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Melting Points of Molten Salt Coolants for Chloride-based Molten Salt Fast Reactor

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1. Introduction

Molten salt reactors (MSR) represent one of the most prominent designs among Gen-IV reactors. In contrast to conventional reactors that use solid fuel, molten salt reactors have an innovative structure where nuclear fuel is dissolved in a molten salt coolant, serving both as fuel and coolant. This design significantly reduces concerns regarding core meltdown accidents, as the nuclear fuel can be isolated and solidified in a drain tank located beneath the core in the event of an accident, thus preventing potential secondary accidents due to radioactive leaks. Additionally, the capability for fuel injection and real-time reprocessing during reactor operation enables economical operation. Furthermore, the absence of various equipment and facilities such as pressure vessels allows for system miniaturization and modularity [1]. Based on these diverse advantages, numerous companies and research institutions in advanced nuclear technology nations are actively pursuing the development of molten salt reactor technology.

During the 1950s and 1960s, projects such as Aircraft Reactor Experiment (ARE) and Molten Salt Reactor Experiment (MSRE) were conducted at the Oak Ridge National Laboratory (ORNL) in the United States, with the aim of operational demonstration of the molten salt reactor. These projects and the various MSR conceptual designs that have been developed were primarily developed based on fluoride-based thermal-neutron spectrum MSR concepts. However, in recent years, research efforts aimed at developing chloride-based molten salt fast reactors (MSFRs).

However, due to the relatively limited research on the thermophysical properties of chloride salts compared to fluoride salts, a significant barrier exists to the development of chloride-based MSFR technology. Furthermore, specific considerations regarding coolant salts in chloride-based fast reactors have not been as thoroughly investigated compared to fuel salts. The selection of suitable coolant salts is a crucial process for ensuring the safe and efficient operation of MSFRs, and it is therefore a vital aspect of MSFR technology development.

Information about the melting point of salts is particularly crucial in preventing solidification issues within the MSFR system. In the case of fuel salts, the presence of residual heat from nuclear fission reduces the concern for solidification. However, if solidification occurs in the flow paths of the coolant salt within the secondary intermediate heat exchanger and the power conversion system, it could lead to internal system breakdown and salt leakage. Therefore, understanding the temperature range that the coolant salt must maintain is critical for the safety and maintenance of the system.

The MSRE Report produced by ORNL specifies that solidification should never occur in any part of the MSR, except for the freeze valve between the core and the drain tank [2]. Moreover, in various ORNL reports, including those for ARE, MSRE, and MSBR (Molten Salt Breeder Reactor), have established a requirement that the system's minimum temperature should be maintained with a margin of over 100 ℃ above the freezing point of molten salts to prevent solidification accidents [3].

The melting point of the salt also influences the design of various system components, including heaters, pipes and pumps. It determines the minimum operating temperature and influences the choice of construction materials and insulation requirements. In MSR systems, it is essential to maintain the temperature of the molten salt significantly above its melting point throughout the operation to ensure fluidity and effective heat transfer.

The objective of this study is to compile melting points of ternary chloride salts for MSFR application. The studied salts are regarded as the next-generation heat transfer fluid for thermal energy storage systems (TESSs), and thus, the thermophysical properties of salts are relatively well known.

2. Melting Point of Salts

The sensitivity analysis of melting point to the compositional changes in $LiF\text{-}BeF_2$, used as a coolant salt in the MSRE, was carried out by Romero-Serrano et al [4]. As shown in Fig. 3, The $LiF\text{-}BeF_2$ has significant variations in the melting point as the composition variations, and due to the uncertainty in heat transfer performance. According to the chemical analysis report of the MSRE, extensive efforts were made to maintain the purity of the coolant salt to address these issues [5, 6].

This study suggests that the composition of the molten salt has a significant impact on the melting point, and it indicates the necessity for an analysis of the melting point sensitivity to compositional changes in the salt.

