent into a shape that resembles the letter C (Fig. 3). The internal volume of the freeze valve, defined as the volume in between the two horizontal surfaces at the top and bottom, is 12.4 cm3. The valve is an integral part of the loop's tubing, i.e. the tubing is continuous up- and downstream of the valve and no special joining of the valve and the rest of the loop is required.



Figure 3. Dimensions of the freeze valve (in mm). Thermocouple positions are shown.

The shape of the valve should ensure that the solidified salt inside the valve can withstand the pressure gradients expected for the loop. Since the salt circuit is a closed system, small pressure increase may arise from density changes and/or increased vapor pressure of the molten salt at high temperature, and the C-shaped valves act to prevent motion of the solid plugs.

The bottom freeze valve, analyzed in this study, is wrapped with an electrical heating tape supplied by BriskHeat; the tape being 13 mm wide and 600 mm long, and with the heating power of 156 W. The heating tape, HT10, is coupled to two RS PRO 1.5 mm thick, type K thermocouples attached to the external walls of the tube at the top and bottom of the valve. These thermocouples are named TC10T and TC10B, respectively. The valve is equipped with its own cooler, F4, which is a model RG90-18/56 air blower made by Ebm-Papst. This air blower has 22 W electric power and 15 m3/h rated flow. It is mounted on the loop support frame to the right side of the valve, with the outlet directed towards the center of the valve. A programmable logic controller is used to automatically control MS1 operations by controlling the cooling and heating functions while maintaining the freeze valve in a closed state (salt frozen) during the experiment or in an open state (salt molten) when draining the loop. There is no flow of salt through the valve during operation, as there is a metal cap placed at the bottom of the valve that is removed only for draining. During the entire experimental campaign, the valves successfully maintained their isolating function. The rather sluggish flow of the salt above the freeze valve has not affected its operation to an observable extent.

2.2. Experimental data

Fig. 4 depicts three different phases of the freeze valve experiment, each of which requires slightly different model settings. The temperatures shown are

measured at the wall of the valve and do not directly describe the temperature of the salt inside the valve. While typically the melting of the salt in the freeze valve would be analyzed, here the freezing was chosen, as it is equally important for the operability of closed-system molten salt loops.

Prior to the experiment, at -700 to -500 s, both the heater HT10 and air blower F4 are turned off (their logic state = 0), the salt inside the valve is cold, but still molten after the previous heating cycle, and the measured temperatures are decreasing. In the first phase of the experiment, at -500 to 666.5 s, the heater is turned on and the temperatures are increasing, first rapidly at both the top (TC10T) and bottom (TC10B) thermocouples, subsequently the temperature rise is slower until the temperature of the top thermocouple reaches the setpoint of 450 °C. This phase takes place to reach a starting condition for the analysis of the active freezing. During the second phase, at 666.5-743.5 s, the air blower is turned on and the heater turned off, in order to rapidly cool down the salt. During the third phase, at 743.5 to 2300 s, the cooling is switched off and the temperature of the environment, while the heater turns on intermittently to maintain TC10T at 250 °C to diminish thermal stresses to the structural material.

In this paper, we examine the behavior of the salt in detail between 0 s and 870 s. Of particular interest is the second phase for which we perform a quantitative sensitivity analysis.

3. CFD model

In order to examine the molten salt phase changes when operating the loop, especially solidification, a model of MS1's bottom freeze valve has been developed in the CFD software STAR-CCM+ (version 2020.2) [17].



Figure 4. Temperature measurements at the wall of the valve during the three phases of the freeze valve experiment. The logic states of the heater HT10 and the air blower F4 are shown.

3.1. Geometry

A full-scale 3D freeze valve model was created in the STAR-CCM+ design tool and subsequently cut vertically in half to exploit the symmetry of the valve. The model is composed of the solid heater material, nickel walls, and the interior of the valve is the fluid (NaOH) domain. The valve is further divided into five sections defined by the boundaries between the straight and bent parts of the valve (Fig. 5).

Point probes representing the tips of the thermocouples TC10T and TC10B are placed at positions (7.15, -22.00, 110.00), measured in mm, and (7.32, -5.00, 22.00), respectively, with the origin located at the center of the tube, at the bottom end of the freeze valve (cf. Fig. 5).

3.1.1. Meshing

Three built-in meshers of STAR-CCM+ were used to discretize the various parts of the freeze valve, cf. Fig. 6; the Surface Remesher with a minimum face quality of 0.05 to mesh the surfaces, Prism Layer Mesher with default settings to refine the meshes at the boundaries, and Polyhedral Mesher to fill up the volumes [17]. A surface and volume extrusion of 1.0 mm thickness comprising 8 equally thick layers (brown in Fig. 6) was added to the external sides of the tube walls to model the heating tape wrapped around the freeze valve. The mesh control parameters were given as:

- Base size 0.3 mm,
- Target surface size 100% of base size,
- Minimum surface size 10% of the base,
- Surface curvature of 72 points per circle,
- Surface growth rate (maximum size ratio of connected mesh edges) of 1.3,



Figure 5. The freeze valve model with its five different sections (the heater layer, modelled in the same fashion, is not shown for clarity). Physical thermocouple positions (TC10T and TC10B) and additional software-based point probes used for sensitivity analysis are indicated.

- 10 prism layers,
- Prism layer stretching of 1.5 (ratio of thickness of subsequent layers),
- Prism layer total thickness of 0.5 mm,
- Volume growth rate (ratio of cell size from the boundaries to the core mesh) of 1.2,
- Maximum tetrahedron size (primal cell size) of 0.5 mm.



Figure 6. Meshes created for each domain – fluid (blue), wall (gray), and heater (brown).

In total, the mesh is described by 582,699 cells in the NaOH domain, 1,198,366 cells in the solid wall domain, and 442,680 cells in the heater domain.

3.2. Physics models

In order to model the phase change of sodium hydroxide induced by heat exchange between the salt and the nickel tubes, as well as by heating and cooling of the surface of the heater, several physics models are included in the CFD model. Fluids and solids are treated separately and the interfaces between the materials are coupled through the software's default conjugate heat transfer relations, i.e. the total heat flux is conserved across the interface and the interface has a zero thermal contact resistance.

The energy and momentum fields are calculated using Navier-Stokes equations with a temperature-dependent density by segregated solvers employing 2nd-order convection in the fluid domain and a time solver employing 1st-order discretization and 5 inner iterations. The time steps used in the different phases of the simulation are: 7.5 s during the first phase (heating, which is used mostly for initialization of temperature and flow fields), 1.0 ms during the second phase (freezing), and 2.5 ms during the third phase (cooling). Corresponding maximum Convective Courant Numbers obtained in the last two simulations are below 0.3.

The fluid is modelled as incompressible and multiphase, with the phase change governed by an enthalpy model [23]. STAR-CCM+'s Melting-Solidification model is accessed through the Volume Of Fluid model. This approach is based on a Eulerian description of multiphase fluids that can be used for phase change problems [24], [25], as it can capture the interface between immiscible phases like solid and liquid with the use of a 2nd-order convection discretization, and predict the temporal distribution of the interface.

We added additional models to account for the specific behavior of a liquid undergoing phase change, which makes it resemble a porous material [26]. When the liquid solidifies, it locally nucleates into small crystals that aggregate into dendrites [27] which create resistance to the flow eventually stopping it once a solid fraction threshold is reached [28]. The flow stop, i.e. imposing a zero value of velocity at a specified solid fraction of the salt called a flowability threshold, is accounted for by the Melting-Solidification Flow Stop feature in the software that prevents creeping flow. While for pure substances the flowability threshold is 1 [17] – solid materials do not flow, the value is not a priori known for impure NaOH; we chose a value of 0.95 as a result of fitting the simulation results to the experimental temperatures. The effective viscosity of the solid-liquid mixture is determined by the Average Slurry Viscosity model that uses the Metzner method [29], and the permeability of that mixture is found by the Mushy Zone Permeability model which utilizes the Carman-Kozeny equation [30], both methods using the software's prescribed default values.

The flow of NaOH in the freeze valve is expected to be laminar due to the very low fluid velocity and the lack of a pressure differential. The Grashof number is smaller than 10⁵ which is below the threshold of the transition to the turbulent boundary layer [31]. The only driving force for the flow is the natural convection which can be modelled with both laminar and low-Reynolds turbulent models [32, 33], each yielding similar results for low Grashof numbers. Due to the higher stability and low computing time, the laminar model was used for all simulations. Volume exchange with the rest of the loop is not accounted for.

A chemical compound which contains impurities does not behave like a pure substance and therefore does not melt at a fixed temperature [34, 35]. The purity of the NaOH salt is specified by the supplier as 98%, i.e. with 2% impurity contents, while corrosion products may also accumulate in the salt during the experiment, thereby increasing the impurity contents. Since the salt in the freeze valve did not mix with the rest of the salt in the MS1 loop in circulation, the concentration of the corrosion products in the freeze valve is not expected to be uniformly distributed. By reference to impure KOH , the melting point depends strongly on the concentration of the impurities [36], with 2.5% impurities lowering the melting point by 5 °C relative to the pure salt. This led us to assume that some NaOH in our experiment could solidify at a temperature differing from the melting point expected for pure NaOH, 323 °C [37]. We assume that our salt has the liquidus point of 323 °C and the solidus point of 318.4 °C as reported in [38], which creates a range over which the phase change can occur, given a conservative estimate of 0.5% fraction of corrosion products is formed on top of the initial 2% impurity content postulated by the supplier.

