Melting Points Comparison of Chloride Salts for Coolant of Molten Salt Fast Reactor

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1. Introduction

The development of Molten Salt Reactors (MSRs), one of the most promising Generation IV reactor technologies, has gained attention due to their inherent safety features and efficient operation. Unlike conventional reactors using solid fuel, MSRs dissolve nuclear fuel in high-temperature molten salt, serving both as fuel and coolant. This design minimizes concerns about core meltdown accidents, as the liquid fuel can be promptly drained and solidified in a dedicated drain tank, effectively preventing further radioactive leakage. Additionally, MSRs enable online refueling and reprocessing, enhancing operational economics. The compactness and modularity enabled by the absence of large pressure vessels make MSRs a highly attractive alternative for future nuclear power systems [1].

Early MSR development was spearheaded by Oak Ridge National Laboratory (ORNL) through projects such as the Aircraft Reactor Experiment (ARE) and the Molten Salt Reactor Experiment (MSRE) during the 1950s and 1960s. These projects primarily focused on fluoride-based thermal spectrum reactors, demonstrating the feasibility of MSR technology through extensive operational tests [2, 3]. However, recent interest has shifted toward chloride-based Molten Salt Fast Reactors (MSFRs), which offer enhanced neutron economy and lower corrosivity towards structural materials compared to fluoride salts. Nonetheless, the relatively limited research on the thermophysical properties of chloride salts remains a significant barrier to their development [4].

A critical aspect of MSFR safety and performance is maintaining the molten salt above its melting point throughout operation. While residual heat generation in fuel salts mitigates solidification risks, coolant salts are particularly vulnerable to freezing within the heat exchanger and power conversion system. Solidification can result in mechanical damage and salt leakage, which would severely compromise reactor safety. ORNL's MSRE report specifies that solidification should never occur within the MSR system, except for the freeze valve between the core and the drain tank, emphasizing the importance of sufficient temperature margins [5, 6].

Although various binary chloride salts have been evaluated for their suitability as coolants, comprehensive studies on ternary chloride salts are still lacking [7, 8]. Ternary chloride salts, expected to provide better thermophysical properties and economic advantages, have been considered promising candidates for heat transfer fluids in thermal energy storage systems (TESSs). Therefore, this study aims to compile and assess the melting points of various ternary chloride salts, focusing on their applicability to MSFR systems. The results of this investigation will contribute to the selection of optimal salt compositions for safe and efficient reactor operation.

2. Previous studies

The study by Romero-Serrano et al. highlights the importance of maintaining the precise composition of FLiBe in MSRE systems, as its melting point is highly sensitive to compositional changes [9]. According to their analysis, as the mole fraction of BeF_2 in FLiBe increases, the melting point initially decreases, reaching a minimum at approximately 47.04% BeF_2, and then increases again, as shown in Figure 1. This non-linear behavior suggests that the mixture reaches a lower energy state at this specific composition, which could be due to unique physical or chemical interactions. Therefore, maintaining consistent composition is critical for minimizing uncertainties in heat transfer performance and preventing operational accidents.

Li et al. conducted a study to compare the predicted melting points of specific NaCl-KCl-$ZnCl_2$ compositions, calculated using the CALPHAD (CALculation of PHAse Diagrams) method, with experimentally measured values. The comparison revealed discrepancies between the predicted and measured melting points, ranging from 6 to 20 ℃, indicating limitations in the predictive accuracy of the CALPHAD method [10].

In addition to melting point analysis, Li et al. performed thermal stability tests by heating various salt compositions to 400 ℃. The results showed that NaCl-KCl-$ZnCl_2$ mixtures exhibited negligible mass loss below 310 ℃, with values remaining under 0.5% [10]. However, since the thermal stability evaluation was not extended to temperatures above 400 ℃, which are critical for MSFR operation, further research is necessary to accurately assess the thermal stability of NaCl-KCl-$ZnCl_2$ salts under high-temperature conditions.