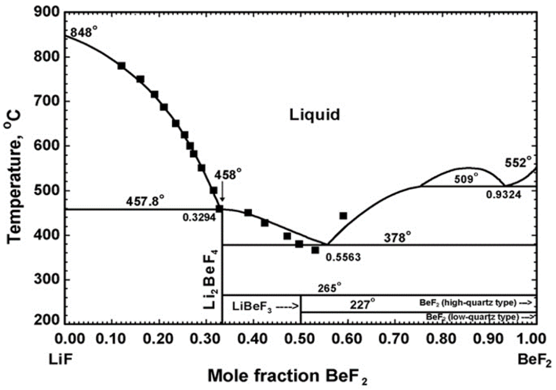

Fig. 1. Phase diagram of LiF-BeF$_2$ [4]

Although there have been proposals to use ternary chloride salts, which are being considered candidates for the next-generation heat transfer fluid in TESSs for Concentrated Solar Power (CSP) systems, no concrete feasibility verification studies have been conducted to ascertain their suitability as coolant salts for MSFR. Ternary chloride salts have the advantage of relatively low melting points and high boiling points. Additionally, they also offer excellent chemical stability and low corrosivity even at high temperatures, which presents significant benefits as coolant salts for MSFRs [7]. Examples of previous research cases concerning the melting point measurement of NaCl-KCl-MgCl$_2$ and NaCl-KCl-ZnCl$_2$ are introduced.

Villada et al. conducted a study comparing the eutectic point of NaCl-KCl-MgCl$_2$ from previous research cases with the eutectic point measured in their study [8]. The experimentally measured eutectic point was found to be similar to previous precedents and predicted values. This research case indicates that the eutectic point of NaCl-KCl-MgCl$_2$ has been measured precisely over several years, suggesting that the eutectic point data for NaCl-KCl-MgCl$_2$ are reliable.

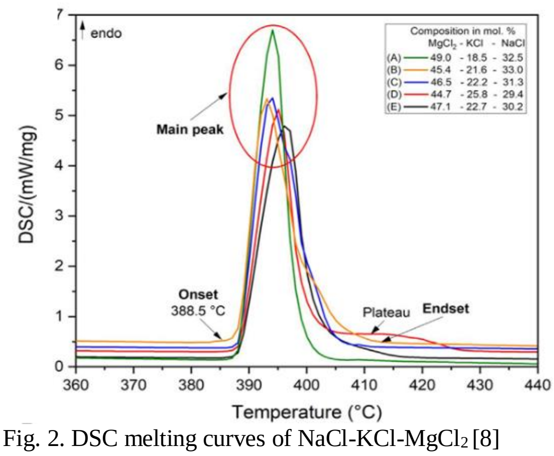

Fig. 2. DSC melting curves of NaCl-KCl-MgCl$_2$ [8]

Table I: Comparison of the previously measured eutectic point data of NaCl-KCl-MgCl$_2$ with the eutectic point measured by Villada et al [8].

Composition [mol.%]	Reported / predicted melting point [°C]	Measured melting point [°C]	Ref.
32.5-18.5-49.0	385	388.20 ± 0.14	Schoilich (1920)
33.0-21.6-45.4	385-387	388.33 ± 0.21	Mohan et al. (2018)
31.3-22.2-46.5	400	388.47 ± 0.06	Podiesnyak et al. (2018)
29.4-25.8-44.7	385	388.45 ± 0.07	Vidal et al. (2019)
30.2-22.7-47.1	385.4	388.55 ± 0.07	Villada et al. (2022)

A study conducted by Li et al. involved comparing the predicted melting points of specific compositions of NaCl-KCl-ZnCl$_2$, calculated using the CALPHAD (CALculation of PHAse Diagrams) method, with the experimentally measured melting points of the same. The results of the study indicated that there were discrepancies ranging from 6 to 20 ℃ between the predicted melting points and the actual measured values [7].

Li et al. also conducted thermal stability analyses by heating samples of each composition to 400 ℃. According to Li et al., for NaCl-KCl-ZnCl$_2$ salts, the mass loss at temperatures below 310 ℃ is less than 0.5%, which is considered negligible [7]. However, since the thermal stability analysis was not conducted under conditions exceeding 400 ℃, which are relevant for the operational temperature conditions of MSFRs, further research appears to be necessary.