Sodium hydroxide's thermophysical and transport properties are therefore set for three temperature regions: the solid, liquid, and the mushy zone. The latter is defined by the salt being in a state between the solidus and liquidus temperatures, i.e. with the solid fraction of the material between 0 and 1. Several materials melt over such a range of temperature, especially mixtures of salts [39–41]; and the phase change in salt is modelled by various authors using the mushy zone approach [9], [10], [12]. The latent heat of fusion of NaOH was set to 209.2 kJ/kg [42]. The properties are summarized in Table 1, with the values for the mushy zone calculated either as a linear interpolation between the solid and liquid state, or extrapolated from the liquid state.

Property /	Solid	Mushy zone	Liquid
State			
Density [kg m ⁻³]	2130 [11]	28678.12 - 83.37978 · T	$1904.4 - 0.489 \cdot T$, adapted from [186] and extrapolated
Thermal	Extrapolated	Extrapolated from liquid	$533 + 0.945 \cdot T$,
conductivity	from liquid	state	adapted from [19]
[10⁻³	state		
W m ⁻¹ K ⁻¹]			
Heat	2125 [187]	$267.136 + 5.83522 \cdot T$	2199 – 0.146 · <i>T</i> [188]
capacity			
[J kg ⁻¹ K ⁻¹]			
Dynamic	N/A	Extrapolated from liquid	$9.25230 - 0.01571 \cdot T$,
viscosity		state	adapted from [189]
[10 ⁻³ Pa s ⁻¹]			and extrapolated

Table 1. Thermophysical and transport properties of sodium hydroxide used in the CFD model. T is the temperature in °C.

Properties of the structural material, Ni-201, were modelled as functions of temperature, while the material covering the heater, fiberglass, was modelled with constant properties (see Table 2). Since the tube walls are kept at very high temperatures with respect to the surroundings, a radiative heat model was added. The Participating Media Radiation model based on spherical harmonics was chosen; the tube was modelled as a gray body with a surface emissivity of 0.4 (for the oxidized nickel [48]) and default values of zero transmissivity, reflectivity being auto-calculated, and no radiation flux between interfaces.

Property /	Ni-201 (adapted from [190])	Heater material
Material		[191], [192]
Density	$8902.475 - 0.12377 \cdot T$	2500
[kg m ⁻³]		
Heat capacity	$453.125 + 0.14375 \cdot T$	700
[J kg ⁻¹ K ⁻¹]		
Thermal	$81.748 - 0.1037 \cdot T + 0.0001 \cdot T^2$	1.0
conductivity		
[W m ⁻¹ K ⁻¹]		

Table 2. Thermophysical properties of the freeze valve's structural and heater material used in the STAR-CCM+ models. T is the temperature in °C.

3.3. Boundary conditions

In all three domains, i.e. the fluid, nickel wall, and heater material, all boundaries are modelled impermeable. The bottom end of the freeze valve is a physical wall, whereas the top end is approximated as one in this first approach to modelling MS1's freeze valve due to the fact that relatively little exchange of mass is expected between the freeze valve and the salt in motion above the freeze valve. Conjugate heat transfer takes place across the different materials' interfaces. The top and bottom ends of the valve are assumed adiabatic for simplicity.

In the first phase of the experiment, all outside walls of the heater material are set to exchange heat with the environment by convection, with the ambient temperature of 20 °C and the heat transfer coefficient of 10 W m⁻²K⁻¹ as suggested by [51]. An energy source is added to the heater domain, corresponding to the heater's rated power of 180 W.
In the second and third phases of the experiment, the freeze valve's boundaries are described using user-defined functions that divide the valve into the top and bottom parts characterized by different heat transfer dynamics due to their positions with respect to the rest of the system. The top part encompasses the middle, top straight, and top regions (cf. Fig. 5), and the bottom part encompasses the bottom straight and bottom regions. The heater walls exchange heat with the environment by convection, with the ambient temperature of 20 °C and the heat transfer coefficients determined by the following functions. After an initialization time of 8 seconds (zero effective power of the fan), the cooling power and the heat transfer coefficients for convection are assumed to linearly ramp up to 220 W m⁻²K⁻¹ and 105 W m⁻²K⁻¹ for the top and bottom parts of the valve, respectively. The heat transfer coefficients for convection from the outside wall of the heater were confirmed experimentally. Keeping the other parameters of the model constant, the coefficients were found by fitting the temperature curve obtained from the simulation to the experimental values.

In the third phase, after an 8-second delay, the heat transfer coefficients decrease linearly over 8 seconds to reach 10 W m⁻²K⁻¹ and 30 W m⁻²K⁻¹ for the top and bottom part, respectively.

3.4. Initial conditions

At 20 °C, the thermal diffusivity for NaOH and Ni-201 is 0.17 mm²/s and 19.47 mm²/s, respectively, while at 400 °C, the thermal diffusivity is 0.25 mm²/s and 12.15 mm²/s for NaOH and Ni-201. It is thus clear that Ni-201 transfers heat much faster than NaOH throughout the temperature range considered. Measurements of the temperature of the NaOH salt inside the tubes are not performed, but the diffusion coefficients suggest that to equilibrate temperature, NaOH requires between 50 and 100 times longer

than Ni-201. The simulations indicate rather steep radial temperature gradients in the freeze valve during the heating and cooling phases, which are also partly caused by the latent heat.

For the first phase, the initial freeze valve temperature distribution was set as a linear transition from 330 °C at the bottom to 470 °C at the top of the freeze valve in the NaOH domain, and from 330 °C to 480 °C in the nickel domain. The heater's initial temperature was assumed uniform at 450 °C. See Fig. 7 for the initial conditions for the first (left) and second (center) phase.

For the sensitivity analysis, only the second phase of the experiment was investigated. At the beginning of the second phase, TC10T showed 452.4 °C and TC10B 375.9 °C. In our model, we have simplified the geometry into a top and bottom part and with initial conditions of temperature accordingly (cf. Fig. 7, right). Using data from the second phase of the experiment, we assumed that the molten salt in the top part of the freeze valve reached the maximum of 450 °C, whereas the salt in the bottom part was at 385 °C, slightly higher than measured by the bottom thermocouple that was affected by higher heat losses to the environment than the top one due to its relative location in the loop assembly. The salt is colder at the bottom than at the top due to the buoyancy effects. The nickel walls of the freeze valve, as well as the heater material, were also set at different temperatures; the top half was set at 452 °C and the bottom at 380 °C. See Fig. 7, right for the simplified initial conditions of the second phase.



Figure 7. Initial conditions of temperature for the salt, tube, and heater regions. Left: initial conditions of phase one. Center: initial conditions of phase two, resulting from the phase one simulation. Right: initial condition for the sensitivity analysis.

3.5. CFD model validation

3.5.1. Comparison of experimental and simulation results

The simulation was carried out with the use of the Niflheim supercomputer at the Technical University of Denmark, using 120 tasks on Intel Xeon40 processors over the course of approximately 24 h.

To ensure that the flow and energy equations are resolved properly, residuals of the iterative evaluation of the equations are kept at levels below 10^{-4} for energy and 10^{-8} for momentum and continuity. The Courant number is controlled as well.

In Fig. 8, the temperature measurements from the experiment are shown together with the simulation results. The entire dataset is provided as a supplement to this article. In Fig. 8, also the average solid volume fraction of NaOH is shown as a function of time.

At the beginning of phase two, the molten salt is continuously heated and at around 670 s the air blower's impeller starts revolving, however with no evident cooling effect during the first approx. 10 seconds. After 10 seconds, the temperature measured by thermocouple TC10T is decreasing faster than the one of TC10B. The temperature decrease is slowing down at approx. 740 s, which is linked to the phase change of molten NaOH. Phase two ends as the fan is turned off at 743 s. After t = 760 s, the top thermocouple sees a temperature increase due to the heat transfer from the NaOH salt. Overall, a good agreement is observed between the CFD model and the experimental data.



Figure 8. Results of the base case simulation compared with the experimental measurements.

For quantitative comparison of the simulation results with the experimental results the Pearson correlation coefficient, maximum difference in temperature (positive or negative), and average absolute value of the temperature difference are given in Table 3. The Pearson correlation coefficient r provides a linear association between two sets of numbers [52].

Thermocouple /	Pearson	Maximum	Average absolute	
Metrics	correlation difference [°C]		value of the	
	coefficient r		difference [°C]	
TC10T	0.9969	13.4	4.7	
TC10B	0.9960	-28.7	5.3	

Table 3. Metrics of the base case simulation results for the time period 500-870 s.

