MOLTEN SALT COOLANTS FOR HIGH TEMPERATURE REACTORS
A LITERATURE SUMMARY OF KEY R&D ACTIVITIES AND CHALLENGES

IAEA Internship Report
INPRO COOL
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NOTE: Text highlighted in red first needs to be cleared by Claude Renault, CEA
(MOST database references [51] [114])
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INTRODUCTION

Scope of Report

This report reviews and summarises key literature on molten salt coolants for high temperature nuclear reactors. This report has been produced as a working material, for the INPRO COOL collaborative project for the IAEA; investigating the technological challenges related to the removal of heat from reactor cores operating at high temperatures (600-1000ºC and beyond) for molten salt and liquid metal coolants.

The focus of this report will be on molten salt coolants, covering the following areas:

1. **Molten salt coolants and nuclear applications of molten salts** (chapter 1). This chapter will give a brief overview of the high temperature nuclear systems that propose the use of molten salt coolants. These include molten salt reactors that were successfully operated in past research projects, and also advanced (Gen IV) designs, with varied types of molten salt. This chapter also further focuses the scope of the present report.

2. **Thermophysical properties of molten salts** (chapter 2). This chapter will summarise the most reliable thermophysical properties data for the different molten salt types (up to the 900-1000ºC range), from selected sources. The data tables in the appendix present consolidated lists of the summarised/referenced thermophysical properties data (and/or data references). Chapter 2 will go through each property, commenting on the level of validation (estimation or measurement methods), summarised from the given literature sources.

3. **Heat transfer in molten salts** (chapter 3). This chapter consists firstly of a review of the basic theoretical relationships, correlations, and unique features regarding heat transfer in high temperature molten salt systems; located in relevant literature. Secondly, a literature survey and summary of experimental and simulation heat transfer tests for different molten salt systems will be presented.

4. **Corrosion chemistry and materials for molten salts** (chapter 4). This chapter first reports the basic corrosion processes and related chemistry given in the main sources, including a summary of some proposed chemistry control and monitoring systems. The second part of this chapter then summarises a range of R&D activities and key research results, sourced from selected research programs. In particular, results of corrosion tests between different salt systems and structural alloy materials are referred.

Objectives of Report

The general aim is to provide an overview of the status of knowledge and key research trends in the listed fields of molten salt coolant technology. This is achieved by summarising a variety of R&D activities and related literature, together with the identification of important research challenges and data gaps. As a result, the report can be used as a reference material.

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1. See “Preliminary list of issues…” (Table 2) in INPRO COOL Terms of Reference document (IAEA, 2008) [1].

2. The report is an IAEA “working material” and is not intended as a publication.
to focus further research in the development of molten salt coolant materials and technologies, for reactor applications.

The literature search for this report was performed using open sources (e.g. internet, journals, books) and other references obtained from experts in the field. This report should be considered as a collection and summary of gathered literature, presenting key results and highlights of research activities reported by other investigators in the references. The reader is therefore expected to refer to the cited sources for more detailed information, using this report as a categorisation and summary of these sources.

**Background**

The main technological goals of high temperature nuclear reactors are improved power plant efficiency and the use of process heat for hydrogen (H₂) production. In particular, new advancements in Brayton power cycles enable the conversion of high temperature nuclear heat (above 550ºC) to electricity, with increased thermal efficiency [2] [3]. Moreover the temperature requirements for thermochemical hydrogen production are in the 700-850ºC range, demanding higher outlet temperatures in reactor design [4]. Generation IV systems that propose temperatures in this higher range include the helium cooled Very High Temperature Reactor (VHTR) (up to 1000ºC), plus molten salt cooled variant designs, and the Molten Salt Reactor (700-800ºC) [5].

The paper “Reactors with Molten Salts: Options and Missions” (Forsberg et al. 2004) [2], outlines that high-pressure gases, such as helium, and low-pressure fluids with high boiling points, traditionally molten salts, are the two main options for high temperature reactor coolants. Liquid metals, and in particular liquid lead or lead-bismuth eutectic, are alternative low-pressure high temperature liquids proposed for Advanced Fast Reactor and Accelerator Driven System coolants [1] [2]. Detailed literature and state of the art knowledge reviews for nuclear applications of lead and lead-bismuth coolants, are performed as part of the OECD/NEA Working Group on Lead-Bismuth Eutectic (WG-LBE) technology [6]. As defined in the previous section, the present report will focus on the low-pressure molten salt coolants, in the areas summarised in the previous section.
1. MOLTEN SALT COOLANTS AND NUCLEAR APPLICATIONS

1.1. Types of Molten Salt

1.1.1. Salt Form

A salt component or compound, such as sodium fluoride (NaF), can be written in general as \( \textrm{M}^+\textrm{X}^- \), in which the \( \textrm{X}^- \) is the “anion” (i.e. F\(^-\) in NaF) and the \( \textrm{M}^+ \) is the “cation” (i.e. Na\(^+\) in NaF); (notation ref [7]). In general, materials compatibility properties usually govern the choice of anion (e.g. fluorides, chlorides etc.), and the choice of cation is usually governed by other “performance issues” such as physical and nuclear properties, and costs etc; as is stated in [7]. Some examples of molten salt components include BeF\(_2\), MgCl\(_2\), NaBF\(_4\) and KNO\(_3\).

A salt mixture (or coolant) consists of different individual salt components mixed together into a multi-component system, such as the binary mixture LiF-BeF\(_2\) or ternary mixture LiF-NaF-KF. The melting points of each individual salt component are too high for coolant applications (e.g. the melting point of NaF is 995ºC [8]), and the mixing of several components into binary/ternary systems reduces the melting point of the resulting salt system to more practical levels [8]. Each mixture also has a certain composition, depending on the different proportions of each component in the mixture. For example, an optimum eutectic composition of LiF-BeF\(_2\) is 67-33 % mol. Each mixture and composition will have different physical and chemical properties, and therefore the choice of molten salt coolant depends on the type of application and related trade-offs.

1.1.2. Salt Types and Applications

Various sources in the open literature provide an overview of the different reactor applications of molten salt coolants (e.g. [2] [9]). Table 1 below summarises the different applications of molten salts and gives the reference molten salt composition for each (table adapted from [10] and [11]).

<table>
<thead>
<tr>
<th>Reactor type</th>
<th>Neutron spectrum</th>
<th>Application</th>
<th>Reference Salt</th>
<th>Useful Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSR Breeder</td>
<td>Thermal</td>
<td>Fuel</td>
<td>(^7)LiF-BeF(_2)-AnF(_4)</td>
<td>[12] [13] [14]</td>
</tr>
<tr>
<td></td>
<td>Fast</td>
<td>Fuel</td>
<td>(^7)LiF-AnF(_4)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Secondary coolant</td>
<td>NaF-NaBF(_4)</td>
<td></td>
</tr>
<tr>
<td>MSR Burner</td>
<td>Fast</td>
<td>Fuel</td>
<td>LiF-NaF-BeF(_2)-AnF(_3)</td>
<td>[15]</td>
</tr>
<tr>
<td>AHTR</td>
<td>Thermal</td>
<td>Primary coolant</td>
<td>(^7)LiF-BeF(_2)</td>
<td>[16] [8]</td>
</tr>
<tr>
<td>VHTR</td>
<td>Thermal</td>
<td>Heat transfer coolant</td>
<td>LiF-NaF-KF</td>
<td>[17]</td>
</tr>
<tr>
<td>MS-FR</td>
<td>Fast</td>
<td>Primary coolant</td>
<td>LiCl-NaCl-MgCl(_2)</td>
<td>[9]</td>
</tr>
<tr>
<td>SFR</td>
<td>Fast</td>
<td>Intermediate coolant</td>
<td>NaNO(_3)-KNO(_3)</td>
<td>[18]</td>
</tr>
</tbody>
</table>

Table 1 Different applications and types of molten salts in nuclear reactors. Table is closely adapted from version given in [10].

From Table 1 it is clear that there are two distinct uses of molten salts in nuclear reactor systems. For the MSR systems, molten salts are used as a fuel-carrier (or “fuel” as given in
the table), in which the liquid salt acts as both fuel and coolant. For the AHTR and the VHTR, the molten salt is simply a coolant; “primary coolant” (AHTR) and “heat transfer coolant” (for AHTR and VHTR). In this report, molten salts acting as fuel-carrier coolants will be referred to as ‘fuel-coolant salts’ or ‘fuel-salts’, and molten salts acting as coolants, will be referred to as coolant salts or ‘clean’ salts [16].

The following three sections will focus on the three principle applications of molten salts, regarding the most prominent advanced reactor designs\[a\]. Section 1.5 will give a brief overview of the application of molten salts in fusion reactor technology.

1.2. Primary Coolant Salts

1.2.1. AHTR Application

The Advanced High Temperature Reactor (AHTR) is one of the principal concepts of a high temperature, molten salt cooled reactor. General descriptions of the reactor and core designs can be found in [16] [19] [20]. The AHTR core uses the graphite-matrix nuclear fuel designs of the high temperature gas cooled reactor (HTGR) [16]. Instead of a gas coolant, the primary loop uses a molten salt coolant to transport the high temperature heat from the core to an intermediate loop; the intermediate loop coolant uses a secondary liquid salt to transport heat either to a Brayton power cycle, for electricity production, or to a hydrogen production plant [19]. Several different reactor core designs are reported to be under consideration in [19], including a “prismatic-block fuel”, a “pebble-bed fuel”, and a “pin type fuel”. Reactor sizes range from compact 100-1000MW(t) to high-power sizes 2000-4000MW(t), with peak coolant temperatures between 700ºC and 1000ºC [20]. For more information on the PB-AHTR, see [21]). Note the AHTR is also called the liquid salt cooled Very High Temperature Reactor, for designs with temperatures greater than 900ºC [8] [22].

Other reactor design studies that propose the use of primary loop molten salt coolants, circulating a solid fuel core, include; the innovative high temperature reactor designs (IHTR-H), studied in India for hydrogen production [4] [23], and the liquid salt pebble bed reactor LSPBR, similar to the PB-AHTR, studied in the Netherlands [24] [25].

1.2.2. Candidate Coolants

The Oak Ridge National Laboratory (ORNL) report “Assessment of Candidate Molten Salt Coolants for the Advanced High-Temperature Reactor (AHTR)” (Williams et al., 2006) [8] gives a detailed review of the molten salts considered for the primary loop of the AHTR, assessing the physical properties, nuclear properties and chemical issues for a wide range of salts. Its data sources include; “open literature”; “internal reports” (deriving from the ORNL molten salt programs in the 1950s/60s/70s); and also “the use of the best available estimation techniques” [8]. For this reason, it is widely referenced across the open literature, and will act as a principal reference for candidate coolant salts and their properties in the following chapters\[b\].

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\[a\] The Molten Salt cooled Fast Reactors (MS-FR) applications will not be covered given the relative lack of literature on these systems; for more information see [9]

\[b\] The ORNL review will be the principal source for the literature summaries in chapter 2 (for thermophysical properties) and chapter 4 (for corrosion chemistry), of the present report.
The primary AHTR candidate salts are fluorides [16]. In general, the key factors favouring fluorides are described across a range of papers, and include: low melting points, chemical stability at higher temperatures (>800°C), compatibility with graphite (i.e. AHTR core matrix), better neutronic properties (i.e. low neutron absorption cross sections and stability in fields of high radiation, in reactor core); and, finally, their successful use and operation during the ARE and MSRE experiments (in particular; 7LiF-BeF2 or “FLiBe” was used for the MSRE) [8] [2] [26].

Chlorides are not considered in the literature, because of their higher thermal-neutron-absorption cross sections [2], and undesirable neutron activation properties (generation of 36Cl, a long lived radionuclide) [16]. Nitrates, sulfates and carbonates are oxygen containing salts, and are also not relevant for the primary AHTR coolant. At the higher temperatures, they are not as stable as fluorides, and they decompose to release oxygen, which corrodes carbon composites [17].

1.3. Heat Transfer Coolant Salts

1.3.1. NGNP/NHI Application

The NGNP/NHI heat transfer loop (USA program) aims to transfer heat from the Next Generation Nuclear Plant (NGNP) to the Nuclear Hydrogen Initiative (NHI) hydrogen production plant, as described in [17]. More general “heat transfer loop” applications include the secondary or intermediate loop of the next generation high temperature reactor (e.g. helium cooled or molten salt cooled VHTR [27]), which functions to carry heat from the primary loop to either the Brayton electricity generator or the hydrogen plant [2] [28].

1.3.2. Candidate Coolants

The separate ORNL report “Assessment of Candidate Molten Salt Coolants for the NGNP/NHI Heat-Transfer Loop” (Williams et al. 2006 ORNL) reviews the candidate heat transfer coolant salts. Again, much of the R&D for these heat transfer salts derives from the considerable data gathered during the past ARE, MSRE and MSBR programs in the USA.

The main screening factors for the primary coolant salts also apply to these heat transfer salts: favourable melting points and vapour pressures, chemical stability above 800°C, compatibility with high temperature alloys [17], and operational experience (ORNL). The neutronic properties (such as low absorption cross section) do not apply to the secondary salts, because the secondary/heat transfer loop will operate outside of the neutron field of the reactor core [17]. Chlorides and fluoroborates are therefore also considered for the heat transfer loop, as well as selected fluoride compositions. Chapter 2 will go into more detail on relevant thermophysical properties.  

1.4. Fuel-Salt Coolants

The main emphasis for this report lies with the ‘clean’ coolant application of molten salts, as in the described AHTR and Heat Transfer Loop (VHTR) systemsvi. However, since there are

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vi The mentioned ORNL review will be the key reference source in chapter 2, for the thermophysical properties of the heat transfer salts, as well as for relevant chemical data, in chapter 4.

vi This focus adheres to the IAEA INPRO COOL collaborative project, which focuses on the ‘clean’ applications of molten salt coolants, and these types of nuclear reactor systems.
overlapping technologies with fuel-salt coolant and clean-salt coolant systems, the fuel-salt category will also be covered to a certain extent.

In an MSR, the liquid salt containing the fuel circulates the primary loop. As the fuel-salt flows through the moderator in the core, fission occurs within the salt [2]. The liquid then flows to the primary heat exchangers, through which heat is transferred to a secondary (or heat transfer) clean salt coolant [2]. This is why the primary salt liquid in an MSR acts as both fuel and coolant.

**1.4.1. Past MSR Programs**

Past MSR research was undertaken at Oak Ridge National Lab. (ORNL) during the 1950s/60s/70s; namely the Aircraft Reactor Experiment (ARE), Molten Salt Reactor Experiment (MSRE) and the Molten Salt Breeder Reactor (MSBR) projects. Key features of each system are presented in Table 2.

<table>
<thead>
<tr>
<th>Key Features</th>
<th>ARE</th>
<th>MSRE</th>
<th>MSBR (Design)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Name and Dates</strong></td>
<td>Aircraft Reactor Experiment 1954</td>
<td>Molten Salt Reactor Experiment 1965-1970</td>
<td>Molten Salt Breeder Reactor (design) 1970-1976</td>
</tr>
<tr>
<td><strong>Peak Power Output</strong> (MW)</td>
<td>~2.5*</td>
<td>~8*</td>
<td>n/a</td>
</tr>
<tr>
<td><strong>Peak Temperature (ºC)</strong></td>
<td>860</td>
<td>650</td>
<td>705</td>
</tr>
<tr>
<td><strong>Solid Moderator</strong></td>
<td>BeO</td>
<td>Graphite</td>
<td>Graphite</td>
</tr>
<tr>
<td><strong>Fuel-Salt Composition</strong> (% mol)</td>
<td>NaF-ZrF$_4$-UF$_4$ (53-41-6)</td>
<td>$^7$LiF-BeF$_2$-ZrF$_4$-UF$_4$ (65-30-5-0.1)</td>
<td>$^7$LiF-BeF$_2$-ThF$_4$-UF$_4$ (72-16-12-0.4)</td>
</tr>
<tr>
<td><strong>Secondary Coolant</strong></td>
<td>Na metal</td>
<td>$^7$LiF-BeF$_2$</td>
<td>NaF-NaBF$_4$</td>
</tr>
</tbody>
</table>

Table 2 ORNL MSR systems and key features; as developed during past research programs. Table closely adapted from version given [29].