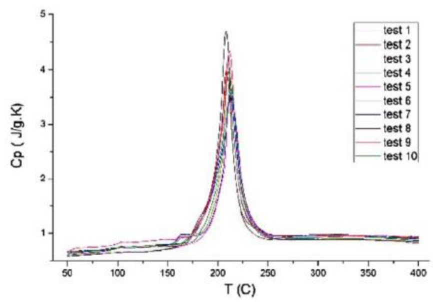

Fig. 3. DSC melting curves of NaCl-KCl-ZnCl$_2$ (13.8-41.9-44.3 mol.%) [7]

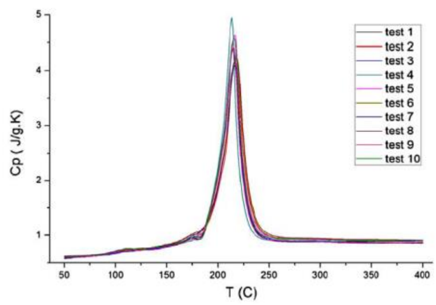

Fig. 4. DSC melting curves of NaCl-KCl-ZnCl$_2$ (18.6-21.9-59.5 mol.%) [7]

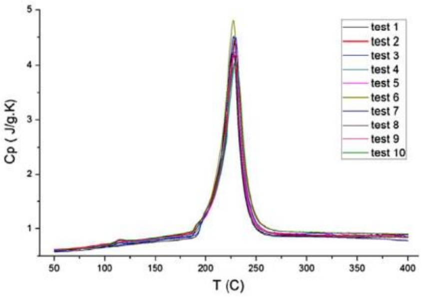

Fig. 5. DSC melting curves of NaCl-KCl-$ZnCl_2$ (13.4-33.7-52.9 mol.%) [7]

Table II: Comparison of the measured melting point data with the predicted melting point using CALPHAD method [9]

Composition [mol.%]	Measured melting point [°C]	Theoretical melting point [°C]
13.8-41.9-44.3	199.3	229
18.6-21.9-59.5	198.7	213
13.4-33.7-52.9	210.3	204

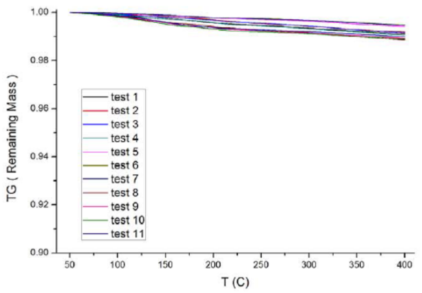

Fig. 6. Thermal Stability Analysis Result of NaCl-KCl-$ZnCl_2$ (18.6-21.9-59.5 mol.%) [7]

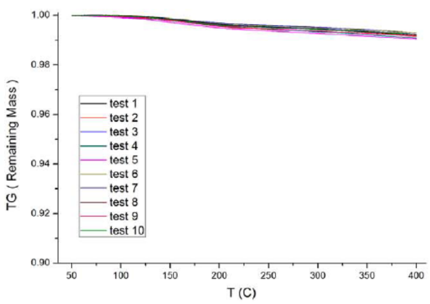

Fig. 7. Thermal Stability Analysis Result of NaCl-KCl-$ZnCl_2$ (13.8-41.9-44.3 mol.%) [7]

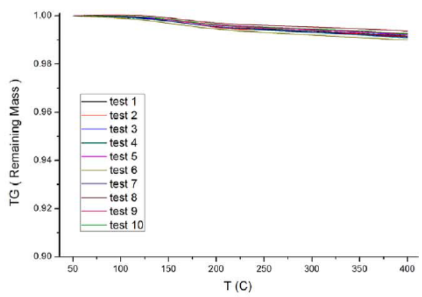

Fig. 8. Thermal Stability Analysis Result of NaCl-KCl-$ZnCl_2$ (13.4-33.7-52.9 mol.%) [7]

3. Summary and Further Works

In this study, the melting point of ternary chloride salts, a next-generation HTF of TESSs, was reviewed for MSFR application. Ternary chloride salts have the advantage of relatively low melting points (below 450 ℃) and high boiling points (above 1200 ℃) compared to Fluoride salts. Additionally, the chloride salts also offer excellent chemical stability and low corrosivity to Nickel alloys at high temperatures, which presents significant benefits as coolant salts for MSFRs.

Due to the limited research on the thermo-physical properties of NaCl-$MgCl_2$, experimental measurements are planned to determine the eutectic point, conduct melting point sensitivity analysis with respect to the compositional change, and compare these with the data from studies on NaCl-KCl-$MgCl_2$ eutectic point measurements. This will allow for a comparative analysis of the thermophysical properties of binary and ternary molten salts. Additionally, since there is a lack of information on the eutectic point in previous studies on NaCl-KCl-$ZnCl_2$, there is a plan to measure this eutectic point and conduct thermal stability analyses at temperatures ranging from 500 ℃ to 700 ℃, which are relevant to the operational temperature range of MSRs.

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