3.5.2. Solid volume fraction distribution

The solid volume fraction is calculated for the entire NaOH salt domain, with the values of 0 representing fully liquid and 1 fully solid NaOH. The average solid fraction shows the freezing dynamics, resembling an S-curve. Salt freezing starts at t = 688 s, first at the inner walls of the freeze valve, even though the liquidus point has not yet been reached by the two thermocouples. At the end of phase two, when the air blower is stopped, the solid fraction has reached the value of 0.77.

As can be inferred from Fig. 9, at the end of the second phase of the simulation, at 743 s, the freeze valve is still open, as the liquid salt can pass through it, under the assumption that flow of NaOH only stops at the solid volume fraction greater than 0.95. Due to the low thermal diffusivity of NaOH, especially in the solid phase, only the volume cells adjacent to the

fully frozen cells (red color) have a high solid fraction. The freezing starts on the walls and continues towards the interior of the tube. The effect of the natural convection can be seen in the difference of thickness of the fully solid layer of NaOH; it is thicker at the bottom parts of the bends and thinner at the top. Moreover, several bumps in the solid volume fraction field in the top parts of the straight sections are visible – the solid fraction distribution is not uniform, which suggests the presence of small vortices that influence the phase change.



Figure 9. Solid volume fraction of NaOH in the freeze valve at 743 s.

Due to the adiabatic nature of the boundary conditions imposed on the top and bottom ends of the freeze valve model, the bottom end solidifies earlier than the top, as warmer salt flows upwards and encounters an inability to cool down through heat exchange with the top surface of the valve (which resembles the real-life scenario).

3.5.3. Temperature distribution

In Fig. 10 the temperature distribution is shown for t = 743 s. In the radial direction, the difference between wall temperature and NaOH temperature at the center of the tube can be as high as 90 °C, with the temperature ranging from approximately 230 °C on the wall to 320 °C in the salt. This implies that the temperature gradient is difficult to resolve numerically on the small distance between the wall and the center of the tube. The temperature gradient inside the walls is not very large due to the high thermal conductivity of the nickel tube; the temperature difference over the axial direction reaches approximately 40 °C. The temperature plot indicates that buoyancy effects are present in the salt as the warmer salt (in red) tends to flow above the cold salt (in orange).

3.5.4. Velocity distribution

The velocity field inside the freeze valve for t = 743 s is shown in Fig. 11. Frozen cells are clearly visible near the walls (in blue), indicating that there is no flow in the NaOH that has reached the flowability threshold (solid volume fraction of 0.95). Overall, the natural circulation velocities in the valve are very small, with the bulk average below 1 mm/s.



Figure 10. Temperature in the freeze valve at 743 s.



Figure 11. Velocity of NaOH in the freeze valve at 743 s.

The influence of buoyancy shows in the recirculation pattern (dark blue) at locations adjacent to the walls of the valve, with the bulk of the salt flowing upwards in the central part of the valve. The valve's shape governs the dynamics of free convection; velocity vectors are more aligned at the bottom parts of the bends and more distorted at the top parts due to the salt being cooled radially, with the colder salt falling downwards and distorting the warmer salt flowing upwards.

The effect of imposing an impermeable no-slip wall boundary condition is discernible at the top and bottom ends of the valve. In the experiment, salt at the top of the valve is not isolated from the rest of the system; mass and energy are exchanged with the salt flowing in the loop above the freeze valve. In the model, salt remains in the top part of the valve, which is seen as recirculation vortices in Fig. 11. The overall effect of this recirculation is not expected to significantly affect the results and due to the inability to measure the flow, the velocity distribution has not been the focus of our research.

3.6. Sensitivity analysis

3.6.1. Methods

To investigate the sensitivity to the model parameters, we carried out a sensitivity study for the base case model of the second phase of the experiment. Two different kinds of sensitivity analyses were performed.

First, a model without radiative heat transfer was studied to select appropriate time step and mesh refinement prior to the subsequent, resource-heavy freeze valve analysis. In each simulation one parameter of the model was varied – either the time step or the mesh base size. For the time step sensitivity analysis, a mesh with the base size of 0.3 mm was used. The performance of the model in terms of convergence of temperatures and flow using time steps

of 1 ms and 5 ms was compared to the one having a 0.5 ms timestep. For the mesh convergence study, a time step of 1 ms was used. The mesh base sizes of 0.3 mm (1,781,065 cells) and 0.6 mm (448,739 cells) were compared against 0.2 mm (4,022,947 cells).

Next, we investigated the effects of the experimental conditions, material properties, and numerical schemes employed. These cases are presented in Table 4.

Case no.	Top/bottom heat	Flowability	Critical	Latent heat
	transfer coefficients	threshold	solid	of fusion
	$[W m^{-2}K^{-1}]$		fraction	[J kg ⁻¹]
base case	220/105	0.95	0.27	209200
1	190/80	0.95	0.27	209200
2	250/120	0.95	0.27	209200
3	220/105	0.50	0.27	209200
4	220/105	0.75	0.27	209200
5	220/105	1.00	0.27	209200
6	220/105	0.95	0.24	209200
7	220/105	0.95	0.30	209200
8	220/105	0.95	0.27	165000

Table 4. Cases of the sensitivity analysis pertaining to the physical parameters of the model.

In case 1 and case 2 different heat transfer coefficients were employed, correspondingly smaller and larger than in the base case: 190 and 80 W $m^{-2}K^{-1}$ for the top and bottom parts of the freeze valve in case 1, and 250 and 120 W $m^{-2}K^{-1}$ in case 2.

After reaching the flowability threshold, the fluid velocity in a mesh cell is set to zero. Four different values of the flowability threshold are studied: 0.50, 0.75, 0.95, and 1.00.

The critical solid fraction used in the Average Mushy Zone Permeability and Average Slurry Viscosity models is a parameter that is used in the switching function of Carman-Kozeny and Metzner models when these are used in combination. The Metzner slurry viscosity model tends to give rise to high viscosities when used above the critical solid fraction, which enhances the effect of the mushy zone permeability [17], therefore the models need to be swapped at the critical solid fraction. Three values of the critical solid fraction are studied: 0.24, 0.27 (default), and 0.30. Lower or higher values make the model unstable.

Several values of the latent heat of NaOH can be found in the literature. We decided to use the highest one [42] in the base case model, whereas the lowest one [37] is shown here for comparison.

The measurements of temperature are performed only at two locations on the freeze valve. These two data points alone do not allow for a detailed understanding of the phenomena affecting the molten salt inside the freeze valve. In particular, the velocity field or local solid fraction cannot be directly inferred from these temperature measurements. Therefore, the measurements of the top (TC10T) and bottom (TC10B) thermocouples are used only to differentiate between the global performance of the models.

To gain a better understanding of what takes place within the molten salt, two additional point probes (cf. Fig. 4) were ascribed to the fluid region at (4, -25, 110) mm (top probe) and (4, -25, 40) mm (bottom probe).

3.6.2. Results

Table 5 summarizes results of the time step and mesh size analyses, using the metrics described above. For convenience, in the following we show the complement (1-r) of the Pearson correlation coefficient, as differences between the cases are rather small.

Case	Thermo- $(1-r) \cdot 1$		Maximum	Average absolute	
	couple		difference [°C]	value of the	
				difference [°C]	
Time	TC10T	0.3	1.3	0.93	
step 1 ms					
1	TC10B	0.5	0.9	0.42	
Time	TC10T	19.1	15.3	10.48	
step 5 ms					
1	TC10B	38.3	10.3	6.04	
Base size	TC10T	3.0	-1.9	1.08	
0.3 mm					
0.0	TC10B	0.3	-0.3	0.11	
Dece size	TC10T	15	2.2	0.00	
Dase size	10101	1.3	-2.2	0.00	
0.6 mm					
	TC10B	3.3	0.8	0.31	

Table 5. Metrics of the time step and mesh sensitivity analysis cases; r denoting thePearson correlation coefficient.

Doubling the time step from 0.5 ms to 1 ms does not introduce any notable differences in the temperature results, whereas the computation time

decreases almost fivefold. Increasing the time step to 5 ms affects the results considerably, hence the time step of 1 ms is used for the base case model.

Coarsening the mesh by increasing the base size from 0.2 mm to 0.3 mm and further tripling it to 0.6 mm only has a small effect on the results, which implies that the mesh produces converged results. The 0.2 mm mesh size requires a computation time 6 times longer than the 0.3 mm case and for this reason, the 0.3 mm mesh was used in the rest of the study.

Table 6 shows the results of the eight simulations, relative to the base case model. In Fig. 12, the temperatures of the two thermocouples are shown. Fig. 13 compares the temperatures of the two internal probes and Fig. 14 compares the velocities in the z direction measured at these probes.