*These values are sourced from [30]

Many references give details of the results and achievements during the successful operation of the MSRE. Key developments included; the successful operation of a molten salt reactor system (MSRE), numerous molten salt test loops and developments in high temperature reactor structural alloys [2] [3 5]. The experience gained during this period, resulting in over 1000 technical reports [2], provides a significant knowledge base for the newer Gen IV MSR systems.

**1.4.2. MSR Applications**

From Table 1 in section 1.1.2, there are two broad types of MSR reactor. The MSR Breeder can be designed to breed fissile uranium ($^{233}$U) from fertile thorium ($^{232}$Th), in a thermal or epi-thermal/fast spectrum, in a circulating molten salt system [32]; in the MSBR (1970s), this fuel-salt was $^7$LiF-BeF$_2$-ThF$_4$-UF$_4$. The MSR Burners are incinerator systems that function to burn and transmute actinides (An), from LWR spent fuel or other sources of long life nuclear waste [2]. The typical fuel-salts for these transmuter systems are fluoride mixtures containing different actinides (An), including plutonium [30]. In the MSR systems, the circulating fuel-salts have to be continually reprocessed on-line, in which fission products are extracted from the circulating fluid; including burned Pu, other minor actinides and lanthanides, and also other poisons like Xe, Kr and tritium [30].
More recent MSR concepts and fuel-coolant salt related technologies have been researched worldwide. In Europe, MOST and ALISIA, under Euratom’s 5th and 6th Framework Programs, have been collaborations between different institutes and countries on molten salt technologies. Research in France (CNRS and also CEA/EDF/AREVA) has focused on thorium molten salt reactor concepts, including the TMSR (Thorium Molten Salt Reactor) [36] and the TMSR-NM (non moderated) [13], in which the breeder and burner concepts are both applied. The Czech Republic (NRI) focuses on the SPHINX (SPent Hot fuel INCinerator by Neutron Flux) MSR system, proposing to operate in the fast spectrum [37] [38]. Other European burner systems included the AMSTER and TIER concepts. Related international programs include the P&T (Partitioning and Transmutation) and MOSART (MOlten Salt Actinide Recycler and Transmuter) collaborative projects, at the OECD/NEA and IAEA. In Russia, the completed ISTC#1606 and underway ISTC#3749 projects have focused on molten salts and related experimental R&D, including the MOSART burner reactor [39]. In Japan, the developmental strategy THORIMS-NES (The Thorium Molten Salt Nuclear Energy Synergy System) includes the FUJI molten salt power reactor concept, proposed as a plutonium burner, as well as the AMSB (Accelerator Molten Salt Breeder) sub-critical system, that utilises thorium [14].

1.4.3. Candidate Coolants

The main empirical data sources for the fuel-salt coolants again derive from extensive ORNL technical reports and databases, given the ARE, MSRE and MSBR experiments. Literature reviews and reassessments of fuel-salt data have been produced under the MOST and ALISIA programs, such as [10] [31]-[34] [40]. Other literature includes ISTC#1606 publications [11] [41], specifically containing experimental and theoretical research on MSR burner fuel salt compositions.

The candidate fuel-salts are fluorides, given their favourable coolant properties (chapter 2). Selection factors specific to the fuel-salts are described in [10] [11]. In particular, they should have a wide range of solubility for the fertile and fissile materials and low neutron absorption properties. From Table 1, the candidate breeder fuel-salts are $^7\text{LiF-BeF}_2-\text{AnF}_n$ mixtures. In particular $^7\text{LiF-BeF}_2-\text{ThF}_4-\text{UF}_4$ is the typical breeder mixture; given that it was chosen for the MSBR design, more properties data exists for this mixture [42]. $\text{LiF-NaF-BeF}_2-\text{AnF}_n$ compositions (containing the NaF component) are the primary fuel-salt choice for the MSR burner; in which different actinides can be dissolved including UF$_4$ and PuF$_3$ for example [11] [41]. Other ZrF$_4$ containing mixtures (NaF-ZrF$_4$-AnF$_n$) are also considered in various sources, given the fact that NaF-ZrF$_4$ fluorides have high solubility for actinides [2].

1.5. Fusion Applications

The molten salt FLiBe has also been recommended as a blanket coolant in the design of fusion reactors. The paper “Molten Salts in fusion nuclear technology” (Moir et al. 1998) [43] gives an overview of the applications and favourable properties of FLiBe in fusion systems, as well some of the key links between molten salts in fission (MSRE) and fusion technologies. In particular;

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\textsuperscript{vii} The mentioned source is one of the key data references for the breeder fuel-salt (thermophysical properties) chapter 2.

\textsuperscript{viii} The mentioned sources are key references for the burner fuel salts in the thermophysical properties chapter 2.
“Most of the reasons for selecting fused fluoride salt for fission are also applicable to fusion, though there are some specific requirements for fusion reactor coolant/blanket materials concerned with the magnetohydrodynamic (MHD) force, tritium breeding ratio (TBR), tritium confinement and so on.” Moriyama et al. (1998) [43]

The most recent molten salt applications are for the Force-Free Helical Reactor (FFHR) program and for the High-Yield Lithium-Injection Fusion Energy-II (HYLIFE-II) project. The FFHR design is pursued in universities and research institutes in Japan (e.g. the National Institute for Fusion Sciences). The second concept, the HYLIFE-II project, falls under the second Japan/US Program on Irradiation Tests for Fusion Research (JUPITER-II). The JUPITER-II collaboration concluded in 2006, with the US proceeding to re-join the ITER project, (a technology which does not include molten salts) [44].
2. THERMOPHYSICAL PROPERTIES OF MOLTEN SALTS

This chapter covers the main thermophysical properties for (i) primary coolant salts (AHTR) (Table A1; source Williams et al. (2006) [8]), (ii) heat transfer coolant salts (loop to H₂ plant) (Table A2; source Williams (2006) [17]), and (iii) fuel-salt coolants (MSRs) (Tables A3(a), A3(b), 4; various noted sources). The data tables presented in the appendix (Tables A1, A2, A3(a), A3(b), A4), are to be used in parallel with this chapter, since the following text is structured to refer/comment on this data.

2.1. Melting Point and Phase Diagrams

The coolant’s melting point is of primary importance for coolants operating in high temperature reactors. [136] identifies freeze protection as a key technology gap for an MSR, because temperature drops, and subsequent partial freezing, can adversely affect heat transport properties in a liquid coolant loop, operating at high temperatures.

2.1.1. Primary AHTR Coolants

The candidate salt coolants are binary or ternary systems, since multi-component mixtures have lower melting points than single salts. The upper limit on the coolant freezing point (or melting point), is set in the region of 400-525°C for the AHTR primary coolant, as reported in [8], based on ARE, MSRE and MSBR limits [12] [45] (given in [8]).

The phase diagrams for each mixture showing phase boundaries at different compositions and temperatures, are important to understand coolant freezing/defreezing behaviour. A full database of phase diagrams for all salt systems is available in the literature [8], which also cites selected original ORNL reports [49] [50]. The Molten Salt Database (MSDB) [46] and the MOST database [51], give a more complete list of different salt types, with corresponding phase data and melting points.

Other recent literature reviews of phase data for the FLiBe salt mixture (LiF-BeF₂) are provided in [10].

2.1.2. Heat Transfer Coolants

Williams (2006) [17] reports that a minimum steady state temperature of the heat transfer loop is ~680°C (NGNP/NHI loop), and that acceptable melting points for the heat transfer salts are 454°C (FLiNaK – reference salt for the secondary loop (AHTR)) and 385°C (NaF-NaBF₄ – a fluoroborate candidate salt). Table A2 (appendix) shows the melting points.

The phase diagrams of each salt mixture can be referred in [17], also presenting phase diagrams for the ternary chloride systems: NaCl-KCl-MgCl₂ and LiCl-KCl-MgCl₂.

[10] present more recent reviews of the thermodynamic properties and phase diagrams of various molten salt mixtures, and include the FLiNaK (LiF-NaF-KF) and NaF-NaBF₄ systems.

2.1.3. MSR Fuel-Salt Coolants

The references for the phase data of the ternary and quaternary MSR-Breeder fuel-salt coolants LiF-BeF₂-ThF₄ and LiF-BeF₂-ThF₄-UF₄ are shown in Table A3(a) in the appendix. The liquidus temperatures for the thorium breeder quaternary melt LiF-BeF₂-ThF₄-UF₄ are
Various studies into the thermodynamic properties and phase diagrams of the ternary fuel-salt LiF-BeF₂-ThF₄ are found in the literature, as shown in Table A3(a). Original references include measured equilibrium diagrams ([52] as referenced in [10]), and more recent references containing calculated phase diagrams using thermodynamic data ([10] [32] [33]).

The second group in Table A3(a) covers the ternary and quaternary combinations of the LiF-NaF-BeF₂-AnFn fuel-salt system. It is reported in [10] that there is a lack of experimental data for this group of (MSR-Burner) fuel-salts. The mixture LiF-NaF-BeF₂ (in which the fuel-fluoride would be dissolved) was selected as a promising solvent system, in which to dissolve the fuel-fluoride components; this is reported as part of the ISTC#1606 (MSR) research project in Russia (ref [41]). Table A3(a) refers to phase diagram reviews in [41], for the fuel-solvent system LiF-NaF-BeF₂, without fuel-fluoride component. Data for the solubility of plutonium trifluoride (PuF₃) in various compositions of this fluoride mixture are given in [11]. No combined quaternary diagram for the quaternary system LiF-NaF-BeF₂-PuF₃ was located in the literature.

Finally, phase data for all the other binary subsystems are reviewed in the MOST database [51]. Konings et al. (2004) [34] analyses the phase diagrams for other binary (LiF-LnF₃ and LiF-AnF₃) and ternary (LiF-PuF₃-AmF₃) systems, using thermodynamic considerations. These are relevant for the MSR-Burner application. The third group in Table A3(a), the ZrF₄ containing fuel-salts, include only the NaF-ZrF₄-UF₄ system; refer to MOST database [51] for selected data.

### 2.2. Boiling Point and Vapour Pressure

After melting point, the boiling point and vapour pressure of the liquid coolant are the major concerns [53]. As a differential property between liquids, in general, the higher the boiling point of a liquid, the lower the vapour pressure of the liquid (i.e. less volatile). Note vapour pressure is defined at a certain temperature.

#### 2.2.1. Primary AHTR Coolants

In general, Forsberg (2004) [2] states the optimal salt coolants should have boiling points high enough to ensure stability during possible temperature transients in reactor operation; i.e. typically above 1300°C. See Table A1 for boiling points of the selected fluorides, given in [8] [46]. These values are extrapolated from lower temperature data (at around 1100°C) [8].

Vapour pressure is heavily dependent upon salt composition. Based on ARE and MSRE experience, Williams et al. (2006) [8] reported that desirable vapour pressures are predicted to be in the region of 1 mmHg, at high temperatures. See Table A1 for vapour pressures at 900°C, as given in [8].

In Fusion research programs there have been vapour pressure studies on certain salts. Peterson et al. (2007) [54] apply the “modified McGlashan-Rastogi” and “Harris-Prausnitz” thermodynamic models to the binary systems LiF-BeF₂ and NaF-BeF₂, and the ternary

\[ (1 \text{ mmHg} \sim 1 \text{ Torr} \sim 133 \text{ Pa}) [53] \]
system LiF-NaF-BeF$_2$, to gain theoretical vapour pressures (in Pa) as a function of composition, temperature range 500-700°C.

The vapour pressures and species have also been studied closely in Olander et al. (2002) [55]. This study modelled high temperature data from ORNL measurements, taken from [56] (as referenced in [55]), and concluded that the modelled data is applicable in the Torr pressure range, at temperatures above 1000°C (1 Torr ~ 133Pa). Zaghoul et al. (2003) [57] use thermodynamic derivations and experimental data (ORNL), to formulate a correlation for the FLiBe vapour pressure, applied over a wide range of temperatures (800-1600K). Also see ref. [57] for vapour pressure and species data for the FLiBe mixture, according to different salt compositions and temperatures (up to 700°C).

2.2.2. Heat Transfer Coolants

Table A2 presents the boiling points and vapour pressures (at 900°C) for the chlorides and fluoroborate candidate heat transfer salts, as given in [17]. As with the primary salts, the boiling points in Table A2 require further study and in particular for the chlorides.

Williams (2006) [17] plots vapour pressure curves for selected salts from each class, over the temperature range 600-1200°C; however the equations were not provided. [17] identifies key ORNL technical reports [58] [59] that examine the practical issues and “nuisance factors” associated with fluoroborates; e.g. the monitoring and control of BF$_3$ cover gas pressures and reactivity.

From Table A2, it is clear that the vapour pressure data (at 900°C) for the chloride mixtures is more lacking than for other salt mixtures. The ORNL review points out that the vapour pressures of MgCl$_2$ containing salts, as well as the MgCl$_2$ vapour species itself, may be problematic [17].

2.2.3. MSR Fuel-Salt Coolants

Data for vapour pressures of the fuel-salt systems was scarce in the located literature, and are therefore not included in Table A3(a).

However, the vapour pressures for the MSBR (breeder) fuel-salts are considered in [42] (dated 1968), for the quaternary mixtures, and are shown in Table A3(b). The source reports that the estimates are empirical, based on the vapour pressures of the LiF-BeF$_2$ and LiF-UF$_2$ binary subsystems, with uncertainty as a factor of 50 in the temperature range 500-700°C.

Konings et al. (2007) [32] provides a more recent review of the thermophysical properties of the ternary fuel-salt LiF-BeF$_2$-ThF$_4$, including vapour pressure.

2.3. Density

Molten salt density $\rho$ decreases linearly, as temperature increases [8]. It is an important property to define for candidate coolants, since it affects heat transfer characteristics (such as volumetric heat capacity and thermal conductivity). Williams et al. (2006) [8] reports that the density is easy to measure, (fluid mass divided by fluid volume, units kg/m$^3$ [60]), and, therefore the existing database retains good experimental validation in this area.
2.3.1. Primary AHTR Coolants

Table A1 gives the set of density equations for each salt mixture. Note that there is some discrepancy between equations in the literature and the data sources [8] [46] [47]. There were two main methods to derive the density equations at ORNL (as discussed in [8]): one using experimental data (LiF-BeF₂, NaF-BeF₂, LiF-BeF₂-ZrF₄, LiF-KF, LiF-RbF, LiF-NaF-KF, NaF-ZrF₄) and another using a predictive method (additive molar volumes method). See [61] (ref given in [17]) for an original analysis of the method.

For the mixture LiF-BeF₂ (or “FLiBe” to which it is commonly referred), Table A1 also presents a density equation taken from a Fusion study [57]. Zaghoul et al. 2003 [53] extended the density equation developed from ORNL experimental data (for temperature range 800-1080K [47] [48]), to the critical temperature of the salt mixture (estimated at 4498.8K [53]), therefore covering a wider temperature range. Other assessments of past literature sources for density data for FLiBe can be found in [10].

2.3.2. Heat Transfer Coolants

Many of the density values in Table A2 for the fluoroborate and chloride mixtures are measured, summarising those given in the ORNL review [17]. The details of the experimental methods are not specified, and should be sought in the original data sources given in [17]; i.e. [62] [63] [64] [65]. As with the primary salts, the method of additive molar volumes was found to be fairly accurate for predicting many of the densities, over a wide temperature range (as reported in [17] [8]); the density equations for two of the fluoroborates (KF-KBF₄ and RbF-RbBF₄) were derived in this way. No temperature range was given either in the ORNL review or the MSDB, for the equations listed. A modified density equation is given for the mixture KCl-MgCl₂, sourced from the [46].