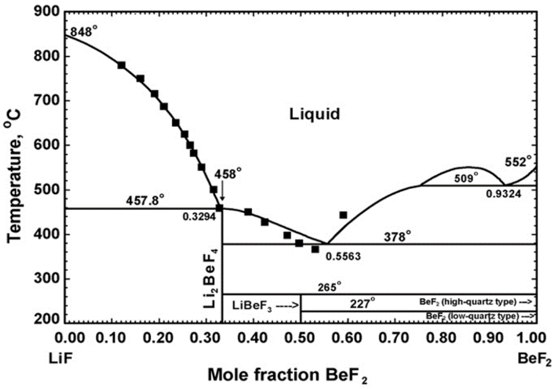

Fig. 1. Phase diagram of LiF-BeF_2 [9]

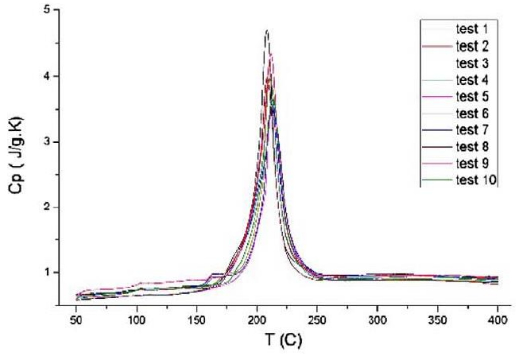

Fig. 2. DSC melting curves of NaCl-KCl-$ZnCl_2$ (13.8-41.9-44.3 mol.%) [10]

3. Methodology

Thermo-Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) are essential analytical techniques for evaluating the thermal properties of chloride-based coolant salts for MSFR systems. TGA measures mass changes of salts under controlled temperature conditions to determine thermal stability, vaporization temperatures, and hygroscopicity. It provides quantitative data on weight loss associated with moisture evaporation, hydrolysis, and chlorine gas volatilization, which are critical factors affecting the suitability of coolant salts.

DSC measures heat flow changes to accurately determine melting points, crystallization temperatures, and latent heat of salts. By comparing the heat flow of a sample with a reference material under controlled heating or cooling conditions, DSC provides precise measurements of phase transitions. This technique also enables accurate calculation of enthalpy changes, contributing to a comprehensive understanding of the thermal behavior of coolant salts.

The combination of TGA and DSC provides essential information for selecting appropriate coolant salts for MSFR systems. TGA identifies thermal stability limits and hygroscopic characteristics, while DSC accurately determines melting points and phase transition behaviors. The integration of these analytical techniques ensures reliable assessment of thermal properties, essential for optimizing the performance of MSFR systems.

For the NaCl-$MgCl_2$ system, the melting points of five compositions, including the eutectic composition predicted by the CALPHAD method and four compositions near it, were measured. The NaCl-KCl-$MgCl_2$ system was assessed using compositions from previous studies by Xu et al. and Villada et al. to verify the accuracy and reproducibility of the DSC method. For the NaCl-KCl-$ZnCl_2$ system, three compositions previously studied by Xu et al. were measured for verification, along with two new compositions within the eutectic region [10, 11].

Due to the high hygroscopicity of each salt sample and the necessity of thorough mixing to ensure data accuracy, specific preparation procedures were undertaken to minimize experimental errors. Prior to mixing, each salt was manually ground using a mortar and pestle for approximately 10 minutes and subsequently subjected to a primary dehydration process in a vacuum oven at 150 ℃ for 7 hours. Following this, the individual salts were weighed according to the target composition, and the mixture was manually ground again for 10 minutes to achieve homogeneity. The homogenized mixture then underwent a secondary dehydration under the same vacuum and temperature conditions for an additional 7 hours.

Given the variation in melting points among the salts, the measurement temperature range was determined accordingly for each sample. The heating rate was uniformly maintained at 10 K/min across all measurements. Throughout the entire experimental process, argon gas, owing to its inertness, was employed as both the purging and protective gas. In this study, the TGA for NaCl-$MgCl_2$ and NaCl-KCl-$MgCl_2$ was conducted using the TG209 F1 Libra, and the DSC analysis was performed using the DSC404 F1 equipment. Both instruments are manufactured by NETZSCH. The simultaneous TGA-DSC for NaCl-KCl-$ZnCl_2$ was conducted using the STA 449 F5 Jupiter model, which is also manufactured by the same company

4. Results

For NaCl-$MgCl_2$, the predicted eutectic composition (57.9-42.1 mol.%) had a predicted melting point of 459.13 ℃, while the experimentally measured melting point was significantly lower at 432.59 ℃. All experimentally analyzed compositions of the NaCl-$MgCl_2$ system exhibited deviations of 25.57 ℃ to 29.79 ℃ from the corresponding predicted melting points. The clearest DSC curve was obtained for the 61.9-38.1 (mol.%) composition, indicating uniform melting.