In Fig. 12, all 8 cases display the same temperature trend and temperature differences remain small, with the exception of cases 1 and 2, in which a large variation is observed as expected. Cases 1 and 2 have the smaller and larger heat transfer coefficients, respectively (dashed lines in Figs. 12, 13), than the rest of the cases, which is why they constitute an envelope around the other results, due to the fact that the heat transfer coefficients have an inherently large influence on the phase change dynamics. The smallest differences are observed for cases 6 and 7, indicating that the results are less dependent on the critical solid fraction within the studied range. In general, changes to the model parameters affect the velocities more than the temperature fields, as is suggested by considerably higher complements of r.

Case	Metrics	TC-	TC-	Probe	Probe	Probe top	Probe
no.		10T	10B	top	botto	velocity	bottom
		[°C]	[°C]	temp.	m	[m/s]	velocity
				[°C]	temp.		[m/s]
					[°C]		
1	$(1-r) \cdot 10^5$	22.1	185.8	220.9	596.2	5447.8	46686.2
	Max.	18.3	18.2	15.9	11.2	3.89E-03	-5.38E-03
	diff.						
•	Ave. abs.	9.40	8.82	3.38	2.47	1.64E-04	-1.75E-04
	diff.						
2	$(1-r) \cdot 10^5$	11.5	54.4	145.6	384.1	3256.4	23965.8
	Max.	-15.9	-12.1	-14.5	-9.7	-3.44E-03	-4.80E-03
	diff.						
	Ave. abs.	-8.64	-5.56	-2.50	-2.12	-9.78E-05	-2.66E-05
	diff.						
3	$(1-r) \cdot 10^5$	64.1	242.4	44.7	239.6	1814.2	18065.9
	Max.						
	diff.	-7.0	-6.1	3.7	4.9	-1.01E-03	3.10E-03
	Ave. abs.						
	diff.	3.0	2.6	0.6	1.3	3.64E-04	6.27E-04
4	$(1-r) \cdot 10^5$	24.7	51.2	14.0	36.3	675.1	3616.3
	Max.						
	diff.	-3.8	-2.5	2.0	2.0	7.41E-04	1.63E-03
	Ave. abs.						
	diff.	1.6	1.0	0.3	0.6	2.15E-04	2.36E-04
5	$(1-r) \cdot 10^5$	2.5	0.5	1.6	30.9	83.5	5266.0
	Max.						
	diff.	1.0	0.3	-0.4	-2.1	3.16E-04	-3.28E-03
	Ave. abs.						
	diff.	0.4	0.2	0.1	0.2	8.18E-05	2.30E-04

6	$(1-r) \cdot 10^5$	0.1	0.2	2.2	6.2	196.4	365.1
	Max.						
	diff.	-0.1	0.1	1.0	1.1	8.40E-04	-7.20E-04
	Ave. abs.						
	diff.	0.0	0.1	0.1	0.1	5.55E-05	6.77E-05
7	$(1-r) \cdot 10^5$	0.0	0.2	0.6	0.8	63.2	1003.2
	Max.						
	diff.	0.1	-0.2	-0.6	0.2	5.85E-04	-9.10E-04
	Ave. abs.						
	diff.	0.0	0.1	0.0	0.0	3.56E-05	1.15E-04
8					1919.		
	$(1-r) \cdot 10^5$	30.5	121.7	10.4	9	614.1	6304.6
	Max.						
	diff.	-6.6	-6.2	-1.2	-9.6	8.31E-04	1.45E-03
	Ave. abs.						
	diff.	2.9	2.5	0.4	1.6	2.07E-04	3.58E-04

Table 6. Metrics of the sensitivity analysis cases of the model parameters; r denoting the Pearson correlation coefficient. For cases 3—8, the analysis only covers the time period from 30 s to 77 s.



Figure 12. Temperature results on TC10T (top) and TC10B (bottom) of the sensitivity analysis cases.

With excluding cases 1 and 2, cases 3 and 8 reach the lowest temperatures at the end of the freezing phase. This indicates that the flowability threshold has a relatively large influence on phase change (case 3). The smaller the flowability threshold, the faster the temperature decrease measured at the location of the thermocouple probes. Once a cell has reached the flowability threshold, the flow in the cell stops due to the extraction of heat through the tube wall with a limited heating effect from the still liquid and flowing salt.

For case 8, the latent heat that was lowered. The difference between the lowest and highest values of the latent heat reported in the literature is more than 25%. As expected, the decrease in the latent heat leads to smaller temperatures at the end of the freezing phase.

In Fig. 13, a noticeable change in the temperature profile of NaOH is observed at the temperature of T = 322.5 °C corresponding to the liquidus point of NaOH. During freezing, between the liquidus and solidus points of NaOH, a smaller value of the flowability threshold results in a slower temperature decrease of the salt, limited by the small heat transfer coefficient of NaOH. For case 8, the small latent heat has a strong effect on the salt, reducing the salt temperatures at the end of the freezing phase.



Figure 13. Temperature results on additional top and bottom probes of the sensitivity analysis cases. The insert shows a zoomed-in section marked with a black rectangle.



Figure 14. Results of the velocity in the *z* direction on additional top and bottom probes of the sensitivity analysis cases.

Fig. 14 shows the velocities at the two probes for the eight sensitivity cases. Movement of the salt within the freeze valve is visible, caused by density changes due to cooling. Similar velocity transients are observed for all cases, while for some of them, the transients are slightly shifted in time, which results in a significantly lower correlation coefficient compared with the coefficients for the temperature. After 60 seconds, a large share of the NaOH salt is frozen and the flow stops in various parts of the valve, resulting in a reduced circulation and velocities close to zero. The sign of the velocity changes a few times, indicating formation of vortices within the freeze valve.

4. Discussion

Our CFD model of the C-shaped freeze valve has been applied to different heat transfer phases of the experiment and compared to temperature recordings at two thermocouples. The temperature profiles of the NaOH salt undergoing phase changes are well captured by the model, however, fine details could not be resolved by the simplified model.

The discrepancies observed between the simulation results and the experimental values, especially at the end of the freezing phase, may be a result of the thermophysical and transport properties of the NaOH salt not being well known, including the salt behavior close to the melting point. The mushy zone has not previously been studied, as it is not trivial to perform any measurements on the phase change process; in particular there is no consensus in the literature on what the melting point is for NaOH, which could not be measured in this experiment, as such measurements require a dedicated apparatus. Additionally, the thermocouple measurements, especially of TC10B, are characterized by a lot of noise, which makes it more difficult to fit the simulation results to the experimental data. A layer of complexity is

added to the present study, as the flow in the MS1 loop and its freeze valves is governed by natural circulation, which is inherently difficult to model [53].

The sensitivity analysis of the model revealed the strong dependence on both the flowability threshold and the latent heat of freezing. For many salts, including NaOH, these parameters are often not well determined as they depend inter alia on the impurity contents of the salt [16–18]. In many applications of molten salts, the impurity content itself is not well controlled as it may change over time, e.g. due to the dissolution of the structural material in the salt and creation of other corrosion products within the salt. An independent verification of how the thermophysical properties of NaOH change depending on the impurity content is needed.

Other parameters of the freeze valve model based on the NaOH salt, such as the critical solid fraction, apparently had only a smaller impact on our simulation results, partly attributed to the fact that many of these parameters are characterized a priori by a high degree of accuracy.

The presence of impurities changes the thermophysical properties of salts and thus influences the heating/cooling requirements and dynamics of phase change in freeze valves in a non-negligible way. Phase change researchers and freeze valve designers should include the effect of impurities on the melting point, heat of fusion, and flowability threshold in their models. To do so, measurements of these properties should be performed with a known and recorded impurity concentration.

The shape of a freeze value is a significant contributor to the dynamics of natural convection. Since freeze values are cooled and heated radially, configurations other than vertical orientations (e.g. bends) distort recirculation vortices, which results in a complex heat transfer. In our case, the buoyancy resulted in the top parts of the bends having a thinner layer of solidified NaOH than the bottom parts during freezing. This effect could be utilized to produce a frozen plug shape that could, for example, speed up melting and subsequent draining of an MSR, where not an entire cross section of the tube would have to melt to open the passage for the salt. Furthermore, for such a solution, we recommend dividing cooling and heating systems into more distributed systems, either of which could have a different power to selectively adjust the thickness of the frozen layer in various parts of the valve.

We acknowledge the need for continuing the research into molten salt phase change and freeze valve modelling. Future computational studies should investigate, among other aspects, melting of NaOH in our freeze valve, addition of components surrounding the freeze valve (e.g. the circuit above it with a molten salt in forced convection to account for volume exchange), and scaled-up models. Additionally, the parameters used in our model should be verified by an independent freezing-type experiment.

5. Conclusions

A STAR-CCM+ enthalpy-porosity model for melting-solidification within the volume-of-fluid multiphase implementation has been developed and applied to a C-shaped freeze valve containing the sodium hydroxide salt. The CFD model was validated against the MS1 experimental loop at Seaborg Technologies being equipped with a C-shaped nickel-based freeze valve.

Overall, the CFD simulations were found to be in good agreement with the experimental temperature measurements taken during the freezing phase of the experimental campaign.