Measured density equations for the FLiNaK and NaF-NaBF₄ heat transfer coolant salts are recommended in [10]. For FLiNaK, an equation is given from previous literature, and for NaF-NaBF₄ the ORNL measured data (Table A2) is recommended.

Theoretical models for density derived from “first principles” can be found in Salanne et al. (2009) [66] [67]. This source determines temperature dependent density equations for FLiNaK and NaF-ZrF₄ using this model, and also compares the results to previous experimental data.

2.3.3. MSR Fuel-Salt Coolants

Table A3(a) shows the references for the densities of the two breeder salt mixtures ⁷LiF-BeF₂-ThF₄-UF₄ and LiF-BeF₂-ThF₄. The density equations for the quaternary system are presented in Table A3(b), for the four compositions studied in Cantor (1968) [42]. These temperature dependent equations are estimated using the additivity of molar volumes method, given for pure-compounds.

The densities for the ternary system LiF-BeF₂-ThF₄ can be referred in various sources, including; original data (experimental calculations using dilatometric method, and estimated methods using additivity of molar volumes) in [68], as reported in data reassessments [10]. Another source (Ignatiev et al. 2002) [41] gives a measured equation (using the method of maximum pressure in a gas bubble) in the temperature range 850-1150K, and compares to earlier ORNL data. Related sources (under ISTC#1606 literature) also present methods to estimate the density, and other thermophysical properties, of various compositions, using a
calculation algorithm ("the additivity principle") based on the properties of constituent salt compounds [11].

The next group in Table A3(a) also shows the above references [11] [41] for estimated density equations for the MSR-Burner fuel-solvent salt LiF-NaF-BeF₂. Scattered data in the MOST database [51], can be found for other subsystems, in the MSR-Burner group of fuel-salts.

2.4. Heat Capacity and Volumetric Heat Capacity

Heat capacity $C_p$ gives the amount of heat energy required to change the temperature of a given mass of coolant by a certain amount (SI units, J/Kg °C). Compared to water, the heat capacities of molten salts are low. However, the volumetric heat capacity of fluoride salts is comparable to that of water, which is a desirable characteristic for a heat transfer coolant [2] [8] [16].

2.4.1. Primary AHTR Coolants

The ORNL database provides a limited set of experimental values and a complete set of predicted values, for the heat capacity of candidate salts (at 700°C) [8] (see Table A1). The units in the table are given in (cal/g °C); 1 cal/g °C is equivalent to 4.184 kJ/kg °C [69]. The experimental method used is reported as relatively unreliable (experimental accuracy ±10%) going by current standards [8]. The predictive method used was that of Dulong and Petit, and is calculated to reach an accuracy of only ±20%, as given in [8]. However, the review reports that the measurement of the LiF-BeF₂ mixture heat capacity is more reliable (±2% accuracy), given that it was the salt chosen for the MSRE [8]. The temperature dependence of heat capacity is indicated as an area in need of further investigation in [8]. Note that Peterson et al. (2008) [70] states that “the specific heat can normally be considered constant over a wide range of temperature”.

The volumetric heat capacities are located in [8], which references original sources [47] [56] [71] [72]. It is calculated (SI units, J/m³ °C) by taking the product of density (experimental value or predicted) and corresponding heat capacity.

2.4.2. Heat Transfer Coolants

Some of the values for heat capacity in Table A2, for the fluoroborates and chlorides, are based on direct experiment on the binary mixtures (see [17]). Where direct experimental data was not available, other values are based on pure-component heat capacities. Original references given in the ORNL review are [47] [62] [63] [73]-[76]. The predicted values in the Table A2 are reported to be calculated from the Dulong-Petit empirical equation.

Literature reviews of heat capacity data for FLiNaK and NaF-NaBF₄ mixtures can be found in [10]. For theoretically determined values for FLiNaK and NaF-ZrF₄, also see [66].

2.4.3. MSR Fuel-Salt Coolants

The liquid heat capacities for the first group of fuel-salt coolants in Table A3(a) are presented in Table A3(b) (for the four MSBR compositions of the MSR-Breeder quaternary fuel-salt). This data is estimated using the mole-fraction additivity method, using values of individual salt components, as reported in [42]. The study checks the validity of the predicted values against measured values of $C_p$, of related salts (e.g. ternary LiF-BeF₂-ThF₄).
An ISTC#1606 paper [41] compares the predicted heat capacity of the ternary breeder fuel-salt (composition 72LiF-16BeF₂-12ThF₄), to the experimental value given at ORNL [42], with good agreement. Other sources are shown in Table A3(a) for estimated and scattered measured heat capacity data, for other fuel-salt mixtures.

2.5. Dynamic Viscosity

Viscosity $\mu$ is an important characteristic because it defines the fluid’s resistance to flow and is therefore fundamental to the convective heat transport properties of the coolant [60]. Viscosity is dependent on temperature, such that as the temperature increases, typical fluid viscosity will decrease exponentially (as shown in [8]); this is a particularly important factor for high temperature applications. Salt composition also affects viscosity, and should be considered when selecting a salt coolant for an application. In general, all the candidate salts show reasonably low viscosities (<10 cP) allowing their use as industrial coolants. Dynamic viscosity is measured in Pa s or cP (Centipoise), where 1 Pa s is equivalent to 1000 cP.

2.5.1. Primary AHTR Coolants

The viscosity equations that were located, together with the data gaps, are shown in Table A1 from [8] [47]. Where there was no available viscosity equation for certain salt mixtures, a data value at 700°C was available in [8]. The validity grounds of these data points are not made clear in the source. The original sources are based on early ORNL measurements, including [77] [78] (refs given in [8]), established via capillary efflux and rotational viscometers experiments. Note [79] is reported to extrapolate viscosity correlations to higher temperatures. It is also stated in [8] that the lighter alkali salt systems give the higher viscosities.

Abe et al. (1981) [80] study the viscosity of the eutectic LiF-BeF₂ (with BeF₂ content of 32.8 % mol) using an oscillating cup viscometer, in the higher temperature range (539.5-1300°C); as shown in Table A1. The source also compares experimental data to previous viscosity data for the same mixture (including the ORNL results).

2.5.2. Heat Transfer Coolants

The chlorides and fluoroborates have low viscosities, even compared to the fluoride melts (see [17] for comparisons). The equations given in Table A2 for the viscosity (as a function of temperature) are based on experimental measurements (sourced from [17]). For the salts without a corresponding viscosity equation (LiCl-RbCl and RbF-RbBF₄), there were no measured results available to the ORNL reviewer [17]. In these cases, viscosity values were calculated using the ideal-mixture viscosity equation based on the viscosity of each component in the mixture, (see [17]).

Reviewed and recommended viscosity data for FLiNaK and NaF-NaBF₄ coolant salts, are given in [10]. Another source [66] also uses simulated model to compute the viscosity relations for FLiNaK and NaF-ZrF₄, and compares to measured data.

2.5.3. MSR Fuel-Salt Coolants

Table A3(a) shows the viscosity data located for the fuel-salts. Results for the quaternary breeder fuel-salts (LiF-BeF₂-ThF₄-UF₄) are presented in Table A3(b). For this quaternary fuel-salt, four exponential equations are given for viscosity, with calculated values at 600°C and 700°C (873-973K) [42]. The equations are estimated empirically from the viscosity
measurements of the ternary subsystem LiF-BeF$_2$-UF$_4$, with a reliability range of 25%; as reported [42].

Table A3(a) shows further viscosity references for the LiF-BeF$_2$-ThF$_4$ ternary system. Three compositions are measured in [68] using oscillating-cup viscometry, and a measured viscosity equation (up to 1300K, using torsional oscillations cylinder) is given in [41], with comparisons to the earlier ORNL data. An analysis of the viscosity of this ternary composition, related to the thermodynamic Gibbs energy coefficients, is given in [32].

Measured data for the MSR-Burner fuel-salt composition (for the solvent system, with no fuel component) is given in the form of an equation (525-800°C) in [41], together with modelled data and comparisons with earlier ORNL measured data (in the same source).

Scattered viscosity data for the other MSR-Burner salt mixtures, including the NaF-ZrF$_4$-UF$_4$ mixture, are located in the MOST database [51].

### 2.6. Thermal Conductivity

Thermal conductivity $k$ (SI units W/m K) must be evaluated for the purposes of heat transfer calculations. The two mechanisms of thermal conduction in molten salts are (a) the vibration mechanism, due to the mechanical behaviour of liquid molecules, and (b) the diffusion mechanism, due to the movement of ions [81] (and [82] as given in [8]). In particular, the design of heat exchangers in direct contact with the coolants requires knowledge of this property [81].

Thermal conductivity is however described to be difficult to measure for molten salts, across the literature. Sources of experimental error identified in the literature derive from underestimated contributions from other modes of heat transfer (thermal convection and radiation) [8] [83]. In general, thermal conductivity of liquid salts decreases with increasing temperature [70].

#### 2.6.1. Primary AHTR Coolants

In terms of experimental measurements, the database is deficient, as reported in [8]. The few measured values are shown in Table A1. More reliable $k$ values are required for a range of the candidate salt mixtures, and especially for the ZrF$_4$ salts. It is generally concluded in [17] that the lighter salts (i.e. with lighter atoms), yield higher thermal conductivities (originally [81]. The most common experimental method for measuring the thermal conductivity uses a variable-gap technique [83].

The ORNL assessment [8] presents two predictive models for thermal conductivity as a function of temperature, which are deemed to be the most reliable models, given the limited results. The first is from Turnbull [81], and the second method is an empirical correlation from Ignatiev and Khoklov (used in Table A1) [41].

Ignatiev et al. (2002) [41] also presents a measured set of values (temperature range 500-750°C), for the ternary eutectic 7LiF-64.2NaF-28.8BeF$_2$. The coaxial cylinder experimental method used for the measurements is described as reliable by the authors [41]. The same study goes on to show good agreement between this measured data and the data predicted from their model (Khoklov correlation).
2.6.2. Heat Transfer Coolants

The earlier problems associated with the measurement of thermal conductivity go for all salts, including the high temperature chlorides and fluoroborates, as reported in [17]; the experimental data gaps are evident in Table A2. The most reliable predictive method uses a mole-fraction average of the thermal conductivity of the pure-compound values, as given in [17] ([84]).

A very recent paper reviews the “Current status of knowledge of the fluoride salt (FLiNaK) heat transfer” (Ambrosek et al. 2008) [83]. Note FLiNaK is the reference salt for the heat transfer loop. The study reviews previous heat transfer models for the salt, and notes discrepancies in the thermal conductivity values used in past experiments. The experimental correlation \( k = 0.36 + 0.00056 \times T(K) \) is taken to be the most accurate in the paper, and is considered as an accurate semiempirical model (cited from Smirnov et al. 1987 [85]). The value at 700°C is calculated and presented in Table A2 (or A1) for FLiNaK, and is close to the value predicted by the Khoklov correlation (used for the other fluorides).

Konings et al. (2009) [10] also reference and recommend the same equation as discussed above for FLiNaK. Thermal conductivity data is also reviewed in this source for NaF-NaBF₄, from past ORNL literature ([42] [68]).

2.6.3. MSR Fuel-Salt Coolants

The thermal conductivities for the first group of fuel-salt coolants in Table A3(a) (thorium breeder cycle) are presented in Table A3(b). Cantor (1968) [42] states a >25% range of uncertainty in each result, and, due to this large range of error, the temperature dependence can be neglected. The source also states that they do not possess adequate experimental validation [42].

For the ternary thorium-salt (LiF-BeF₂-ThF₄) in Table A3(a), a literature review of thermal conductivity data, together with linear extrapolations (850-1000K) and recommended values, is found in [10]. The ISTC#1606 report [41] compared their predicted value for \( k \) at 866K (for composition 72LiF-16BeF₂-12ThF₄) to the ORNL measured values (by variable gap method), reporting significant discrepancy.

For the MSR Burner fuel-salt carrier system LiF-NaF-BeF₂, Table A3(a) shows references for estimation methods.
3. HEAT TRANSFER IN MOLTEN SALTS

The value of the heat transfer coefficient \( h \) is based on (i) the conditions of operation, including channel geometry, flow rate, heat flux and system temperature, and (ii) the physical properties of the coolant fluid. The first section (3.1) will outline the basic theoretical definitions (equations, coefficients, correlations) and concepts (heat transfer performance comparisons, high Pr fluids, mixed flow regimes) that are found in the literature to apply to high temperature, molten salt coolants.

Using the theory as an introductory/reference section, a literature review of the existing experimental studies and results, plus scaled simulation studies, will be covered in the second half of this chapter (3.2).

3.1. Theoretical Factors

3.1.1. Basic Relationships

**Heat Flux and Heat Transfer Coefficient**

Molten salts are assumed as Newtonian fluids [8]. Therefore, Newton’s law of cooling is used to describe the heat transferred \( q \) between a coolant and a surface (notation from [86] and [87]).

\[
q'' = \frac{q}{A} = h(T_w - T_f)
\]  

Where, \( q'' \) (in W/m²) \(^\text{x}\) is the heat flux, \( q \) (in W) is the heat transferred, \( A \) (in m²) is the area across which heat flows, \( h \) (in W/m²·°C) is the coefficient of heat transfer by convection, or “surface conductance”, \( T_w, T_f \) (in °C) are the wall-surface and fluid bulk temperatures respectively.

**Pumping Power and Pressure Drop**

The pumping power \( W \) (in W) is essentially equivalent to the power required by the coolant to overcome pressure losses through the loop. Pressure drops derive from a range of sources, such as friction, and can be calculated using the sum of the losses \( \Delta p \) (in Pa = N/m²), as shown below:

\[
W = \Delta p A_c u
\]  

\[
\Delta p = f \frac{L \rho u^2}{D_e 2g_c}
\]  

(Darcy formula)  

Where, \( A_c \) (in m²) is the cross section of the coolant passage, \( u \) is the coolant velocity, \( f \) (dimensionless) is the friction factor – this is a property of the particular conditions of the coolant loop, varying with channel surface (smooth/rough), and flow regime (level of turbulence), \( L \) (in m) is the channel length, \( g_c (= 1 \text{kg m/N s}^2) \) is the conversion factor, \( D_e \) (in m) is the “effective” or “hydraulic” diameter of the channel passage, which may deviate from

\(^{\text{x}}\) Original source [86] uses non-SI notation, for the following units: energy (Btu), length (ft), time (hr), temperature (°F), mass (lb). Conversions to SI units have been made, for all units taken from this source.
a circular shape. \( D_e \) can be defined as \( 4A_e/P \), if \( P \) (in m) is the wetted perimeter; \( \rho \) is the fluid density (kg/m\(^3\)).

For more complex geometries than smooth circular pipes, other friction factor equations were located in the literature applied to liquid salt systems. In a scaled experimental analysis of the liquid salt, pebble bed core design of the PB-AHTR [88], the pressure loss equation used is Darcy’s formula (3), with a theoretical friction factor based on the available correlations in packed beds (i.e. Ergun’s equation). Ergun’s equation is further identified in other sources related to molten salts, in applied simulation experiments (in packed bed geometries) [89], and in the parameter design analysis of the LSPBR (Liquid Salt Pebble Bed Reactor; variant of the AHTTR) [24]. From [88]:

\[
f = \frac{1 - \varepsilon}{\varepsilon^3} \left( \frac{a}{\text{Re}_s} + b \right)
\]

(Ergun’s equation) \hspace{1cm} (4)

Where, \( \varepsilon \) is porosity, \( \text{Re}_s \) is defined with a superficial velocity \( u_s \), (a,b) use values of either (180,1.8) or (150,1.75); as given in [88].

**Dimensionless Coefficients**

The most fundamental coefficients commonly used in heat transfer correlations, are the first three in Table 5A (in appendix). The Nusselt number is defined as the ratio of convective heat transfer \( hD_e \), perpendicular to the direction of fluid flow (i.e. along channel diameter \( d_e \)), to conductive heat transfer \( k \). The Nu number is a function of the Pr and Re numbers \( \text{Nu} = f(\text{Re Pr}) \), and it is this correlation (used in various forms) that is usually used to calculate heat transfer in a coolant system.