The results, however, and hence the performance of freeze valves, proved sensitive to the flowability threshold of the liquid and its latent heat of freezing, parameters that are often not well accounted for in applications of molten salts.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi: 10.17632/gdj64y22dz.1.

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224

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228

MS1 operations

The operations of MS1 followed similar procedures to ones followed in NS1 experiments. Solid NaOH pellets were loaded into the top vessel of the loop (see Figure 54 for reference) and melted there, after which a mechanical valve below the top vessel was opened and the molten salt dropped into the lower part of the circuit. Figure 55 shows the loading procedure and temperature measurements of thermocouples placed on top of the loop's side opposite to the side below the top vessel (TC4B, TC4T, and TC8T) and of thermocouple TC10B which should measure the greatest temperature increase. The hot salt dropped to the bottom of the loop (see the steep increase in TC10B around t = 550 s) and filled the loop up to the top freeze valves (see the temperature increase at the highest point of the loop, TC4T).

Subsequently, freeze plugs were created with the use of external air cooling, and the temperature of the heaters was adjusted so that the loop could reach its steady-state conditions with NaOH circulating inside the tubing. Figure 56 depicts measurements from all thermocouples which plateau at around t = 6500 s after the initiation of the procedure.

After 300 h of the corrosion experiment, the freeze valves were melted and the salt was drained into a crucible placed below the drain tube (see Figure 57). The drained salt was analyzed using inductively coupled plasmaoptical emission spectrometry for presence of corrosion products; the loop was cut (see Figure 58) and samples of the nickel tubing were analyzed under a scanning electron microscope with energy dispersive spectroscopy. The analysis of the loop samples proved that the salt circulated in the loop, as nickel was found to be removed from the hot sections through dissolution in the salt and deposited in cold sections of the loop. This also indicated that corrosion of the tubes exposed to molten NaOH was a result of the thermal gradient between the hot and cold legs of the loop.



Figure 54. MS1 with locations of all thermocouples marked.



Figure 55. Chosen temperature measurements taken during the loading procedure.



Figure 56. Temperature measurements from all thermocouples showing the approaching of MS1's steady state conditions.



Figure 57. Salt drained from the loop after 300 h of exposure, solidified.



Figure 58. Samples of the loop after cutting.

Closing remarks

The author's analysis of the experimental data collected and further corrosion sample analysis performed by Seaborg's corrosion specialists proved that the C-shaped freeze valves isolated circulating NaOH from the atmosphere, thus satisfying their intended function. This success allowed for the freeze valves to be implemented in further loop facilities that are being developed in the company, benefitting molten salt R&D through simplification and cost reduction of the design of the experimental apparatus. Although the issue of this component not working as a passive safety valve has not been tackled in MS1, another advantageous application of the freeze valves was found and verified, which, in fact, enabled more advanced studies on molten salt multiphysics and corrosion, which are two of the company's main focus areas of development. The design of MS1 is being utilized as a platform for further studies of long-term corrosion. This data is, however, not ready to be published at the time of writing this dissertation.

9. NaOH thermophysical and transport properties

Introduction

Any model can be only as good as input data used for calculations. To predict the behavior of a material, high-quality data on thermophysical and transport properties across a given temperature range is needed, with an assumption of a certain quantity of impurities influencing the final result to a known degree. With NaOH being a salt whose properties are less known than the other salts' intended for use in MSRs, the author's research on properties of salts was limited to NaOH.

To increase the understanding of salt phase change and molten salt flow and to increase the accuracy of numerical models, the author reported measurements of molten NaOH viscosity and density that are described in a manuscript submitted for publication, presented in the following section.

Viscosity and density of molten sodium hydroxide at temperatures between 623 and 973 K

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ABSTRACT Molten salts are increasingly used as heat storage and transfer fluids, with sodium hydroxide being one of the promising candidates for energy production and storage applications. Dynamic viscosity and density are among properties which govern the flow of melts. Viscosity and density of a pure sodium hydroxide melt are experimentally determined within a temperature range between 623 and 973 K under atmospheric pressure, for the first time utilising a simultaneous measurement method on a molten salt. An improved formula for viscosity is derived from the data by means of an
exponential fit. A linear fit found for treated density data agrees with previously obtained measurements. The results increase the understanding of the dynamic behavior of molten NaOH and allow for predictions at higher temperatures than before.

1. Introduction

Sodium hydroxide has long been of interest for use in industrial processes such as nuclear, energy storage, and others [1]–[7]. Already in the 1950s molten NaOH was seen as a potential high-temperature heat transfer medium, but the corrosive nature of the salt inhibited its industrial application [1], [8]. Interest in the use of molten NaOH in industry has seen a recent resurgence, particularly at Seaborg Technologies and Hyme Energy, due to the development of a novel corrosion control method [9]. NaOH is being considered for molten salt energy storage systems [10], [11] to support a transition from fossil fuel-based power production to one based on intermittent green energy sources [12]. Table 1 compares properties of various molten salts used for energy storage. Because of its relatively high heat of fusion and heat capacity, NaOH is a good choice for both sensible and latent heat storage systems, with its price outcompeting other salts.

236

Property	NaOH	Solar salt (60 NaNO ₃ -40 KNO ₃)	Hitec (7 NaNO ₃ – 53 KNO ₃ – 40 NaNO ₂)	NaKMgCl (20.5 NaCl– 30.9 KCl– 48.6 MgCl ₂)
Melting point <i>T_m</i> /K	593 [13]	494 [14]	415 [6]	656 [6]
Heat of fusion $H_{fus}/(10^3 \text{ J kg}^{-1})$	160 [13]	96 [14]	80 [16]	207 [17]
Specific heat capacity $c_p/(J \text{ kg}^{-1} \text{ K}^{-1})$	2131 [18]	1620 [14]	1560 [19]	1023 [20]
Density $\rho/(\text{kg m}^{-3})$	1709 at 673 K [21]	1900 at 573 K [22]	1933 at 473 K [19]	1729 at 673 K [20]
Volumetric latent heat storage density $\rho H_{fus}/(10^8 \text{ J m}^{-3})$	2.7	1.8	1.5	3.6
Volumetric sensible heat storage density $\rho c_p/(10^6 \text{ J m}^{-3} \text{ K}^{-1})$	3.6	3.1	3.0	1.8
Specific cost/(USD kg ⁻¹)	0.21 [23]	0.72 [24]	0.93 [25]	0.35 [26]

Table 1. Comparison of Properties of Molten Salts Used for Energy Storage

Molten NaOH is also planned to be used by Seaborg Technologies in the Compact Molten Salt Reactor (CMSR). The CMSR is a molten salt reactor which proposes the use of molten NaOH as a neutron moderator (a material increasing the probability of nuclear fission in thermal-spectrum nuclear reactors) and/or a heat transfer fluid [27]. Compared with graphite used historically as a moderator in nuclear reactors, molten NaOH cannot experience structural deformation and cracking due to radiation typical for graphite and is a much more efficient moderator, allowing for a more compact reactor core. With a view to novel corrosion control methods being developed prior to commercialization of such new energy systems, a strong need exists to revisit previously published data on thermophysical and transport properties of molten NaOH, which are scarce.

Data and correlations for NaOH viscosity available up to now have been based on measurements from 1926 and only up to 823 K [28]–[30]. The new applications of molten NaOH require higher operational temperatures [31], with precise knowledge of viscosity being needed for proper sizing of pumped systems and calculations of heat transport in accident scenarios [15]. Density of NaOH was measured up to 1173 K more recently, in 2004 [21]. However, an independent verification of the few existing datasets is necessary to confirm their accuracy.

Rotational rheometry is a standard technique for measuring the viscosity of molten salts [32]–[34]. Common techniques for density measurements are the Archimedean method and pycnometry [35]–[38]. However, recently it has been shown for liquid metals [39] that viscosity and density can be experimentally determined simultaneously by using a rotational rheometer in

combination with the Archimedean method [40]. The simultaneous nature of the measurement enables economizing in terms of time, material amount, and the number of instruments used. In this paper, we present results of simultaneous viscosity and density measurements of molten NaOH between 623 and 973 K. We derive a new equation for the viscosity and tentatively confirm previous measurements of density.

2. Experimental Section

2.1. Materials

The chemicals used in the experiment were NaOH pellets (99.99%, trace metals basis, Thermo Scientific) and high-purity argon; their characteristics are summarized in Table 2.