The Reynolds number gives the ratio of inertial forces to viscous forces. A low \( \text{Re} \) represents a laminar flow, in which flow-disturbances are dampened. A critical \( \text{Re} \) represents the transition from laminar to turbulent flow, in which flow-disturbances are no longer dampened. A high \( \text{Re} \) represents a highly turbulent flow, in which there is a high degree of mixing and convective heat transfer [86].

The Prandtl number is the ratio of kinematic viscosity, a measure of the rate of momentum transfer between molecules, to the thermal diffusivity, a measure of the rate of heat transfer to energy storage by molecules. To refine the definitions further, the kinematic viscosity of the fluid (in m\(^2\)/s) is given by \( \nu = \mu/\rho \) and the thermal diffusivity of the fluid (also in m\(^2\)/s) is given by \( \alpha = k/\rho c_p \). The Pr number is the only coefficient based only on the thermophysical properties of the coolant fluid, which depend on fluid temperature, and to a lesser extent, the pressure [86].

**Standard Correlations**

The textbooks “Nuclear Heat Transport” (El-Wakil, 1981) [86] and “Fundamentals of Heat and Mass Transfer” (Incropera and DeWitt, 2002) [90] were used to source a set of standard heat transfer correlations, and are presented in Table 3.
The correlations themselves calculate the local Nu number (which can be used to get a value of convective heat transfer \( h \)). Note the correlations can be applied for both the uniform surface temperature and heat flux conditions, for fully developed turbulent flow in a smooth circular pipe [90]. The ranges of validity for the correlations, in terms of Pr (fluid properties) and Re (turbulent conditions), are also presented in the table. It should be understood that these Pr ranges are only theoretical, and the validation of the correlations for high temperature molten salt systems would be required.

### 3.1.2. Heat Transfer Comparisons between Coolants

**Pr Number**

Table 4 shows the Pr and thermal conductivity values of three selected molten salt coolants (FLiBe, FLiNaK and a fluoroborate heat transfer salt), along with three other standard coolants for comparison. For a more complete list of candidate salt mixtures and corresponding Pr numbers, see [8] (calculated at 700°C).

<table>
<thead>
<tr>
<th>Coolant</th>
<th>Temperature (°C)</th>
<th>Thermal Conductivity k (W/m K)</th>
<th>Pr No. ((C_p \mu/k))</th>
<th>Data Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>300</td>
<td>0.54</td>
<td>0.967</td>
<td>[8]</td>
</tr>
<tr>
<td>Sodium liquid (Na)</td>
<td>550</td>
<td>62</td>
<td>0.004</td>
<td>[8]</td>
</tr>
<tr>
<td>Helium gas (He)</td>
<td>827*</td>
<td>0.36</td>
<td>0.66</td>
<td>[70]</td>
</tr>
<tr>
<td>2LiF-BeF₂</td>
<td>700</td>
<td>1</td>
<td>13.525</td>
<td>[8]</td>
</tr>
<tr>
<td>LiF-NaF-KF</td>
<td>700</td>
<td>0.92</td>
<td>5.938</td>
<td>[8]</td>
</tr>
<tr>
<td>NaF-NaBF₄</td>
<td>700</td>
<td>0.5</td>
<td>2.64</td>
<td>[8]</td>
</tr>
</tbody>
</table>

* at 10MPa pressure.

Molten salt fluids are in the class of high Pr number fluids (Pr in the order of 10); compared to liquid metals (Pr much lower than 1), and water and gas coolants (Pr around 1), all given at typically operating temperatures. The high Pr property of a molten salt, therefore results in
Heat transfer mechanisms unique to molten salt fluids (i.e. different from lower Pr fluids). These effects will be discussed in section 3.1.3.

**Heat Transfer Performance FOM**

Heat transfer performance indicators are used to provide a comparative analysis between candidate salts and other coolants (water, sodium, lead). Williams et al. (2006) [8] states “generalised heat-transfer metrics are a useful tool for grouping coolant performance in the absence of more detailed system designs”. Essentially, a “figure of merit” (FOM) for each flow regime is calculated for each coolant, based on certain thermophysical properties ($\mu$, $\rho$, $c_p$, and volume expansivity $\beta$ (in $1/\degree C = 1/\rho \cdot d\rho/dT$) of the coolant or particular salt mixture (see Table 6 below). The FOMs of each fluid are then ranked in order of performance, with a lower value correlating with better performance. The principle behind the model is that the “minimal pumping power for a given coolant temperature rise as the objective function for forced convection” [8].

<table>
<thead>
<tr>
<th>No.</th>
<th>Equation</th>
<th>Regime Basis Of FOM</th>
<th>Refs. citing FOM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$FOM = \mu^{0.2}/(\rho^{2}c_{p}^{2.8})$</td>
<td>forced convection, turbulent</td>
<td>[8] [17] [66], originally [91]</td>
</tr>
<tr>
<td>2</td>
<td>$FOM = [\mu/(\beta c_{p})]^{0.36}$</td>
<td>natural convection, turbulent</td>
<td>[8] [17] [66], originally [91]</td>
</tr>
<tr>
<td>3</td>
<td>$FOM = [\mu/(\beta c_{p})]^{0.5}$</td>
<td>natural convection, laminar</td>
<td>[8] [17] [66], originally [91]</td>
</tr>
<tr>
<td>4</td>
<td>$FOM = \mu^{0.2}/(c_{p}^{0.6}k^{0.6}\rho^{0.6})$</td>
<td>heat exchanger area*</td>
<td>[8] [17] [66], originally [45]</td>
</tr>
</tbody>
</table>

Table 6: Figures of Merit - theoretical equations used to rank salt/coolant performance, according to a particular flow regime, or to the area required for the primary heat exchanger*.

*It is recommended that the last FOM be used to compare coolants within a group (e.g. salts) rather than between different groups [8].

### 3.1.3. High Pr Effects

Molten salt fluids have high Pr numbers, which affect the heat transfer capabilities. The influence of high Pr on fluid heat transfer was found in various sources.

The basic features of high Pr fluids are well summarised in a paper on experimental heat transfer of molten salts in circular pipe flow (in a study on FLiBe as a blanket coolant for a fusion reactor, JUPITER-II program):

“The low thermal conductivity and high viscosity of FLiBe make it a high Prandtl number medium – meaning heat transport from a heated wall into the core of the coolant flow is dominated by turbulent motion rather than thermal diffusion. Near wall flow structures are especially important because thermal boundary layer is much thinner than the momentum boundary layer. In the case where the thermal boundary layer lies within the viscous sub-layer, the heat transfer through the wall decreases considerably. This makes the investigation of the fluid mechanics and heat transfer of high Prandtl number fluid compared to low Prandtl number fluid very important from the design point of view in order to assess the applicability of FLiBe to high heat flux removal system as well as the prospect for heat transfer enhancement mechanisms.”

Takeuchi et al. (2007) [92]

These considerations are mirrored in a theoretical analysis of molten salts heat transfer in [87], where it is explained that the thermal resistance in the high Pr fluid is “primarily close to the wall yielding an almost square temperature profile”. In laminar flow conditions the effect is explained to decrease, to some degree (see [87]).

These properties of high Pr fluids are described as a disadvantage of using molten salt coolants; since it is reported “a high Pr fluid flow has less heat transport capability because of
low thermal conductivity and very thin thermal boundary layer” [93], and “high Prandtl-number (Pr) fluid leads to low heat transfer performance” [94]. In the fusion related molten salt studies, heat transfer enhancement mechanisms are investigated [93]. Examples of techniques used to increase thermal mixing are packed bed tubes; further details and results of these experiments (TNT Loop, Japan) will be covered in the part 3.2.

### 3.1.4. Mixed Convection

Mixed convection effects should be considered in molten salt heat transfer systems. A (previously cited) research study from UCB (2006) describes the Design and set-up of a high temperature flow loop for the investigation of heat transfer and pressure loss in a mixed convection regime flow of higher Prandtl number molten salt simulants [87]. The reference contains a detailed theoretical background and literature review, covering many theoretical aspects of high temperature, molten salt coolant systems.

#### Natural Convection and Buoyancy Effects

Rather than treating forced and natural convection separately, it is stated that

> “Due to temperature difference that must be present for heat transfer there are always density differences that cause buoyancy effects and as a result some natural convection forces. Especially for high temperature differences the impact of free convection can become considerable even for cases that seem to be ruled only by forced forces at first glance.” Hauk (2006) [87]

A detailed literature analysis is then performed, of recently proposed equations that determine whether there is dominating forced convection, or non-negligible buoyancy force. It is stated that “designing engineers are interested in a border that tells them up to where the influence of natural convection is negligible” [87]. Some key aspects of this review are summarised in Table 7:

<table>
<thead>
<tr>
<th>Inequality / Border Method</th>
<th>Details</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Gr^{1/3} / (Re^{1/2}Pr^{2/15}) &lt; 1)</td>
<td>- If inequality is true, there is dominating forced convection.</td>
<td>[87], citing [95] (as original ref.)</td>
</tr>
<tr>
<td>Graphical Approach</td>
<td>- A “map” indicates whether forced, free or mixed convection dominates heat transfer.</td>
<td>[87], citing [96] (as original ref.)</td>
</tr>
</tbody>
</table>

#### Table 7 Summary of literature review in [87] to determine the point of influence of buoyancy and natural convection forces.

In general, the research study reports that these relations need to be validated with experimental data for higher Pr fluids:

> “No data of fluids of Pr above 5 (for water) has been tested with this criterion as far as it was found in the literature and the upset experiment should allow to collect proper data to fill this gap.” Hauk (2006) [87]

Validating these buoyancy considerations for molten salt coolants requires further work. The referred “upset experiment” (which is the main subject of the UCB project [87]) constitutes an obvious data source and should be followed up.

#### Mixed Convective Correlations

To derive more accurate (mixed) convection correlations, for molten salt (high Pr fluids), [87] uses and compares two methods, namely Aicher and Martin [97] and Celata et al. [98]. The
resulting correlation \( (\psi = \frac{Nu_4}{Nu_{Op}}) \) is compared to present experimental data in the same source, and the following evaluation is given, with reference to high Pr coolants:

“The comparison shows quite good prediction quality with most data points estimated within ±20%, however it is still not sufficient to predict the heat transfer for critical design problems like nuclear reactors. Additional data from an experiment using a fluid in the Prandtl number range of interest is required in order to validate existing or establish new correlations.” Hauk (2006) [87]

3.1.5. Two Phase Flow

No theoretical (or experimental) treatments of multi phase flow in liquid salt reactor coolants were located in the reviewed literature. In the paper “Options for Scaled Experiments for High Temperature Liquid Salt and Helium Fluid Mechanics and Convective Heat Transfer” (Peterson et al. 2008 [70]), a design and pre-analysis of scaled thermo-mechanic experiments for the molten salts is presented. In this source it is stated that:

“Because liquid salts have a very high boiling temperature (>1300°C) and a very low volatility, phase change phenomena are typically not important. However, in cases where free surfaces exist between the liquid and a gas, as at the free surface of liquid pools or centrifugal pump bowls, or in cases where gas bubbles are entrained or liquid jets or droplets are sprayed through a gas, gravity forces may play an important role.” Peterson et al. (2008) [70]

3.1.6. Thermal Radiation

Heat transfer by thermal radiation in liquid salts is considered in the paper on scaled experiments for high temperature liquid salt heat transfer [70] and in the FLiNaK data reassessment studies [83] [109] (both sources used in next part of chapter 3.2). The results of these two analyses are summarised in turn. First, it is identified that:

“Helium and liquid salt applications involve temperatures where thermal radiation heat transfer has the potential to be significant. Therefore, in all cases the potential effects of thermal radiation must be considered in the design of experiments.” Peterson et al. (2008) [70]

The cited source identifies that heat transfer by radiation depends on a complex set of factors, including system geometry, absorptivity, emissivity, temperature, chemical compositions, etc. See [70] for a more detailed review of thermal radiation effects on convective heat transfer (e.g. a more recent reference, cited in [70], is [111]).

Liquid fluoride salts are transparent in the visible/near-infrared spectral region, as reported in [70]. However, the paper clarifies that “data and modeling for the effects of infrared absorption on liquid salt heat transfer are not well developed” [70].

In Ambrosek et al. (2009) [83], a radiation heat transfer coefficient is included in the model for convective heat transfer, using the method described in Adams and Rogers (see [83]). Initially it was observed that the heat transferred by radiation is small compared to convection (only ~ 0.6% of heat transferred to salt). A theoretical model was also run to test at what point the contribution of radiation would become significant (>10% of total h term); changing temperature and Re parameters in the modelled flow [109]. The results indicate that “radiation heat transfer in high-temperature applications is not negligible as the flow moves to the laminar regime” [83]. Also, it is observed that “as the corrosion products from the container
material increase in the salt, the absorption increases. A more detailed understanding of the absorption coefficient of these salts is needed” [83].

3.2. Heat Transfer Experiments

Empirical investigations into the heat transfer of molten salts is limited in the literature, both in general, for fluids with higher Pr (in the order of molten salts), and also across each of the candidate salts. Ambrosek et al. (2009) [83] recently states that “there have been only a handful of measurements for forced convective heat transfer of liquid salts in the open literature”, and Hauk (2006) [87] states that “almost no experimental data is available for heated up flow in channels at Prandtl numbers of the order of 10”. Validating heat transfer correlations for convective heat transfer therefore remains a key research objective, for the development of molten salt coolants in reactors.

Table 8 (overleaf) summarises various experimental studies located in the literature, and also relevant simulation studies as a pre-test for molten salt cooling systems in reactor systems.
### Table 8: Literature survey of heat transfer experiments and simulations of molten salts.

*Each earlier study on FLiNaK is re-evaluated in Ambrosek et al. 2009 [83]. Therefore, most of the original experimental data was sourced from this more recent paper; however, the only original source not available to the present review was Grele and Gedeon 1954 [102].

1. No date for publication is given in original source.
2. Original values $q'' = 22,000-560,000$ Btu/hr. ft$^2$. Conversion factor [86] 1Btu/hr.ft$^2 = 3.155.10^{-4}$W/cm$^2 = 3.55.10^{-3}$kW/m$^2$."

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Institute / Program / Refer.</th>
<th>Type Of Experiment / Simulation (and Experimental Conditions)</th>
<th>Advised Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td>FLiNaK</td>
<td>Wisconsin (USA)</td>
<td>Ambrosek et al. 2009 [83]</td>
<td>Data re-evaluation and modelling of previous experimental results</td>
</tr>
<tr>
<td></td>
<td>(Russia)</td>
<td>Ignatiev et al. 1983 [99]*</td>
<td>Heat exchange experiment in a circular tube: Kh18N10T: iron based steel, $T_{fluid} = 550-650^\circ$C, $Re = 5000-15000$, $q''$ (Heat Flux) = 30-60kW/m$^2$</td>
</tr>
<tr>
<td></td>
<td>Delft, (Netherlands)</td>
<td>Vriesema [100]*</td>
<td>Heat transfer experiment in vertical apparatus: Inconel 600 alloy, $T_{fluid} = 575-675^\circ$C, $Re = 14000-93000$</td>
</tr>
<tr>
<td></td>
<td>ORNL (USA) “MSRE”</td>
<td>Hoffman and Lones 1977 [101]*</td>
<td>Forced convection heat transfer experiment in a circular tube: Inconel, Nickel, Type 316 SS alloy pipes, $T_{fluid} = 646-702$, 527-734, 722-745$^\circ$C respectively for each pipe alloy, $Re = 2800-8337$, 2400-5600, 6600-9500, $Pr = 6.0-8.0$, 5.1-17.1, 4.9-5.4, $q''$ = 29-540, 73-604, 25-355kW/m$^2$</td>
</tr>
<tr>
<td></td>
<td>ORNL (USA)</td>
<td>Grele and Gedeon 1954 [102]*</td>
<td>Forced convection experiment: Inconel X system, $T_{fluid} = 540-729^\circ$C, $Re = 2000-20000$, $Pr = 5.2-15.6$, $q''$ = 28-606kW/m$^2$</td>
</tr>
<tr>
<td></td>
<td>ORNL (USA)</td>
<td>[8] (Cooke and Cox 1973 [103])</td>
<td>None given</td>
</tr>
<tr>
<td></td>
<td>Salts in general</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>UCB / INL (USA) “PB-AHTR”</td>
<td>Peterson et al. 2003 [88], 2007 [104], 2008 [70], Hauk 2006 [87]</td>
<td>Scaled heat transfer experiments for molten salts, using simulant fluids, and pebble bed core design (PB-AHTR).</td>
</tr>
<tr>
<td></td>
<td>Tohoku / NIFS / Kyoto / Toyama, (Japan):</td>
<td>Chiba et al. 2006 [94], Kunugi et al. 2001 [93]</td>
<td>Numerical research and simulation (DNS) of high Pr fluid flow and heat transfer enhancement. 2D thermofluid simulations and computational visualisation. Packed bed and cylinder geometries analysed to enhance thermal mixing in flow.</td>
</tr>
<tr>
<td></td>
<td>Tohoku / NIFS, (Japan): “TNT Loop”</td>
<td>Satoh et al. 2007 [106], Chiba et al. 2002 [107], 2005 [89]</td>
<td>Experimental studies of heat transfer in high Pr and high temperature molten salt fluids. Experimental studies of heat transfer enhancement in high Pr fluids. KNO$_3$-NaNO$_2$-NaNO$<em>3$ stimulant used: SUS316 alloy, $T</em>{fluid} = 200-300^\circ$C, $Re$ ~ 3500-13000, $Pr = 13-27$, $q''$ ~ 30kW/m$^2$</td>
</tr>
<tr>
<td></td>
<td>Tohoku / Tokyo / Kyushu / Kyoto (Japan), and UCB (USA): “FLIHY”</td>
<td>Takeuchi et al. 2006 [92], 2008 [108]</td>
<td>Study of heat transfer enhancement/suppression for molten salt flows in a large diameter circular pipe. Potassium hydroxide (KOH)-water stimulant: SUS304 alloy, $T_{fluid} = estimated using equation, no value given, Re ~ 22,500$, $Pr = 7$, $q''$ ~ 5kW/m$^2$</td>
</tr>
</tbody>
</table>
The following sections will provide a short review of the relevant conclusions of the studies in Table 8, related to molten salt heat transfer properties.

3.2.2. University of Wisconsin (Heat Transfer Salt)


Reassessment of FLiNaK Heat Transfer Data

Ambrosek et al. (2009) [83] re-evaluates experimental data from the 1950s and 1960s from three forced convective heat transfer experiments using FLiNaK (see refs in table). Computer models (2-D) of each test section and material set ups of the previous experiments were performed in FLUENT, to simulate and re-predict the heat transfer results using more up to date thermal properties data (as reported in [109]). Note that brief details of the past experiments are shown in Table 8.

• For forced convective, turbulent flow (10,000<Re<100,000), using the data from experiments conducted in tubes made of Inconel alloy, Ambrosek et al. (2009) reports “with the use of correct properties, the heat transfer of fluoride salts, in particular FLiNaK, can be modelled using the DB correlation” [83].

• For the laminar region of flow (Re<2300), for constant heat flux, [83] used a heat transfer correlation given by Gnielinski (see Table 3, or [83] for slightly modified version). The heat transfer for the transitional region of flow (2300<Re<10,000) is interpolated from the laminar and turbulent values.

Design of Molten Salt Flow Loop

The University of Wisconsin has designed a forced convection, molten salt flow loop; “the purpose of the loop is to examine flow similar to conditions expected for the NGNP application” [109]. More specifically, the loop is designed to simulate the conditions in the intermediate heat exchanger (IHX) and to study heat and mass transfer [109]. Details of the loop design are given in [109], however, key features are summarised from this source as follows: maximum outlet and inlet (target) temperatures of 850°C and 715°C respectively; stainless steel 316 as selected structural material; temperature rise in test section of 122K; vertical cantilever, centrifugal pump (operable at 600°C, with FLUENT code used to calculate the temperature profile of the pump shaft and bearings); and mass flow, temperature and pressure drop measurement components.

3.2.3. ORNL (Fuel-Salt Coolant)

ORNL Review

The recent ORNL (2006) assessment [8] states that “molten salts exhibit normal fluid behaviour. They are Newtonian fluids and exhibit typical exponential decrease in viscosity, $\mu$, \ldots
with reciprocal temperature”. The ORNL review then refers to the “detailed forced-convection heat-transfer measurements” [8] in Cooke and Cox 1973 [103], as a good source to confirm this heat transfer behaviour.

Other ORNL Reports

The ARE, MSRE and MSBR database of reports provides more specific information with regard to heat transfer analyses in core designs; these should be researched.

3.2.4. UC Berkeley (Simulant Coolants)

Scaling Options

On-going research initiatives at UCB (USA) have studied the fluid mechanics and convective heat transfer of high temperature molten salts, using simulant fluids and scaled experiments to model reactor conditions:

“For these reactors [NGNP, AHTR, MSR and future fusion energy systems], high temperature convective heat transport phenomena with liquid salts…will play important roles in the steady-state, transient, and accident response. Ideally, these fluid mechanics and convective heat transport phenomena can be studied using scaled experiments with reduced size, temperature, and power. Data from scaled experiments can then be used to validate analytical models and benchmark numerical codes.” Peterson et al. (2008) [70]

The cited paper “Options for Scaled Experiments for High Temperature Liquid Salt and Helium Fluid Mechanics and Convective Heat Transfer” (Peterson et al. 2008 [70]) outlines the scaling parameters and heat transfer coefficients that must be matched, when using a scaled system to simulate a prototypical reactor system. The heat transfer coefficients to be matched include the Nusselt Nu, Reynolds Re, Prandtl Pr, Strouhal St, Froude Fr, Grashof Gr, Weber We and Biot Bi* numbers [70]. In general, this source provides a good general overview of the important aspects and considerations for a model for high temperature, liquid salt fluid mechanics and convective heat transfer.

The above source identifies and evaluates two types of simulant fluids, as feasible for matching the scaled fluid mechanics of high temperature liquid salts: light oils (to match FLiBe at 600ºC and 900ºC, and NaF-ZrF4 at 700ºC) and water (useful when the fluid mechanics, and not the convective heat transfer phenomena, is modelled) [70]. Simulant structural (container) materials are also identified for the model of a prototype liquid salt reactor cooling system.

Pebble Recirculation Experiment (PREX)

Out of the three proposed fuel geometries of the molten salt cooled AHTR (prismatic, pebble and stringer core designs for the TRISO fuel), experiments at UCB have been performed on the pebble bed design (PB-AHTR). Essentially PREX is a scaled model of the AHTR pilot plant, using (i) water (around 20ºC) to simulate the hydrodynamic behaviour of FLiBe [88] (see [70]), and (ii) polypropylene spheres to simulate the hydrodynamic behaviour of the fuel pebbles. The choice of these simulant materials is reported, since “the density ratio of the salt to the pebbles can be matched with water and polypropylene spheres” [88]. Further details on the conditions and uncertainty factors in using such a scaled and simulated set up, are provided in the relevant papers.
The main aims of the series of PREX tests were to confirm fundamental buoyant pebble hydrodynamics; i.e. injection in and extraction from the bed, pebble motion around the bed, and packing density and pressure loss measurements in the pebble bed arrangement [88]. From the results, it is concluded that:

“The PREX experiments confirm the viability of pebble recirculation in liquid salt cooled high temperature reactors, and provide the basis for designing the pebble recirculation system for the PB-AHTR” Peterson et al. (2003) [88]

Closed Flow Loop

A closed flow loop examining the heat transfer and pressure drop of molten simulant fluids (synthetic oils) in a vertical pipe, has also been set up and is currently under operation, at UCB. See Hauk (2006) [87] for relevant experimental design details and calculations. Published results from the closed loop experiments were not available at the time of writing this report; however, preliminary results indicate the temperature dependence of the thermophysical properties (in particular, viscosity) lead to an enhancement of the forced convection heat transfer coefficient, as compared to existing correlations [110].

3.2.5. Fusion Studies (FLiBe Simulant Coolants)

A summary of the previous theoretical and experimental developments, in selected fusion publications relevant to molten salt coolants, are given in the previous Table 8. This section will outline the key experimental results.

Numerical Simulation Studies

The first group of fusion related molten salt studies in Table 8 is the numerical research.

• In Kunugi et al. (2001) [93], Direct Numerical Simulation (DNS) of turbulent free-surface flow in various Pr fluids was performed, giving turbulent statistics and computational visualisations of the flow structure. The conclusion is drawn that “it is necessary to consider some turbulent heat transfer and thermal mixing augmentation for high Pr fluid flows” [93].

• In Chiba et al. (2006) [94], numerical simulations were performed to estimate effects of using cylinders as obstructions for heat transfer enhancement in high-Pr fluid flow [94]. Pressure drop calculations are also studied, according to the different geometries. The main result indicates that the “heat transfer of high-Pr fluid flow strongly depends on the effect of flow stirring caused by obstructions” [94].

TNT Loop

The references shown in the second group in Table 8, present the experimental activities and results related to the TNT loop. In Chiba et al. (2002) [107], it is described as a “high temperature molten salt loop (MSL)”; it was designed to use FLiBe as a coolant, however, due to difficulties in the handling of Be and the high melting point of FLiBe, it was chosen to use a heat transfer salt (HTS) simulant, KNO₃-NaNO₂-NaNO₃ (53-40-7 %mol) [107]. The advantage of the HTS simulant is that it can be adjusted to match the Pr of FLiBe at 560°C (Pr ~ 30), at the lower temperature ~170°C, as reported in [107]. The main experimental objectives of the TNT loop are: to validate empirical heat transfer correlations for molten salts, study the thermofluid structure, and study heat transfer enhancement (thermal mixing) techniques using packed bed tube designs [107] [89]. For more information on the TNT loop
and test section details (structural properties, heating parameters, and system design) please see references. Some important results are summarised as follows.

- Chiba et al. (2002) [107] gives preliminary experimental results and experiences, in the operation of the MSL and in the handling of molten salts. Also, the need for optimum mixing chamber and modified-test section designs was found.

- In Chiba et al. (2005) [89] heat transfer results in the packed bed tube design are presented with the following relevant conclusions.

  - “It is clarified that a molten-salt fluid flow through a circular tube can be enhanced with metallic packed bed” Chiba et al. (2005) [89]

- In Chiba et al. (2007) [106], the modified TNT loop is used to evaluate heat transfer performance for high Pr and high temperature molten salt flow in a circular pipe, and a sphere packed pipe. The modified loop has a much longer entrance region, in which the thermal boundary layer becomes fully developed; therefore yielding “more precise heat transfer data” [106]. The empirical correlations from the reference are shown in Table 8; Modified Hausen was applied to $3500 \leq Re \leq 10000$, Sieder-Tate to $10000 \leq Re$, and Modified Petukhov to $3000 \leq Re \leq 5,000,000$. Heat transfer characteristics of the HTS in a circular pipe agreed with the standard empirical correlations. Refer to the given sources for more details of the results and findings.

**FLIHY Facility**

The final group of fusion related FLiBe studies in Table 8 are undertaken in the FLIHY test facility at UCLA under the US-Japan JUPITER-II program. Similar to the numerical and experimental analysis, the work involves the visualisation and quantitative turbulence measurements for the FLiBe simulant (potassium hydroxide-water solution). In fact key parameter ranges and geometrical design accord with the TNT loop. However the main objectives of these experiments are specific to fusion reactors, involving study of the effects of the MHD force on the coolant [108], and are therefore not relevant for coolants in advanced nuclear reactors. Takeuchi et al. (2006) [92] does on the other hand present useful information regarding high Pr flow structures. Plus the results of the heat transfer data gathered using the simulant experiments agree with the well known correlations (Dittus Boetler, with ±10% certainty) [92].
4. CORROSION CHEMISTRY AND MATERIALS FOR MOLTEN SALTS

The interaction between fluoride salts and the reactor materials is a principal concern in the development of high temperature, molten salt coolant technologies. The chemical properties of molten salts and their effects on container alloys, along with procedures to reduce corrosion (purification and chemistry monitoring and control methods) are reviewed in the first part (4.1). Principle sources for the corrosion chemistry (general issues, and more specific experimental data) are again the ORNL literature reviews [8] [17]. The materials and compatibility tests are reviewed in the second part of this chapter (4.2), and gives summaries of related studies from selected research programs.

4.1. Corrosion Chemistry

4.1.1. Thermodynamic Free Energies

Knowledge of the thermodynamic free energy of formation of the relevant fluoride compounds is particularly important for corrosion assessments:

“Fluoride salts are fluxing agents that rapidly dissolve protective layers of oxides and other materials. To avoid corrosion, molten salt coolants must be chosen that are thermodynamically stable relative to the materials of construction of the reactor; that is, the materials of construction are chemically noble relative to the salts.” Forsberg (2004) [2]

Forsberg (2004) [2] also states that a difference in free energy of >20 kcal/mol°C is needed for compatibility between the salt and the container alloy.

A review of the literature gives the following data sources for thermodynamic free energies, for respective fluoride/chloride/fluoroborate component salts, as well as for the formation (and dissolution) of container metal fluorides:

<table>
<thead>
<tr>
<th>Range of Compounds</th>
<th>Refs for Data of Thermodynamic Free Energy of Formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoride constituents (e.g. LiF, BeF₂, NaF etc.)</td>
<td>[2] [12]</td>
</tr>
<tr>
<td>Corrosion product fluorides (CrF₂, FeF₂, NiF₂, MoF₆)</td>
<td></td>
</tr>
<tr>
<td>Fluoride constituents (inc. UF₄, ThF₄ etc.)</td>
<td></td>
</tr>
<tr>
<td>Corrosion product fluorides</td>
<td></td>
</tr>
<tr>
<td>Other impurity fluorides (HF, VF₂, TiF)</td>
<td>MOST database [114] [12]</td>
</tr>
<tr>
<td>Chloride constituents (secondary coolants)</td>
<td></td>
</tr>
<tr>
<td>Corrosion product chlorides</td>
<td></td>
</tr>
<tr>
<td>Fluoroborate constituents (NaF-NaBF₄ secondary coolant)</td>
<td></td>
</tr>
<tr>
<td>Corrosion product fluorides (from fluoroborate)</td>
<td>[17][46]</td>
</tr>
</tbody>
</table>

Table 9 Useful references for thermodynamic free energy properties, for the corresponding type of salt compounds.

Further electrochemical properties and related details of various fluorides and fuel fluorides can be sourced from earlier ORNL technical reports e.g. [12].

A more recent source [7] reports the need for a thermodynamic screening of chloride salts for materials compatibility. Williams (2006) [17] also suggests the need for further work in the fundamental chemistry of fluoroborates, if they are to be serious molten salt heat transfer coolant candidates.
Other more detailed sources on selected molten salts, and their thermodynamic modelling and free energy coefficients (including fuel-salt compositions) are [31] [34].

Acid-base chemistry is fundamental to the thermodynamic activity coefficients, as is reported in [8]. Knowledge of this underpins a full understanding of the corrosion processes and corrosion control methods, in molten salt coolants. In general, the ‘basic’ salt compounds easily give up fluoride ions (F⁻), and the ‘acidic’ salts react with the free fluoride ions to form complexes. The complexation process then results in a decrease in the thermodynamic activity values [8]. Typical basic compounds include the alkali metal fluorides [8] and acidic compounds include the ZrF₂ and BeF₂ [8] [11].