Chemical name	CAS no. ^a	Mass fraction purity ^a	Melting point ^a /K	Purification method	Supplier
NaOH	1310-73-2	0.9999	589.15	Used as purchased	Thermo Scientific
Ar	7440-37-1	0.99999	N/A	Used as purchased	Widmann Gase GmbH

^aProvided by suppliers

2.2. Methods

Rheological and density measurements were performed with an air-bearing Modular Compact Rheometer (MCR 702) from Anton Paar (Anton Paar GmbH, Graz, Austria). The device is equipped with an additional lower linear drive and a water- and air-cooled Convection Temperature Device (CTD 1000). Measurements were conducted with a concentric cylinders (CC) absolute measuring geometry [41] made of Inconel 600, with a diameter of 24 mm for the rotating bob and 26 mm for the fixed cup (CC 24). The material and the geometry were selected considering the corrosiveness of liquid NaOH and the expected sample viscosities in the lower mPass range, and density around 1600 kg m⁻³, based on existing literature data [7], [29]. Samples were loaded under a fume hood as pellets at room temperature, and the contact time with atmosphere was limited to less than one minute due to the hygroscopic nature of NaOH, with the argon gas flowing over the samples. The sample chamber was continuously flushed with argon during heating (5 K min⁻¹ up to 623 K) and in the course of all subsequent high temperature measurements. The steady heating of the sample up to 623 K prior to measurements led to the removal of any absorbed water in the sample. Sample melting at about 595.15 K (with reference values for pure NaOH ranging from 591.55 K [42] to 596.15 K [43]) was determined based on softening of the sample by monitoring the normal force (F_N) and the vertical gap distance between bob and cup, while pushing with the bob from the top onto the solid sample. After melting of NaOH, the bob was moved to measuring position at a 4 mm vertical gap distance and viscosity curves and density were determined at 623 to 973 K in 50 K steps. Samples were thermally equilibrated for 10 min at each temperature after the set temperature of the CTD was reached. Viscosity curves were measured with the upper rotational drive from shear rate 1 s⁻¹ to 100 s⁻¹ in logarithmic spacing (13 data points) with measuring point duration decreasing logarithmically from 20 s to 5 s, and a resulting total test time of 142 s. For density measurements, the shear rate was set to 0 s⁻¹ with the upper rotational drive and normal force was recorded with the lower linear drive; 25 data points were recorded in 300 s.

Viscosity was derived as the ratio between torque and rotational speed recalculated to shear stress and shear rate based on geometry factors of the CC measuring geometry [41]:

$$\eta = \frac{\tau}{\dot{\gamma}} = \frac{M}{\omega} \frac{k_{\tau}}{k_{\dot{\gamma}}} \tag{1}$$

where k_{τ} (in m⁻³) is the shear stress factor to convert torque *M* into shear stress τ and $k_{\gamma'}$ (in rad⁻¹) is the shear rate factor to convert rotational speed ω into shear rate $\dot{\gamma}$. Both factors are specific for the used measuring geometry (CC 24).

The density of NaOH, ρ was derived based on the inverted Archimedes principle [194], where the buoyancy of a body depends on the density of the medium in which it is immersed, corrected for the buoyancy in air, but disregarding other boundary conditions:

$$\rho = \frac{F_N}{gV_{CT}} - \rho_{air} \tag{2}$$

with F_N being the normal force (due to buoyancy, measured either from top or bottom), g is the gravity constant, V_C^T is the volume of the submersed cylindrical bob at measurement temperature, and ρ_{air} is the density of air. The F_N sensitivity of the lower linear drive is 0.0005 N, resulting in a relative accuracy of 0.3% and a sensitivity of 5 kg m⁻³ when measuring liquid NaOH (about 1600 kg m⁻³) with a CC 24 measuring geometry.

3. Results and discussion

3.1. Viscosity

Two replicate datasets were collected during measurements of dynamic viscosity, η , with temperature increments of 50 K applied between 623 and 973 K. Measurements above 973 K deviated considerably due to volatilization and creep of the salt melt and could not be used.

For each temperature in a dataset, viscosity was measured at multiple shear rates. Viscosity is constant over a range of intermediate shear rates; at low shear rates it is affected by a lower torque limit, and at high shear rates the viscosity is affected by a turbulent flow occurring in place of a required laminar flow. To determine the region with a constant behavior, a linear fit with a zero slope was applied at each temperature and outliers with standard residuals higher than 1.75 were excluded. The data collected for all the measurements excluding the outliers are shown in Fig. 1.

The data points from both replicates were used to derive a formula for a temperature-dependent viscosity of NaOH in the measured temperature range, utilizing the Vogel-Fulcher-Tammann equation that has been used to model viscosity of nitrate and chloride salt mixtures [44]–[47]:

$$\eta = A \exp\left(\frac{B}{T-C}\right) \tag{3}$$

where *A*, *B*, and *C* are empirical parameters. The final formula derived from the combined datasets is characterized by very low reduced χ^2 values and R^2 values very close to unity (see Table 3).

243



Figure 1. Definition of the linear region for viscosity measurements via linear regression and exclusion of data points based on their residuals, using data from two different Data Sets (DS). Outliers are not shown. The relative standard uncertainty of the shear rate is $u_r(\dot{\gamma}) = 0.0001$ and of the temperature is $u_r(T) = 0.0075$. The total uncertainty specification of the measuring device is below $U_s(\eta) = 0.01$ for the viscosity.

Table 3. Parameters of the Fit to the Vogel-Fulcher-Tammann Equation for Viscosity

$A/(\text{mPa}\cdot\text{s})$	B/K	С/К	Reduced χ^2	R^2	Adjusted R^2
0.47834	726.23405	273.66788	0.00587	0.99114	0.99096

Standard uncertainties of the constants are: u(A) = 0.04256 mPa·s, u(B) = 79.52473 K, and u(C) = 23.78811 K.

The resulting expression for viscosity of NaOH in the range from 623 to 973 K goes as follows:

$$\eta/(\text{mPa} \cdot \text{s}) = 0.47834 \exp\left(\frac{726.23405}{T/K - 273.66788}\right)$$
 (4)

In Fig. 2, our correlation is compared with a formula from Janz et al. [30], pointing to original measurements of Arndt and Ploetz [28], where the viscosity was calculated from five points obtained with the use of a vertical capillary viscometer. In the case of our measurements, the width of the confidence band increases up to 2.3% at the highest temperatures. The confidence intervals shown for the mean at each temperature are highest at 923 K reaching 3.9%. While both correlations agree between 623 K and approximately 675 K, the expression found in the literature deviates strongly from the new expression at high temperatures (1.807 mPa s at 820 K for the new vs. 1.491 mPa s for the old expression, yielding a 21% difference). A source for the deviation is currently unknown. High-temperature creeping of molten NaOH is unlikely to account for an overestimation of viscosity in our experiments, as in such a case the viscosity would be expected to decrease due to a loss of material from the system being measured leading to a lower shear stress. Slow decomposition of NaOH at high temperature and under vacuum has been observed previously forming Na₂O and H₂O [48]. Accordingly, varying extent of decomposition of the melt due to different

heating programs may lead to small deviations in between different studies. Additionally to the viscosity study of the NaOH melt, the relevant sources [28]–[30] examined viscosity of KOH melts. However, no more recent data could be found, which impedes the analysis of a possible source of deviation through a comparison to viscosity data of a similar salt.



Figure 2. Comparison of the newly obtained and original correlations [29] for viscosity of NaOH. The new expression is shown with its two-sigma confidence band and the confidence intervals of the mean at each temperature. The literature correlation is shown with a reported 0.02 uncertainty.

In comparison with other salts, viscosity of NaOH is slightly larger than viscosity of KOH [30] and nitrate-based salts [49] and approximately half that of ternary chloride salts [20]. Lower values of viscosity are preferred to reduce pumping requirements of a heat storage system [15], which corroborates the feasibility of using NaOH as a heat transport fluid.

3.2. Density

Similar to the viscosity measurements, two datasets were obtained for density of NaOH in the same temperature range. While the viscosity was measured with the upper rotational drive of the instrument, the density was measured with the lower linear drive, resulting in the measurements being performed simultaneously and without an influence on each other. One of the datasets seemed to have yielded erroneous measurements, likely due to sample creep, and was discarded from a further analysis. The data collected is shown in Fig. 3.

Table 4. Parameters of the Linear Fit for Density

Intercept $a/(\text{kg m}^{-3})$	Slope $b/(\text{kg m}^{-3} \text{ K}^{-1})$	Residual sum of Squares	Pearson's <i>r</i>	R^2	Adjusted R ²
1869.378	-0.29964	39455.64216	-0.90454	0.81819	0.81700

Standard uncertainty of the intercept *a* is u(a) = 8.87147 kg m⁻³ and of the slope *b* is u(b) = 0.01142 kg m⁻³ K⁻¹.



Figure 3. Experimental density data measured at different temperatures.

As in the case of other molten salts, a linear behaviour of density with respect to temperature changes was assumed. The dataset was treated to remove outliers and improve statistics of the linear model; points with standard residuals greater than 2.5 were not included in the fit. This led to the exclusion of 45 out of 200 datapoints. The resulting parameters of the model can be seen in Table 4.