4.1.2. Redox Corrosion

Basic Redox Reactions

Molten salt corrosion is usually induced by reduction/oxidation (redox) reactions, of impurity fluorides in the salt [113] [43]. The fluorides act as the oxidants and the container metal elements act as the reductants [29].

The literature sources [8] [12] [114] plus many other chemical studies during the ORNL R&D period, give details of the main redox reactions. Knowledge of these reactions is required for use and development of redox control methods that are necessary to minimise corrosion. Important reactions are briefly summarised in Table 10:

<table>
<thead>
<tr>
<th>Redox Reaction</th>
<th>Comment</th>
<th>Summised From Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2HF + M(element) ↔ MF₂ + H₂</td>
<td>Salt impurity reduces metal element (M) in structural alloy. (M is typically Ni, Fe, Cr).</td>
<td>[8] [12] [114]</td>
</tr>
<tr>
<td>2UF₄ + M(element) ↔ 2UF₄ + MF₂</td>
<td>UF₄ (fuel fluoride) reduces structural metal elements (M)</td>
<td>[8] [12] [114]</td>
</tr>
<tr>
<td>XF₂ + Cr ↔ CrF₂ + X</td>
<td>Dissolved corrosion products (X is for e.g. Ni, Fe) / impurity fluorides, reduce Cr in structural alloy.</td>
<td>[8] [12] [114]</td>
</tr>
</tbody>
</table>

Table 10 Key redox reactions between fluoride components and structural metal components, inducing corrosion; these are summarised from the given references.

For the clean fluoride coolants, the second reaction is not applicable, since it involves uranium [8]. For the other non-fluoride coolants for secondary/heat transfer loop (e.g. chlorides), similar chemical issues also apply [17]. However, important differences and particular chemical issues are noted (refer to source).

More detailed accounts and experimental data of the oxidation states/stabilities of the corrosion products and salt constituents (e.g. uranium in an MSR fuel salt), should be researched.

Cr Corrosion

The chromium (Cr) element in typical nickel based alloys used for molten fluoride systems increases the air oxidation resistance of the material. However, it is also the most thermodynamically unstable element in the alloys, with respect to fluorides. Previous experiments with molten salt test loops have demonstrated that the corrosion of Cr and its chemical transport from hot to cold regions is a key limiting factor [8] [29]. Temperature dependent corrosion of this type is particularly applicable to high temperature reactor systems, in which large temperature differences are possible [2]. This consideration is more serious for
an MSR, because dissolved uranium fluorides will selectively attack the Cr on the metal surface.

In clean salt coolants (AHTR, heat transfer loop, fusion coolant) the main methods to avoid these corrosion mechanisms are explained:

“In clean-salt applications, these types of corrosion mechanisms can be reduced or eliminated by (1) using purified salts that do not contain chemical species that can transport chromium and other alloy constituents or (2) operating under chemically reducing conditions. Under chemically reducing conditions, chromium fluoride has an extremely low solubility which limits chromium transport.” Forsberg (2004) [2]

In Williams et al. (2006) [8], dissolved chromium concentration data and its temperature dependence (given at 600°C and 800°C) sourced from the ORNL database is reviewed and should be referred. It is also stated that “we expect that fuel systems that experience minimal corrosion would also be better coolants” [8].

4.1.3. Impurities and Purification

Purification Methods

Table 11 summarises the details of the procedures taken to purify the molten salts (according to type) before use, in the some of the selected studies.

<table>
<thead>
<tr>
<th>Research Program</th>
<th>Salt Type(s)</th>
<th>Purification Methods</th>
<th>Summarised from Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>ARE &amp; MSRE / US (ORNL)</td>
<td>Fluorides</td>
<td>HF/H₂ sparging of salt and use of active metal (e.g. ZrF₄) to reduce salt</td>
<td>[8]</td>
</tr>
<tr>
<td></td>
<td>Fuel-Fluorides</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Chlorides</td>
<td>Drying under vacuum and HCl gas treatment. Improved methods required (see text below).</td>
<td>[17]</td>
</tr>
<tr>
<td></td>
<td>Fluoroborates</td>
<td>Improved methods required (see text below)</td>
<td>[17]</td>
</tr>
<tr>
<td>ISTC#1606 / Russia</td>
<td>LiF-NaF-BeF₂</td>
<td>Hydrofluorination, electrolysis, and treatment with Be (active metal)</td>
<td>[112]</td>
</tr>
<tr>
<td>NERI / US (University of Wisconsin)</td>
<td>FLiNaK</td>
<td>Three purity grade salts, procured from different sources, were used in corrosion tests, representing industrial conditions.</td>
<td>[109]</td>
</tr>
<tr>
<td></td>
<td>KCl-MgCl₂ (chloride)</td>
<td>Mg addition, CCl₄ bubbling. HCl/H₂ bubbling</td>
<td></td>
</tr>
<tr>
<td>JUPITER-II / US-Japan (INL)</td>
<td>FLiBe (for fusion reactor coolant)</td>
<td>Drying of salt and purging with He gas. After melting, purging salt with He/H₂/HF (520°C) gas mixtures. Then, filtering of salt though metal mesh frit. Tests of Be redox treatment of salt were separate.</td>
<td>[113]</td>
</tr>
</tbody>
</table>

Table 11 Summary of purification methods for liquid salts from selected sources.

During the ARE and MSRE programs, experience was gained in the preparation and handling of molten salts. A range of original sources describing purification methods of the liquid salts are given in the ORNL review [8], and are well reviewed in [12]. Table 11 presents purification measures located in other recent studies. Note nuclear fusion related chemical studies are included in the table, given the application of the FLiBe molten salt as a blanket coolant for a fusion reactor. This work was specifically conducted at the Idaho National Laboratory, Safety and Tritium Applied Research (STAR) facility.

For the chloride and fluoroborate candidate liquid salts (heat transfer coolants to hydrogen production plant), it is reported in [17] that there is a need for improved methods for oxygen
removal. References for suggested purification methods are given in [17]; for the chlorides (carbochlorination), these are [115] [116], and for the fluoroborates (carbofluorination); [117].

Impurities

The main impurities in salts that must be removed are oxides and water, because these cause corrosion of the container alloy [12]. Particularly at the high temperature range, fluorides will slowly react with any steam (H₂O) that is present producing further impurities such as hydrogen fluoride (HF), oxygen (O₂), and oxide compounds. Other typical impurities derive from the corrosion products (and their oxides), which dissolve into the salt. In the case of fuel-salts, fission products also contribute. Many of the reviewed sources give information on typical molten salt impurities and their effects (MOST database [114]).

4.1.4. Chemistry Monitoring and Control

Redox Control and Other Methods

Various research programs have focused on the development of chemistry control and monitoring techniques in molten salt systems. It has been mentioned that chemically reducing conditions are desirable to decrease corrosion reaction rates [8]. Table 12 summarises some of the redox control methods, including measuring and monitoring systems for molten salt coolants, as reported in the given references.

<table>
<thead>
<tr>
<th>Redox Control and Monitoring Methods</th>
<th>Reactor Concept / Research Program and info source used (Ref.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control redox by use of metallic beryllium (Be) immersed in the salt, as an active redox agent</td>
<td>Mod PB-AHTR (UCB) [119] MOSART (ISTC#1606) [112] Fusion coolant (JUPITER-II) [113]</td>
</tr>
<tr>
<td>Control of oxide formation by use of high purity He cover gas</td>
<td>MSRE (ORNL) [35]</td>
</tr>
<tr>
<td>Use of U(III)/U(IV) (i.e. UF₃/UF₄) ratio to control optimum oxidation state (redox potential) in fuel-salt</td>
<td>MSRE (ORNL) [8]</td>
</tr>
<tr>
<td>High temperature electrochemical measurements of corrosion concentrations in FLiNaK, using Anodic Stripping Voltammetry and chemical analysis; research to develop probes for online monitoring of corrosion in molten salts</td>
<td>NHI/NGNP (UW) [109]</td>
</tr>
<tr>
<td>Measurement of redox potential in thermal convection loop; research to demonstrate feasibility of online measurements of redox potential in high temperature molten salt loops</td>
<td>MOSART (ISTC#1606) [112]</td>
</tr>
</tbody>
</table>

Table 12 Summary of redox control and monitoring (measuring) methods for liquid salts, in selected sources.

Note the method of U(III)/U(IV) control is only applicable to fuel salt systems. For clean salt coolants, the reduction of the chemical potential is achieved by contact with an active (beryllium) metal. The principal behind this method is described in [113]; in which, to briefly summarise, the redox agent (beryllium) reacts with the free fluorine in the salt system (F₂), and offsets the reactions with the container alloy metals. Other redox agents include Ce and HF/H₂ ([113], [114] MOST database).

Other chemistry control methods are mentioned in a UCB design project for the Modular Pebble Bed AHTR [119]; including the use of a cover gas to prevent the salt reacting with contaminants such as air, and also a salt filtering system.

Tritium production and removal in the salt coolants are also of concern, and can result from the reaction between Be and captured neutrons [16] [113]. These issues are discussed in more
length in [16] [113] [119]. A method to remove tritium, involving He sparging of the salt flow, is described in a design paper of the Modular PB-AHTR [119].

Some beneficial effects of redox control were identified during the MSRE (fuel-salt) system operation. It was reported that radiation embrittlement and intergranular cracking effects were observed, as a result of chemical attack from the fission product tellurium (Te) [12]; and “it was seen that the control of molten salt oxidation potential had dramatic effects on the extent of cracking" [8]. More recent research into Te cracking effects in Ni based alloys, coupled with free/controlled chemical potential conditions in tested salt systems, has been conducted under the CEA MSR programs [135] (see section 4.2.4). Note that Te material embrittlement is only a factor in an MSR (fuel-salt coolant) systems; with regard to clean salt coolant systems (e.g. AHTTR), the main issues are Cr corrosion.

**Fission Products Treatment**

In AHTR systems with a clean salt coolant, the key factors related to the removal of fission products in the molten salt are discussed in the AHTR summary report [16]. The extensive experience gained during the ARE and MSRE (fluid fuelled) reactor programs, and in particular the document [120] is reported to be “the most complete source of information on fission product behaviour in molten fluorides” [16]. Another useful source for chemical research for the (fuel-salt coolant) MSBR is [12].

The chemical processing and treatment of the fuel salt and related fission products in MSR systems is a much more complex challenge than for the solid fuel / clean molten salt coolant reactors. Fuel salt processing, extraction of fission products (e.g. gaseous fission products), the reprocessing and separation of actinides and lanthanides from the fuel salts, along with other wastes, forms a more complex base of research and development, and are not reviewed in this report. Sources that detail more information in these areas include reports from Euratom MOST program (with focus on MSR research), Russian ISTC#1606 reports (MOSART research), and CNRS studies in France (TMSR-NM research).

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**4.2. Materials and Compatibility Tests**

**4.2.1. General Types and Requirements**

Forsberg (2004, 2005) [2] [9] summarise the main issues and development needs for all the molten salt reactor materials for high temperature service (including AHTTRs, MSRs and LSFRs). The four key issues are outlined as follows (from [2]):

- Strength over time
- Long-term creep
- Corrosion resistance to air
- Corrosion resistance to molten fluoride salts

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\[x\] Quoted ref cites original source [77] (given in [8])
Note that particularly above 800°C, corrosion resistance to air is a major limitation, even compared to high temperature fluoride salt environments [2] (and [121] as cited in [2]).

The publication “Status of Preconceptual Design of the Advanced High Temperature Reactor (AHTR)” (Ingersoll et al. 2004) [16] organises the materials for the molten salt cooled AHTR reactor into four broad categories. The following points summarise these (from [16]):

- Graphite and Carbon-Carbon Composites. These materials operate in core, reaching from 500-1100°C, or even higher.
- Reactor Vessel Materials. These operate around 500°C, possibly to 800°C during transients.
- High-Temperature Metals. These are needed for components operating up to 1000°C, in molten fluoride environments, e.g. piping, heat exchangers, pumps.
- High Temperature Melt-Infiltrated Composites. These include new LSI C-C composites, for components (e.g. heat exchangers) needing to withstand very high temperatures, up to 1400°C.

**Graphite**

Forsberg (2004) [2] provides a brief overview of molten salts and graphite compatibility. In general, it is reported that “a large experience base has demonstrated the compatibility of molten fluoride salts and graphite in radioactive and nonradioactive systems”. [2] reports this is backed up by the MSRE post-irradiation examination and other chemical loop tests (up to 1400°C). Other advantages include non-wetting effects. Graphite is therefore a key in-core material for both molten salt fuel and coolant applications (i.e. MSRs and AHTRs). In AHTR design review (2004) [16], it is reviewed that “extensive prior work has demonstrated that graphite is compatible with molten fluoride… however, a database of properties needs to be developed for design use” [16].

**C-C Composites**

C-C composites are referred in various sources as promising materials for high temperature, molten salt reactor applications (both AHTRs and MSRs). For AHTRs, [16] (status review of AHTR design) compares C-C composites to graphite, and they potentially show “similarly good properties in the presence of molten fluoride salts and better mechanical properties” [16]. In the paper “Recommendations for a restart of molten salt reactor development” (Moir, 2008) [137], it is stated that “carbon composite research is recommended for molten salt reactor applications”.

Liquid-silicon-impregnated (LSI) carbon-carbon composites (included under the fourth category material, in the AHTR materials from [16]), are advanced high temperature materials. Desirable properties of LCS C/C-SiC materials that are reported across sources include retention of mechanical strength at very high temperatures, low porosity and fabrication simplicity (allowing use for flow-loop components such as heat exchangers) (refer to [16] [122] for more detailed information). [16] states the need for compatibility tests with molten salts to evaluate corrosion performance.

**Metal Alloys**

A summary of the proposed high temperature, high strength alloys suitable for the AHTR needs, is given in Ingersoll et al. (2004) [16], and can be used as a reference for the main candidate structural metal alloys for molten salt cooled reactors. The data tables in the source
categorise the metals as either coated (i.e. needing a Ni coat for surfaces exposed to liquid salts) or monolithic. Corresponding properties for each alloy given in the referred tables are: salt corrosion resistance, air corrosion resistance, long term strength, highest usage temperature, metallurgical stability, irradiation resistance, fabricability, maturity, code status, and applications (vessel or specified components).

For example, the baseline design of the pebble bed molten salt cooled AHTR is reported to use “Alloy 800H as the structural material for reactor vessel and for components that operate in salts (hot legs, primary pumps, IHX’s, DHX’s, core support structures), with a cladding of Hastelloy N on surfaces exposed to salts” [119].

With regard to molten salt compatibility and corrosion, nickel based alloys (e.g. Hastelloy N, composition 68% Ni, 17% Mo, 7% Cr and 5% Fe) have demonstrated very good performance in higher temperature molten salts [35].

The general R&D requirements for metal alloys (and the other category materials) are given in the status review of the AHTR [16]. Refer to the source for more specific development needs; for current purposes:

“In general, mechanical properties of irradiated and unirradiated materials in the presence of chosen molten fluoride salt, high-temperature oxidation behaviour, and salt compatibility data need to be generated.

For the lower temperature AHTR-IT version, compatible code materials already exist such as Hastelloy N.

However, the 1000ºC coolant outlet temperature required by the AHTR-VT for the NGNP application will require considerable material testing and qualification” Ingersoll et al. (2004) [16]

4.2.2. Studies in U.S.A.

Corrosion Loop Database in ORNL Reviews [8] [17]

The ORNL programs (ARE, MSRE and MSBR) 50s, 60s and 70s resulted in “a large database [that] exists on interactions between molten salts and materials” [123].

Results of the relevant corrosion/materials compatibility tests conducted for the coolant salts during these ORNL programs are consolidated in [8] [17], as follows. The corrosion data table for the fluorides is extensive, and includes many different compositions; test loop materials include 316SS, Inconel and INOR-8 (i.e. Hastelloy-N), with peak temperatures reaching between 607ºC and 815ºC (see ORNL review [8]). Corrosion data for the chloride melts LiCl-KCl and NaCl-KCl-MgCl₂ are given for stainless steel tests loops (peak temperatures between 494 and 575ºC), in Williams (2006) [17]. Finally corrosion data for the fluoroborate melt NaF-NaBF₄ is given in [17], for various natural and forced convection loops (peak temperatures 607-688ºC).

More recent corrosion testing at Oak Ridge with molten salts include a FLiNaK loop operated at 815ºC (for 3000h, Hastelloy N) [29]. Results briefly reported in [29] showed that much less Cr was dissolved in the salt, compared to previous data from the ARE loop (2003, source).

Resulting Trends in ORNL Reviews [8] [17]
It is reported that Hastelloy N emerges as the best choice for both the coolants and the fuel salts, in [8]. All fluorides showed low corrosion rates and the following trends are drawn:

“Very basic (FLiNaK) and very acidic (LiF-ZrF₄) salts showed the worst performance. Nevertheless, the proper control of redox factors... can make even these salt mixtures acceptable with respect to corrosion.” Williams et al. (2006) [8]

The limited results for the chlorides secondary coolants “do not conform to any expected or predictable trends” [17]. However, the chloride corrosion rates even at lower temperatures (~550°C), are identified as “much higher” than those for fluorides in Hastelloy N at higher temperatures (815°C) [17]. In general, it is stated that there is no data or experience for these types of secondary coolants in the range of temperatures anticipated for the NHI loop; however, data exists for fluorides in the 800-900°C range [17].

**University of Wisconsin: NHI Loop**

The Nuclear Heat Transport Loop studies at the University of Wisconsin under the NERI initiative in the US, focused on materials corrosion of FLiNaK salt. Relevant open references include [109] [124] [125]. In this research, static corrosion tests were performed on selected secondary salts FLiNaK and KCl-MgCl₂, using graphite crucibles to house alloy test samples and salt media; at 850°C for 500 hours. A range of alloy samples were chosen to test for corrosion performance in the salts, based on their potential as AHTR materials; as briefly summarised in Table 13:

![Table 13 Materials tested for corrosion in molten FLiNaK in the study at University of Wisconsin (data source and table adapted from [109])](image)

*Refer to data source for full composition details

*Alloys identified as potential candidate materials for the AHTR

*Included on the grounds that Ni is very resistant to thermodynamic dissolution of fluoride salts

Materials characterisation of the samples before and after the tests are reported in the mentioned sources, including: weight loss measurements, analysis of the samples using various techniques (e.g. optical microscopy) and also chemical analysis of salts were performed (to deduce, for example, dissolved Cr content).

Some key findings, as paraphrased from [125], include:

- High Cr content in the alloy causes greater corrosion;
- Nickel is very resistant to corrosion attack and Ni plating improves fluoride salt corrosion resistance;
• Chemical analysis of the salt in conjunction with materials analysis “provides a comprehensive picture of corrosion” [125].

For more details, refer to [109], in which ranked performances of sampled alloys are given, along with more detailed analysis in other areas (air oxidation tests; in depth analysis of Ni-electroplated Incoloy 800H; and also the interaction of graphite in the high temperature corrosion tests).

Identified research needs are briefly summarised in [125]. These include (from [125]): further work on incorporating tests with reducing agents; improved production methods and corrosion testing of the KCl-MgCl₂ salt; the study of corrosion product transport in small channels; high speed erosion and corrosion of pumping components; enhanced plating technologies with Ni-plated 800H; and heat exchanger design to handle creep at high temperatures.

Advanced Composites Studies

The sources [122] [126] [128] [129] can be referred for an overview of relevant research being undertaken in US research institutes, for carbon-carbon composites. For example, the paper “Advanced CSiC composites for high-temperature nuclear heat transport with helium, molten salts, and sulfur-iodine thermochemical hydrogen process fluids” (Peterson et al. 2003) [122] outlines key properties, fabrication methods and compatibility performance (including molten salts) for the advanced CSiC composite.

The main development and testing studies of these advanced materials are undertaken at UCB [16] [126]. The source [129] gives a brief overview of the UCB/collaborative activities in the area.

The compatibility between PyC coated SiC composites and FLiNaK salt has also been a part of the experimental activities at the University of Wisconsin molten salt research [125], summarised in the previous section.

4.2.3. Studies in Europe

The European programs focus mainly on the development of molten salt and materials technology for MSR (fuel-salt) applications. However, large parts of the materials research overlap with general requirements for high temperature molten salt coolant technology.

MOST Database and ALISIA

The Euratom MOST research program addressed key issues related to structural materials. For the reactor, the main structural material to be analysed is modified Hastelloy N, and the main nuclear reactor material is graphite [40].

In the database, there is a review of the existing knowledge base and developments, with focus on the nickel based alloys (in particular Hastelloy N) and their physical properties. In the context of MSR (liquid fuelled) systems, particular issues addressed include irradiation embrittlement and post-irradiation properties. The database includes detailed data on the physical, chemical, mechanical and corrosion properties of these alloys and their various compositions. Experimental data from different corrosion tests loops (of varying temperatures, up to 750°C), and salt compositions are included [114].

The 6FP Euratom project ALISIA [130] following on from the MOST FP5 program, also offers updated information on existing and required technology developments. The most
significant contributions in these areas came from the Czech Republic (MONICR SKODA), CNRS and CEA programs, and foreign participants from Russia and US.

**MONICR SKODA**

A key contribution in the area of structural materials for molten salt applications in the Euratom programs is the project SKODA JS a.s., under the national SPHINX program of the Czech Republic [132]. The aim of the relevant SKODA JS a.s. project is the “Development of Structural Materials for the Transmuter MSR Primary and Secondary Circuits on the Basis of Fluoride Salts, for Service Temperatures up to 750ºC” [131] [37]. The development of the nickel superalloy MONICR series for MSR systems, produced and developed in the Czech Republic, is a main focus.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Applications</th>
<th>Comments</th>
<th>Status</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MONICR</td>
<td>Future plans for reactor service in fluoride salt media, up to 750ºC (e.g. MSR). Planned research to extend to 750-1000ºC range applications.</td>
<td>Very good corrosion resistivity, convenient creep strength and excellent toughness.</td>
<td>Licensing stage</td>
<td>[112] [134] MOST database [114]</td>
</tr>
</tbody>
</table>

Table 14 *Brief details of MONICR (SKODA) alloy*

A range of developments and activities are in process and are planned under SKODA, with the general goals of experimental and computer analysis (for temperature ranges shown in the table) [131]. Systematic analyses of the thermo-mechanic properties of processing regimes, macro-, micro and sub-structures, and other physical measurements are underway and planned, as reported in [131]. More detailed metallography analysis and recrystallisation (formation) investigations of the MONICR alloy are detailed in [134].

Further activities in the Czech Republic that extend the materials testing to experimental loops fall under the ADETTE loop experimental program, in the ADTT (Accelerator Driven Transmutation Technology). [133] reports the construction of a small experimental loop (ADTT-0), tested with fluoride salts (NRI Rez plc and SKODA JS a.r.o). The same source also outlines planned loops (natural convection ADDT-1 and forced convection ADDT-2/3) using the MONICR material of construction. The envisaged research objectives include: loop and circuit operation, testing of structural materials properties (mechanical and thermal), chemical and thermal properties of media, basic components, auxiliary systems, and thermal hydraulics – from [133].

**CEA and CNRS**

Collaborative projects at the CEA and CNRS in France related to TMSR (Thorium Molten Salt Reactor) technologies include chemical and materials corrosion testing in molten salt environments. In particular, studies reported at ALISIA project meeting (Euratom) include experiments performed on the deleterious effects of Tellurium (Te) (a fission product in fuel-salts) on nickel based alloys [135]. In addition, the feasibility of controlling the chemical potential of salt system was studied and effects on rates of intergranular cracking were assessed.

Other recent CNRS activities have focused on the less common Ni-W-Cr alloys (Mo substituted with W tungsten) [13]. This composition holds potential in terms of increased creep resistance and reduced long term activation problems [13]. Initial laboratory studies and
larger scale production are planned, and work in progress involves fluoride corrosion and air oxidation tests, as reported in [13].

In general, it is concluded in the 2008 CNRS Molten Salt Program Summary Report [13] that “very reasonable solutions exist for structural materials for a molten fluoride reactor operating below 750°C”. Future research needs include (paraphrased from [13]):

- Irradiation effects on Ni based alloys. In particular, the effects of He atoms (produced after transmutation of Ni under neutron flux) and their diffuse in the material should be studied.
- Corrosion studies in secondary loop systems (NaBF₄-NaF) and also chloride (batch processing fluids).
- Other materials studies/concepts, including ZrC materials, and graphite studies.

### 4.2.4. Studies in Russia

As part of the ISTC#1606 project to investigate the feasibility of the Molten Salt Actinide Recycle & Transmuter (MOSART) in Russia, an extensive materials tests program has been undertaken. The source “Compatibility of Selected Ni-Based Alloys in Molten Li,Na,Be/F Salts with PuF₃ and Tellurium Additions” (Ignatiev et al. 2008) [112] provides a consolidated review and analysis of materials studies for high temperature molten salts, under the mentioned projects. Other related information sources are [39] (ISTC#1606/3749 involvement in ALISIA).

The three structural materials chosen for study are all nickel based alloys i.e. with Ni (base), Mo (12-16%) and Cr (~7%). In particular, the three tested alloys are HN80M-VI (with 1.5% Nb), HN80MTY (with 1% Al), and MONICR (with 2% Fe) [39] [112]. In brief, compatibility tests in LiF-NaF-BeF₂ (15-58-27 % mol) were conducted and reported [112], in a natural convection loop for 1200hr (hot leg temperatures 620-695°C), together with redox potential measurements. Other compatibility tests, that are only relevant to MSR (fuel-salt) systems, included: additions of PuF₃ (fuel-fluoride component) and Te (fission product in fuel salts) to the salt mixture [39].

A full analysis of the procedures and results are given in [112], including experimental data for corrosion rates, mass losses of the alloy specimens, periodic redox potential measurements, and ICG effects (Te). It is concluded that:

“Specimens of the HN80M-VI and HN80MTY alloys from the hot leg of the loop exposed at temperatures from 620 to 695°C showed a uniform corrosion rate from 2 to 5 µm/yr. For the MONICR alloy, this value was up to 20 µm/yr.” Ignatiev et al. (2008) [112]

In the fuel-salt corrosion tests, “no significant change” was reported with addition of the PuF₃ component [112]. Other performed examinations on the sample alloy include metallographic studies using microscopy techniques.

Future R&D needs are outlined in the sources and in the frame of ISTC#3749. To paraphrase from [112]; further testing of Ni-based alloys with different salt compositions is required, to enhance Te ICG resistance; for the MOSART (MSR Burner) and thorium fuelled MSR systems. This effect is not relevant for clean salt applications (i.e. AHTR and secondary/heat transfer coolants).
SUMMARY AND CONCLUSIONS

The report has presented existing knowledge and R&D activities for molten salts and their application in high temperature reactors. The following sections highlight the key trends and outline areas that require further research.

(1) Molten Salts and Nuclear Applications

The choice of molten salt depends on the application (Table 1). Three broad categories of molten salts were evaluated in the present review: (a) Primary coolant salts (AHTR) (b) Heat transfer coolant salts (nuclear hydrogen production) (c) Fuel-salt coolants (MSRs).

(2) Thermophysical Properties

A significant amount of thermophysical properties data was gained during the early Oak Ridge ARE, MSRE and MSBR programs during the 1950s, 60s and 70s. In addition, more recent ORNL reports provide literature reviews of this early data, for the revived AHTR and NGNP/NHI (nuclear hydrogen) heat transfer loop applications [8] [17]. These are crucial sources for thermophysical properties data, giving measured values above and around 700°C across the range of coolant salts. Other key sources, especially for fuel-salt coolant compositions applicable to the MSR Burner and Breeders, include literature produced under the European (MOST) [10] [40] and Russian (ISTC#1606) [11] molten salt research programs. Online data bases documenting different mixtures of molten salts and their corresponding properties include the Molten Salt Database (project) [46]. Collaboration and data exchange between these various programs should be considered.

- **Density** values are generally well validated in the data tables presented in chapter 2 (and tables in the appendix), also including temperature dependent equations.
- **Melting point, vapour pressure and viscosity** for molten salt coolants were qualitatively analysed in [8] as; “accurate” in measurements but “difficult to predict”. In chapter 2, the dependence of both vapour pressure and vapour species on temperature and salt composition require further evaluation for certain candidate salts (e.g. fluoroborates and chlorides). Temperature dependent equations especially for viscosity are needed to fill gaps in the data bases; this is important for understanding how properties behave in the higher temperature range (up to and beyond 1000°C).
- **Heat capacity and thermal conductivity** data are more deficient in the data base [8]. Heat capacity requires more experimental validation, and values need to be assessed in the higher temperature range. Thermal conductivity is the most prominent gap in the measured properties data, as is clear in the literature and in the summarised data tables (chapter 2 and appendix). Prediction methods for the thermal conductivity do exist [11] [41], however considerable validation efforts are required.

In addition, it was found that more extensive studies have been undertaken for certain salt mixtures: ⁷LiF-BeF₂ (FLiBe) given its choice as a coolant/fuel-solvent for the MSRE/MSBR and as a nuclear fusion coolant [57]; LiF-NaF-BeF₂ (FLiNaBe) given its choice as fuel-solvent for the MSR Burner (ISTC#1606) [11]; and also LiF-NaF-KF (FLiNaK) [83].

(3) Heat Transfer

*Basic theoretical features* of heat transfer in molten salts were covered in the first part of chapter 3. Molten salts were shown to be in a class of high Prandtl (Pr) number fluids,
compared to other coolants which have a lower Pr number (liquid metals, water and helium gas). The general trend across various existing literature sources is that liquid salts are described to behave as normal (Newtonian) heat transfer fluids. Certain studies showed high Pr effects, as well as buoyancy and mixed convection effects, to be important considerations for the heat transfer models for high temperature salt systems.

Experimental heat transfer studies were covered in the second part of chapter 3. In general, the literature shows limited experimental measurements for convective heat transfer in liquid salts [83]. A literature survey (Table 8) of various experimental studies showed the use of standard correlations to model molten salt heat transfer data (e.g. Dittus Boelter, Sieder Tate and Modified Petukhov correlations). Further experimental research is required to validate heat transfer models for molten salts (and/or high Pr simulant fluids), in higher temperature conditions. Both forced and natural convective flow regimes need to be assessed.

Chapter 3 also provided summaries of the relevant research activities being performed for different molten salt systems and flow geometries; including scaled experiments for molten salt cooled pebble bed systems, and various heat transfer flow loops; University of Wisconsin and UCB flow loops (USA) [109] [87], FLIHY and TNT loop facilities (fusion coolant studies) [108] [106] [107]. More details and research collaborations should be followed up.

CFD codes and their application to molten salt system designs were not covered in any depth in this report; therefore further reviews in this area are required. It is clear however that development and benchmarking of CFD codes for molten salt coolants remains an important research objective.

(4) Corrosion Chemistry and Materials

Corrosion processes and related fundamental theory were covered in the first part of chapter 4. Redox reactions were shown to be key considerations in molten salt systems [113], especially since passive layers are dissolved in fluoride environments [83]. In particular, the corrosion of chromium (Cr) in nickel based alloys needs to be minimised, to develop more stable molten salt/metal container contact at high temperatures [8]. To achieve this, various optimised purification methods and chemistry control/monitoring systems exist, to remove oxides and maintain chemically low oxidising conditions. Further development of control systems and their testing in high temperature salt loops is needed. Purification procedures also need to be improved for fluoroborates and chlorides [17].