The resulting linear correlation for density, ρ , of molten NaOH between 623 and 973 K is:

$$\rho/(\mathrm{kg}\,\mathrm{m}^{-3}) = 1869.378 - 0.29964\,T/\mathrm{K} \tag{5}$$

The new expression is compared with previously derived formulae from [28] and [21] in Fig. 4. The confidence band of the fit increases with temperature with a width of 0.33% at the highest temperature of 973 K. Likewise, the confidence interval of the mean at each temperature is the widest at 973 K with a width of $\pm 0.5\%$. Considering the relatively low density of NaOH, the precision can be considered high, as low density decreases the precision of the technique. It can be observed that the data lies largely within the 0.02 uncertainty span as given for the reference data from Patrov and Yurkinskii from 2004 [21]. There seems to be no agreement with the data from Arndt and Ploetz from 1926 [28], however, the uncertainty of Arndt and Ploetz's correlation was missing from the original report. Patrov and Yurkinskii did not indicate the number and variance of repetitions, and neither volatilization, creep, water content, nor thermal decomposition were addressed, which limits the evaluation whether the newly measured density correlation is of higher accuracy. However, were the creep a significant issue in the case of our measurements, our density data would be expected to lie lower at high temperatures than the reference values from Patrov and Yurkinskii, since smaller volumes would be measured due to the salt melt loss and resulting lower buoyancy. Importantly, the good overlap with the literature correlation can be considered a first validation of using this

technique for density measurements of molten salts and is a confirmation that the actual density is in the order of the previously reported expression for NaOH.



Figure 4. Comparison of newly obtained and original correlations for density of NaOH. The new correlation is shown with a two-sigma confidence band and the confidence intervals of the mean of the experimental datapoints at each temperature. The data from Patrov and Yurkinskii [21] is attributed an 0.02 uncertainty; no uncertainty was reported in Arndt and Ploetz [28].

Density of a heat storage medium should be as high as possible to increase volumetric heat storage capabilities [15]. Compared to other salts (cf. Table 1) and KOH [30], NaOH has a lower density. However, higher heat of fusion and heat capacity compensate for it and render NaOH a favorable heat storage material due to high volumetric heat storage densities.

To improve the quality of the density measurements using this method, greater dimensions (volumes) of both the cup and the bob of the measuring device could be used in future research campaigns. The measurement accuracy increases with the bob volume due to the greater normal force signal. The influence of the container and the bob materials should be better understood, as possible corrosion products would change results of the measurements; nickel might perform better [50] than Inconel which was utilized in the present study.

4. Conclusion

New measurements of viscosity and density of molten NaOH at temperatures between 627 and 973 K were made and respective correlations derived. The temperature range in which viscosity of NaOH is known was extended by 150 K. The newly obtained viscosity data is likely of greater accuracy than that published in 1926, which was almost a century ago, implying the use of outdated measurement techniques. The results of the density measurement correlate with the previous expression, validating the measurement technique and the published values. However, more data is necessary to measure the density of NaOH more accurately.

Measurement of density and viscosity within a single measurement run using one device has several advantages: Comparability is increased by obtaining data from just one sample, characterized at identical temperature, and two parameters being measured at the same time allows for economic advantages and efficiency. Hence, a further exploration of this technique for molten salts is desirable.

Difficulties in performing measurements on volatile molten salts should be addressed and discussed in more detail in future research to allow for an estimation of how the choice of the method influences the accuracy of results. Furthermore, it should be addressed if the decomposition of NaOH in the molten state is significantly influencing its properties. Increased dimensions of the measuring geometry may allow for higher accuracy measurements of low-density molten salts, and corrosivity of the materials used should be considered.

The measured properties confirm that NaOH is a promising material for a heat transfer fluid and especially for a heat storage medium. Its favourable properties and very low price have a high potential for increasing profitability and efficiency of heat storage systems, as long as corrosivity of the melt is addressed by a choice of a right container material and corrosion control method.

ASSOCIATED CONTENT

Supporting Information

Supplementary data associated with this article can be found, in the online version, at doi: <u>10.17632/62xpjw8jph.1</u>.

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Author Contributions

L. V., D. C., and J. A. conceived the project. L. V., D. C., J. A., and D. S. designed and planned the study. Conceptualization of experiments, viscosity and density measurements, data evaluation and reduction were performed by C. G. and D. S. Data processing was performed by L. V. with help of J. A.. M. P. wrote the first draft of the paper. The final manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. ‡L.V. and M.P. contributed equally to this paper and are both to be considered first authors.

Notes

The authors declare the following financial interests which may be considered as potential competing interests: Laura Voigt, Mateusz Pater, James Amphlett, and Daniel Cooper report relationships with Seaborg Technologies that include employment. Daniela Schwarz and Christopher Giehl report relationships with Anton Paar GmbH that include employment.

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Phase transition enthalpy

Among researchers within the field of thermal hydraulics, there is a widespread lack of understanding of a crucial phenomenon occurring in the solid state of some materials, namely polymorphic transformations that are changes in the crystal packing. Microscopically speaking, a substance can have different crystal modifications, also called phases, which are represented in phase diagrams.

The transition from one phase to another, just like from the solid to the liquid state, is tied to a change in enthalpy, meaning that this discontinuous process can be endo- or exothermic – energy is required for it to take place or energy is released during the process, respectively. Additionally, the heat capacity and thermal expansion of the material differs, depending on the phase it is in [199]. Even more importantly, for some materials, the heat required for phase transition is comparable with the latent heat of fusion (melting), which means that it must not be forgotten in the enthalpy balance equation which is the principal law of thermodynamics. Knowing all possible phase transitions happening in a range of pressure and temperature conditions of interest and their corresponding enthalpies is a necessity in designing a process that utilizes thermal energy.

Specifically for NaOH, the enthalpy of the so-called $\beta \rightarrow \alpha$ transition that occurs at 293 °C under atmospheric pressure has exactly the same magnitude as that of the transition from α to the liquid state (6.36 kJ/mol according to Bale and Pelton [200]), which takes place at the temperature higher by just around 30 °C. It has serious consequences in terms of the energy balance; to bring 1 kg of NaOH from room temperature to 400 °C, not including the enthalpy of the $\beta \rightarrow \alpha$ transition in calculations, roughly 780 kJ of heat is needed, whereas this number goes up to 940 kJ (20% increase) when the transition enthalpy is included. The implications are that in an experiment – or in a reactor – such a process would take 20% longer than expected assuming a constant heating power, which could result in erroneous sizing of the heating system, compromise safety of the installation, or lead to downtime. Whereas for other salts the difference between the enthalpy of fusion and of the polymorphic phase transitions is usually smaller, it is still of the same order of magnitude [200]. The possible explanation for this oversight in the thermal hydraulics community might stem from the fact that it is mostly the liquid to gas phase change that has been investigated and modelled in depth – predominantly for water, where there is no crystallographic effects taking place. Additionally, for common ice, the transition from one solid phase to another occurs only at extremely high pressures. Other phase change materials than salts are characterized by very small enthalpies of phase transformations compared to the heat of fusion [119], which are, therefore, negligible.

The author suggests a review and update of existing calculations of transients dealing with phase change and heating or cooling of molten salts, and possibly an addition of the polymorphic transition heat to CFD models of phase change. For materials where the phase transition temperature lies very close to the melting point, latent heat could be increased by the value of the phase transition enthalpy, with a simultaneous extension of the mushy zone to the lower temperature (and keeping the flowability threshold very high), which should model the behavior of the molten salt better than what has been done to date.

Closing remarks

A holistic understanding of materials properties is required to properly account for changes to the behavior of salts and especially of NaOH. The author's research contributed to increasing the knowledge of viscosity, density, and phase transitions of NaOH.

10. Conclusions

10.1. Numerical models

Analytical solutions of phase change problems exist only for ideal cases that do not occur in nature. Numerical methods are used instead for simplification of reality and approximating complex fluid thermodynamics equations. The enthalpy method is reported to be one of the most accurate methods for solving phase change problems and is implemented in the STAR-CCM+ software that was used by the author in modelling phase change. There exist a few experimental facilities for validation of phase change models, however, there is still a lot of room for improvement, as the results agree mostly only qualitatively with the predictions. More advanced measurement techniques are required to properly validate the phase change models coupled with free convection.

During the PhD project, a numerical benchmark was created. It can be used for comparison of capabilities of modelling salt phase change by different codes and with the use of different models. The benchmark can be used for choosing software most suited for e.g. MSR licensing purposes. STAR-CCM+, OpenFOAM, and DGFlows were compared with each other and the results showed small discrepancies between them that could be explained by different numerical schemes being used to solve the same problem. Specifically, addition of conjugate heat transfer to the phase change models introduced the differences.

The author's CFD models of NS1 and MS1 loops built at Seaborg Technologies proved essential in the experiment design, as temperature conditions required to reach a chosen temperature distribution across the loop could be deduced from simulation results. The models could also be used for transient simulations and yield information on the dynamic behavior of the setups. The multiphase CFD model of NS1 satisfactorily modelled natural convection of the molten salt with a flowing cover gas, at the same time stressing the importance of care needed in the assembly of the thermocouples onto the loop's tubing. The model of the MS1 freeze valve tackled the difficulty in modelling phase change through incorporation of multiple heat transfer modes, implementation of a temperature range of melting to simulate impurity contents in molten NaOH, and validation of the model with data from a new facility. Specific dynamics of the freeze valve cooling was reproduced, and the experimental data agreed qualitatively with the model.