Materials developments and compatibility tests performed as part of various research activities are summarised in the second part. Graphite for in-core materials, high temperature metal alloys for structural materials, and also advanced carbon-carbon (and melt infiltrated) composites, are the main types proposed for high temperature molten salt cooled reactors (see AHTR design in [16]). The ORNL molten salt reactor programs made significant advances in the technology, resulting in both corrosion test data for various salt coolants and also in the development of more compatible alloys, up to 750°C (Hastelloy N) [8]. Other recent R&D is then summarised, based on literature from various international programs. Developments in the USA include new materials and testing of alloys/composites for components (e.g. heat exchangers) in even higher temperature, molten salt conditions [109] [122]. R&D in Russia and the Czech Republic has focused on materials for MSR technologies (fuel-salt coolants), including modified alloys (HN80M-VI, HN80MTY and MONICR) [112]. Clearly, further testing and code qualification of developed materials at temperatures to 1000°C and beyond is necessary, for the envisaged reactor/coolant conditions.
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### Table A1 Thermophysical properties of the candidate molten salts for the primary AHTR coolant:

*Summary of Data from (Williams et al., ORNL, 2006; [8]) (unless other refs. given)*

<table>
<thead>
<tr>
<th>Salt Class</th>
<th>Composition (% mol)</th>
<th>Melting / Boiling Point (°C)</th>
<th>Vapour Pressure at 900°C (mm Hg)</th>
<th>Density ρ (g/cm³)</th>
<th>Heat Capacity Cₚ (cal/g-°C)</th>
<th>Viscosity μ (cP)</th>
<th>Thermal Conductivity k (W/m K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkali Fluorides</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Equation</td>
<td>Measured (at 700°C)</td>
<td>Predicted (at 700°C)</td>
</tr>
<tr>
<td>LiF-KF (50-50)</td>
<td>LiF-RbF (44-56)</td>
<td>492 / See [46]</td>
<td>See [46]</td>
<td>2.460-0.00068 T(°C)</td>
<td>2.407-0.0005362 T(K) Refs [8]</td>
<td>0.44</td>
<td>0.381</td>
</tr>
<tr>
<td>LiF-NaF-KF (46.5-11.5-42)</td>
<td>470 / ?</td>
<td>3.300-0.00096 T(°C)</td>
<td>T range 500-750°C Refs [8] [46]</td>
<td>0.284</td>
<td>0.226</td>
<td>use equation 0.0212.exp(4678/T(K)), T range 873-1073K</td>
<td>?</td>
</tr>
<tr>
<td>LiF-NaF-RbF (42-6-52)</td>
<td>454 / 1570</td>
<td>-0.7</td>
<td>2.530-0.00073 T(°C)</td>
<td>T range 940-1170K Refs [8]</td>
<td>0.45</td>
<td>0.387</td>
<td>2.9 0.04.exp(4170/T(K)), T range 873-1073K</td>
</tr>
<tr>
<td>LiF-NaF-ZrF₄ (58-42)</td>
<td>435 / ?</td>
<td>-0.8</td>
<td>3.261-0.000811 T(°C)</td>
<td>T range 500-700°C Refs [8] [46]</td>
<td>?</td>
<td>0.236</td>
<td>2.6 ?</td>
</tr>
<tr>
<td>LiF-ZrF₄ (51-49)</td>
<td>NaF-ZrF₄ (59.5-40.5)</td>
<td>500 / -1350 (extrapolated)</td>
<td>5</td>
<td>3.650-0.00088 T(°C)</td>
<td>T range 550-700°C Refs [9] [46]</td>
<td>0.28</td>
<td>0.275</td>
</tr>
<tr>
<td>LiF-ZrF₄ (58-42)</td>
<td>NaF-ZrF₄ (58-42)</td>
<td>410 / -1450 (extrapolated)</td>
<td>1.3</td>
<td>3.923-0.00100 T(°C)</td>
<td>T range 500-700°C Refs [8] [46]</td>
<td>?</td>
<td>0.200</td>
</tr>
<tr>
<td>RbF-ZrF₄ (58-42)</td>
<td>KF-ZrF₄ (58-42)</td>
<td>390 / -1450 Ref [17] (extrapolated)</td>
<td>1.2 Ref [17]</td>
<td>3.416-0.000887 T(°C)</td>
<td>T range 873-1073K Refs [8] [46]</td>
<td>?</td>
<td>0.251</td>
</tr>
<tr>
<td>LiF-NaF-ZrF₄ (58-42)</td>
<td>436 / ?</td>
<td>-5</td>
<td>3.533-0.000870 T(°C)</td>
<td>T range 873-1073K Refs [8] [46]</td>
<td>?</td>
<td>0.296</td>
<td>6.9</td>
</tr>
<tr>
<td>NaF-BeF₂ (57-43)</td>
<td>LiF-BeF₂ (67-33)</td>
<td>460 / -1400 (extrapolated)</td>
<td>1.2, see text for other studies</td>
<td>2.280-0.000488 T(°C)</td>
<td>T range 500-650°C Refs [8] [46]</td>
<td>0.577</td>
<td>0.566</td>
</tr>
<tr>
<td>NaF-BeF₂ (57-43)</td>
<td>340 / -1400 (extrapolated)</td>
<td>1.4</td>
<td>2.270-0.00037 T(°C)</td>
<td>T range 450-550°C Refs [8] [46]</td>
<td>0.52</td>
<td>0.440</td>
<td>7</td>
</tr>
<tr>
<td>LiF-NaF-BeF₂ (31-31-38)</td>
<td>315 / ?</td>
<td>1.7</td>
<td>2.313-0.000450 T(°C)</td>
<td>T range 450-550°C Refs [8] [46] also see [41]</td>
<td>?</td>
<td>0.489</td>
<td>5</td>
</tr>
</tbody>
</table>

Literature Summary IAEA.doc
### Table A2  Thermophysical properties of the candidate molten salts for the Heat Transfer Loop:
Summary of data from (Williams et al., ORNL, 2006; [17] (unless other ref. given)

<table>
<thead>
<tr>
<th>Salt</th>
<th>Class</th>
<th>Composition (% mol)</th>
<th>Melting Point / Boiling Point (°C)</th>
<th>Vapour Pressure (at 900 °C)</th>
<th>Density ρ (g/cm³) Equation</th>
<th>Heat Capacity C&lt;sub&gt;p&lt;/sub&gt; (cal/g°C) Equation</th>
<th>Viscosity μ (cP) Equation</th>
<th>Thermal Conductivity k (W/m K)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chlorides</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiCl-KCl</td>
<td>LiCl-RbCl (58-42)</td>
<td>313 / ?</td>
<td>?</td>
<td>2.7416-0.000689.T(ºC)</td>
<td>0.213</td>
<td>0.212</td>
<td>1.3</td>
<td>0.0286.exp(1441/T(K))</td>
</tr>
<tr>
<td>NaCl-MgCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>NaCl-MgCl&lt;sub&gt;2&lt;/sub&gt; (68-32)</td>
<td>445 / &gt;1465</td>
<td>&lt;2.5</td>
<td>2.2971-0.000507.T(ºC)</td>
<td>0.258</td>
<td>0.262</td>
<td>1.36</td>
<td>0.0431.exp(3060/T(K))</td>
</tr>
<tr>
<td>KCl-MgCl&lt;sub&gt;2&lt;/sub&gt; (68-32)</td>
<td>KCl-MgCl&lt;sub&gt;2&lt;/sub&gt; (68-32)</td>
<td>426 / &gt;1418</td>
<td>&lt;2.0</td>
<td>See equation in Ref [46]</td>
<td>0.276</td>
<td>0.229</td>
<td>1.4</td>
<td>0.0146.exp(2230/T(K))</td>
</tr>
<tr>
<td><strong>Fluoroborate salts</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaF-NaBF&lt;sub&gt;4&lt;/sub&gt; (8-92)</td>
<td>NaF-NaBF&lt;sub&gt;4&lt;/sub&gt; (8-92)</td>
<td>385 / 694</td>
<td>9500</td>
<td>2.2521-0.000711.T(ºC)</td>
<td>0.36</td>
<td>0.435</td>
<td>0.9</td>
<td>0.0877.exp(2240/T(K))</td>
</tr>
<tr>
<td>KF-KBF&lt;sub&gt;4&lt;/sub&gt; (25-75)</td>
<td>KF-KBF&lt;sub&gt;4&lt;/sub&gt; (25-75)</td>
<td>460 / 1070</td>
<td>100</td>
<td>2.258-0.0008026.T(ºC)</td>
<td>0.312</td>
<td>0.367</td>
<td>0.9</td>
<td>0.0431.exp(3060/T(K))</td>
</tr>
<tr>
<td>RbF-RbBF&lt;sub&gt;4&lt;/sub&gt; (31-69)</td>
<td>RbF-RbBF&lt;sub&gt;4&lt;/sub&gt; (31-69)</td>
<td>442 / &gt;1070</td>
<td>&lt;100</td>
<td>2.946-0.001047.T(ºC)</td>
<td>0.218</td>
<td>0.258</td>
<td>0.9</td>
<td>?</td>
</tr>
<tr>
<td><strong>Alkali Fluorides</strong></td>
<td>LiF-NaF-KF (46.5-11.5-42)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>See Table A1</td>
</tr>
<tr>
<td><strong>ZrF&lt;sub&gt;4&lt;/sub&gt; salts</strong></td>
<td>NaF-ZrF&lt;sub&gt;4&lt;/sub&gt; (59.5-40.5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>See Table A1</td>
</tr>
<tr>
<td></td>
<td>KF-ZrF&lt;sub&gt;4&lt;/sub&gt; (58-42)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>See Table A1</td>
</tr>
<tr>
<td></td>
<td>LiF-NaF-ZrF&lt;sub&gt;4&lt;/sub&gt; (26-37-37)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>See Table A1</td>
</tr>
</tbody>
</table>
Table A3 (a) Data references (e.g. [42]) for thermophysical properties of the fuel-salt coolants for the MSR

<table>
<thead>
<tr>
<th>Salt</th>
<th>Phase Diagram (Refs.)</th>
<th>Density $\rho$ (Refs.)</th>
<th>Heat Capacity $C_p$ (Refs.)</th>
<th>Viscosity $\mu$ (Refs.)</th>
<th>Thermal Conductivity $k$ (Refs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF-BeF$_2$-ThF$_4$-UF$_4$</td>
<td>Liquid boundaries diagram [31]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiF-BeF$_2$-UF$_4$</td>
<td>Phase data [51]</td>
<td>Measured data [51]</td>
<td>?</td>
<td>Measured data [51] [42]</td>
<td>?</td>
</tr>
<tr>
<td>LiF-NaF-BeF$_2$-AnFn$_x$ mixtures (MSR-Breeder)</td>
<td>Phase data for various optimal compositions (LiF-NaF-BeF$_2$) [41]</td>
<td>Predicted data (800-1000K) (with no fuel component) [41] Estimation methods [11] Limited measured data [51]</td>
<td>Predicted data (800-1000K) (with no fuel component) [41] Estimation methods [11] [41] Limited measured and estimated data [51]</td>
<td>Predicted and measured data (800-1000K) (with no fuel component) [41] Estimation methods [11] [41] Estimated methods (800-750°C) (without fuel component) [41]</td>
<td>Predicted (800-1000K) and measured data (500-750°C) (without fuel component) [41]</td>
</tr>
<tr>
<td>Salt Composition (% mol)</td>
<td>Liquidus Temperature (°C)</td>
<td>Phase Diagram</td>
<td>Vapour Pressure P (Torr)</td>
<td>Density ρ (g/cm³)</td>
<td>Heat Capacity C_p (cal/g-°C)</td>
</tr>
<tr>
<td>--------------------------</td>
<td>----------------------------</td>
<td>---------------</td>
<td>--------------------------</td>
<td>------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>LiF-BeF₂-ThF₄-UF₄ (73-16-10.7-0.3)</td>
<td>500 ±5</td>
<td></td>
<td></td>
<td>3.628-0.00066,T(°C)</td>
<td>0.34 ±4</td>
</tr>
<tr>
<td>LiF-BeF₂-ThF₄-UF₄ (72-21-6.7-0.3)</td>
<td>500 ±5</td>
<td>See Table A3(a)</td>
<td>log P = 8.0 - 10,000/T(K)</td>
<td>3.153-0.00058,T(°C)</td>
<td>0.39 ±4</td>
</tr>
<tr>
<td>LiF-BeF₂-ThF₄-UF₄ (68-20-11.7-0.3)</td>
<td>480 ±5</td>
<td></td>
<td></td>
<td>3.687-0.00065,T(°C)</td>
<td>0.33 ±4</td>
</tr>
<tr>
<td>LiF-BeF₂-ThF₄-UF₄ (63-25-11.7-0.3)</td>
<td>500 ±5</td>
<td></td>
<td></td>
<td>3.644-0.00063,T(°C)</td>
<td>0.33 ±3</td>
</tr>
</tbody>
</table>

1Temperature range around 873-973K (see text for details)
Table A4 Thermophysical properties of individual salts (with refs given: e.g. [8])

<table>
<thead>
<tr>
<th>Compound</th>
<th>Melting Point (°C)</th>
<th>Normal Boiling Point (°C)</th>
<th>Density $\rho$ (g/cm³)</th>
<th>Vapour Pressure at 900°C (mm Hg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Equation (worked out using additive molar volume method)</td>
<td></td>
</tr>
<tr>
<td>LiF</td>
<td>845 [8]</td>
<td>1681 [8] [47]</td>
<td>2.3581-0.0004902.T(K) T range 1140-1310K [46] [47]</td>
<td>0.1 [17]</td>
</tr>
<tr>
<td>KF</td>
<td>856 [8], 858 [47]</td>
<td>1502 [8] [47]</td>
<td>2.6464-0.0006515.T(K) T range 1150-1310K [47]</td>
<td>1.2 [17]</td>
</tr>
<tr>
<td>RbF</td>
<td>775 [8]</td>
<td>1408 [8] [47]</td>
<td>?</td>
<td>0.75 [17]</td>
</tr>
<tr>
<td>ThF₄</td>
<td>Ref [51]</td>
<td>?</td>
<td>[51]</td>
<td>Equation (theoretical) [32]</td>
</tr>
<tr>
<td>PuF₃</td>
<td>Ref [51]</td>
<td>?</td>
<td>?</td>
<td>?</td>
</tr>
</tbody>
</table>
Table A5 *Dimensionless coefficients (adapted from table in [87] and formulae in [70]).*

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Formula</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nusselt (Nu)</td>
<td>$h d_e / k$</td>
<td>thermal convection to thermal conduction (along $d_e$)</td>
</tr>
<tr>
<td>Reynolds (Re)</td>
<td>$uL / \nu$</td>
<td>inertia to viscous forces</td>
</tr>
<tr>
<td>Prandtl (Pr)</td>
<td>$\nu / \alpha = c_p \mu / k$</td>
<td>viscous momentum transfer to thermal conduction</td>
</tr>
<tr>
<td>Grashof (Gr)</td>
<td>$g L^3 \beta \Delta T / \nu^2$</td>
<td>buoyancy to viscous forces</td>
</tr>
<tr>
<td>Rayleigh (Ra)</td>
<td>$g \beta \Delta T L^3 / \alpha \nu$</td>
<td>buoyancy to thermal and viscous momentum transfer</td>
</tr>
<tr>
<td>Froude (Fr)</td>
<td>$u^2 / gL$</td>
<td>inertia to gravitational forces</td>
</tr>
<tr>
<td>Biot (Bi*)</td>
<td>$k l / \lambda L$</td>
<td>heat transfer at the liquid-solid interface</td>
</tr>
<tr>
<td>Strouhal (Sr)</td>
<td>$\tau u / L$</td>
<td>transient phenomena to convection timescale</td>
</tr>
<tr>
<td>Fourier (Fo)</td>
<td>$L^2 / \alpha \tau$</td>
<td>thermal diffusion to convective diffusion (of heat)</td>
</tr>
<tr>
<td>Weber (We)</td>
<td>$\rho u^2 L / \sigma$</td>
<td>inertia to surface forces</td>
</tr>
</tbody>
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