Phase change models that are coupled with conjugate heat transfer proved extremely sensitive to mesh refinement and also to the choice of the numerical solver. Sensitivity of the phase change models analyzed depended greatly on the heat of fusion and, in the case of STAR-CCM+, flowability threshold.

The research goal of improving the understanding of salt phase change physics was reached, with a commentary that modelling thereof is extremely difficult and sensitive, and should be coupled with experiments equipped with a high-quality data acquisition system that is based on more than temperature measurements only.

10.2. Freeze valves and molten salt loops

The scarcity of mechanical valves available for extended, low-maintenance use with molten salt based energy conversion and production systems impairs the attractiveness thereof due to the issues with materials corrosion and frequent leakage. To prolong the lifetime of mechanical valves, the following features have successfully been tested in the past: elongated stem, bellows seal, rotary packing seal, backseating, and usage of cermet materials for the valve seat and plug. There is, however, still much room for improvement in the molten salt valve design.

Freeze valves, being free of moving parts, are promising solutions to the problem of corrosion of the mechanical valves that could benefit the molten salt power industry. Tens of freeze valve designs have been investigated and even more molten salt loops have been built and operated to study the flow characteristics and corrosivity of molten salts. The research on freeze valves has centered on their passive safety function in MSRs, but no successful demonstration of a fully passive device has been made to date. Various

methods of increasing the heat transfer into the frozen plug are being considered, including an implementation of a narrower section of a pipe that becomes the freeze valve or an addition of a thick metal mass around the valve. There are other unsolved issues with freeze valves, such as thermal cycling often resulting in valve failure, which need to be addressed in these designs as well.

Molten salt loops are used primarily for corrosion studies, high-temperature component development, and numerical model validation. Being relatively simple in construction, molten salt loops are versatile test beds that can even be treated as prototypes of circuits of a nuclear reactor. A high-degree of customization and self-made devices are, however, often required to extend the lifetime of off-the-shelf components that are in contact with molten salts or are needed to increase the understanding of what happens inside the loops.

The author's impact on the research area included creation of two entirely new research facilities devoted to studies of molten salt thermal hydraulics. NS1 and MS1 loops produced results that were used for validation of numerical models of molten salt natural circulation and phase change, for freeze valve and other component tests, and for corrosion studies. A research platform that was created by the author directly benefitted the studies on heat storage and MSR salts, contributing to the United Nations' sustainable development goals [201], especially towards climate action and affordable and clean energy.

Whereas the passive operation of the freeze valve in an accidental scenario in an MSR could not be achieved with the loops tested by the author, the freeze valve's usefulness for system part isolation in molten salt loops was extensively demonstrated. The freeze valves allowed for simplification of the design and cost reduction, as the usage of (still unreliable) mechanical components was avoided. The C-shaped freeze valve designed by the author enhanced the isolating function of the freeze valve compared to the cylindrical shape, at the same time being easily manufacturable. The freeze valves used prove that energy conversion and production systems can utilize them for maintenance purposes, when one part of a circuit needs to be disconnected from the other, or during operation, when no contact of the HTF with the gas atmosphere is desired.

10.3. Properties of NaOH

Knowledge of thermophysical and transport properties of a HTF is necessary for prediction of a system's dynamic behavior under all possible conditions and scenarios, and for proper sizing of the system and its components. With NaOH being the main R&D focus at Seaborg Technologies, its viscosity and density were described by the author, and crucial information on its crystallographic phase change was collected. The temperature range in which the viscosity had previously been known was extended by 150 K, with the measurements performed with a rotary rheometer yielding a new correlation for the viscosity. Previous measurements of the density were in agreement with our new measurements at high temperatures, but more independent result verification efforts are required. The author pointed out that the energy requirements for melting of the salts are significantly higher specifically for NaOH due to a usually omitted crystallographic phase transition enthalpy term.

10.4. Recommendations

With this PhD project covering both theoretical and experimental studies across physics, chemistry, and engineering, a list of recommendations has been made that suggests improvements in a few different areas.

Molten salt valves

What regards the choice of mechanical valve candidates for industrial development specifically for molten salt systems, bellows seal valves, or even more general, packing-free valves are superior to valves with packings and are therefore preferred. The molten salt bellows valves should be equipped with an integrated heater that keeps the bellows' temperature above the salt's melting point, which would eliminate the possibility of damage to the seal. High-nickel alloys seem to experience much lower corrosion rates than stainless steel or graphite, so their usage in the valves

should be increased to lower the frequency of failure. Finally, the mating surfaces should be made of different materials, ideally cermets.

A simple way to make it more possible for the tested C-shaped freeze valve to work in a passive way is to make the valve from a thicker tube and with the same outer diameter as the rest of the loop's tubing. Such a thicker valve could be easily welded to the rest of the loop and perform its function in a more efficient way, with a lower volume of the salt required to be melted in an emergency drain scenario. The greater volume of the metal that conducts heat faster than the salt would enable the passive draining. Also, alternative shapes that speed up the passive draining should be studied, and numerous separate heating or cooling zones should be included in such a study.

Due to the still unsolved issues with both the mechanical and freeze valves, it is worth considering reviving the research on the hybrid valves, which have not received enough attention despite having the advantages of both. The hybrid valve's design would not have to be system-specific like the freeze valves tend to be and it would avoid the problem with the mechanical valve's seat and poppet fusing.

Modelling

Although CFD models can yield very interesting and useful information on the behavior of a given loop, it is time-consuming to create and test them, and full 3D multiphysics and multiphase simulations require a considerable amount of computational resources. To do a so-called pre-analysis that aids designing the loop and its thermal requirements, implementation of 1D thermal hydraulics models instead can come in handy to iteratively define the geometry and heating power of the loop [165], with much lower computational requirements.

Phase change modelling using CFD codes requires very fine meshes and is characterized by stricter requirements for convergence than models without phase change, especially if the analyzed problem is multidimensional or includes conjugate heat transfer or flow calculations. It is recommended that a detailed sensitivity analysis of a phase change model is carried out every time a new addition to the model has been implemented, so that the results are always converged and correct, even though it might seem redundant. If one were to accurately model changes in properties of HTFs over time due to corrosion, first experimental data must be produced that could form a basis for a correlation to be included in the models. It is possible to couple CFD and corrosion models, but it is still necessary to verify and include the changes in properties of the HTF in the software's database. It is particularly important for phase change processes, as both the melting point and heat of fusion are affected by the impurity content. All data on the thermophysical and transport properties should be recorded with associated information on detected impurities.

It is suggested that the crystallographic phase transition enthalpy be added to the models of salt phase change, since it is a significant contributor in the energy balance for situations where the salt is heated up to the melting point from room temperature. Negligence of this fact results in erroneous results. The addition of the transition heat can be included in the latent heat if the polymorphic transition occurs around the melting point; at the same time, the mushy zone could be extended to the transition temperature with the flowability threshold being very high, which should result in a more realistic behavior of the model.

Experiments

To potentially decrease discrepancies between models and measurements, thermocouples that are used for temperature measurements of the loop's tubing should ideally be welded to the tube so that it is impossible for them to detach and move during assembly of heaters and insulation. The effect of welding, however, needs to be evaluated. It can prove vital to test the response dynamics of the installed thermocouples before the loop is loaded with salt. It can be done by turning on a heater associated with the thermocouple of interest and observing how fast the temperature measured increases. If there is a deviation with respect to the other thermocouples, i.e. a slower increase, it is likely that the thermocouple is not in direct contact with the tubing and repositioning or replacement is required.

Experimental code validation facilities should use more sophisticated methods to validate the accuracy of models than just compare temperature data and predictions. Due to the high temperatures and corrosiveness of molten salts, the amount of available instrumentation is scarce. Since it is

not possible to use visual techniques with molten salts to measure velocity, it is recommended that surrogate liquids are used instead and e.g. particle image velocimetry is utilized. The analysis carried out on the surrogate liquids can be translated into the behavior of the molten salt of interest through appropriate dimensionless number scaling techniques.

Concerning the properties of NaOH, especially to improve the quality of the density measurements, it is suggested that the rotational rheometer used for the measurements be upgraded with a larger cup and a larger bob. The container for the salt should be made of a material that does not corrode significantly, e.g. nickel. Apart from that, more independent measurements should be made to confirm the results, and quantification of salt volatility should be included in the description of the results.

Furthermore, as this entire dissertation showed, molten salt based systems' physicochemical phenomena or characteristics cannot be decoupled from each other like in the case of processes based on water being a HTF. High corrosivity of molten salts induces changes to the materials' properties, which in turn affect the salts' behavior. Unexpectedly high enthalpies of crystallographic phase transitions affect energy requirements, which influences the design of the heating system considerably. The passive safety function of the freeze valve depends on its placement in the system due to the flow and temperature of the molten salt above the valve. To conclude, only with a holistic approach is it possible to succeed in designing a molten salt based energy production or conversion system, as in such a harsh environment like inside a molten salt loop there is no room for imperfections.

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270

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272

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276

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