For NaCl-KCl-$MgCl_2$, three compositions were measured: 30.2-22.7-47.1 (mol.%), 30-20-50 (mol.%), and 27.5-32.5-40 (mol.%). The experimentally measured melting points were 399 ℃, 384.45 ℃, and 383.85 ℃, respectively. The 27.5-32.5-40 (mol.%) composition showed the smallest discrepancy, aligning well with the predicted value (383 ℃), suggesting that this mixture acts more stably as a eutectic system.

For NaCl-KCl-$ZnCl_2$, five compositions were analyzed, including three previously studied and two new compositions. The experimentally measured melting points were generally consistent with previous studies but differed from the predicted values by the CALPHAD method. The observed supercooling effect, indicated by temperature deviations ranging from 27.86 ℃ to 39.57 ℃, was primarily attributed to nucleation delays induced by rapid cooling rates. These deviations represent the differences between the experimentally measured melting points and the theoretically predicted melting temperatures. This study confirms the limitations of the CALPHAD method in predicting melting points and highlights the importance of experimental verification.

The thermal stability of NaCl-$MgCl_2$, NaCl-KCl-$MgCl_2$, and NaCl-KCl-$ZnCl_2$ salts was evaluated using TGA in an argon environment with a flow rate of 50 mL/min. To minimize equipment contamination, the temperature range was adjusted for each salt sample. For NaCl-KCl-$ZnCl_2$, two samples were prepared: one in ambient air and the other in a glovebox with moisture and oxygen levels below 5 ppm.

The NaCl-$MgCl_2$ sample exhibited high thermal stability with less than 5% weight loss up to approximately 700 ℃, indicating strong structural integrity and minimal decomposition. The NaCl-KCl-$MgCl_2$ mixture demonstrated the highest thermal stability, with weight loss remaining below 4% when heated up to 700 ℃. This superior stability is attributed to the stronger ionic bonding in the ternary mixture, even though it contains hygroscopic $MgCl_2$.

In contrast, NaCl-KCl-$ZnCl_2$ displayed poor thermal stability, with noticeable weight loss beginning around 500 ℃ even under glovebox conditions, suggesting severe instability at high temperatures. The air-exposed sample showed even greater weight loss due to the highly hygroscopic nature of $ZnCl_2$, which undergoes hydrolysis at lower temperatures than $MgCl_2$. The results indicate that NaCl-KCl-$MgCl_2$ is the most suitable coolant salt for MSFR systems, while NaCl-KCl-$ZnCl_2$ is not a viable candidate due to its instability and high sensitivity to moisture.

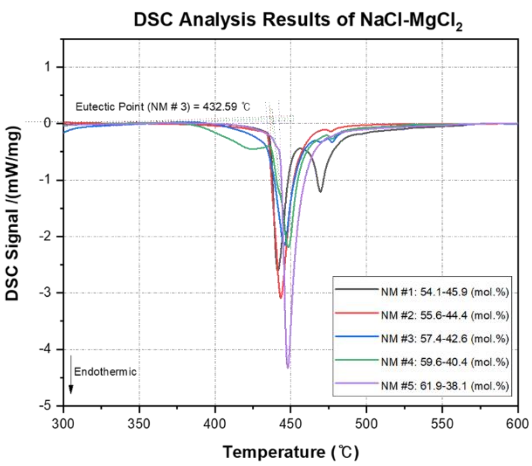

Fig. 3. DSC melting curves of NaCl-$MgCl_2$

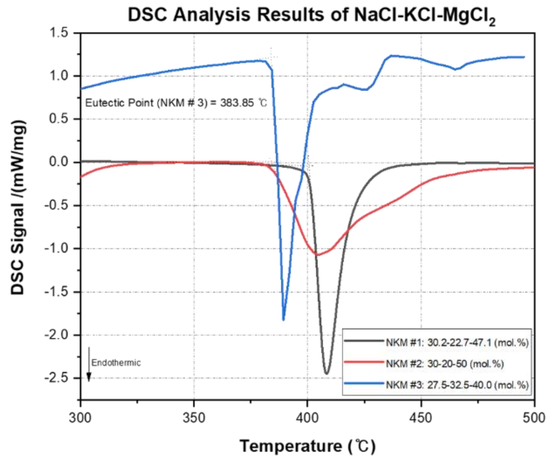

Fig. 4. DSC melting curves of NaCl-KCl-$MgCl_2$

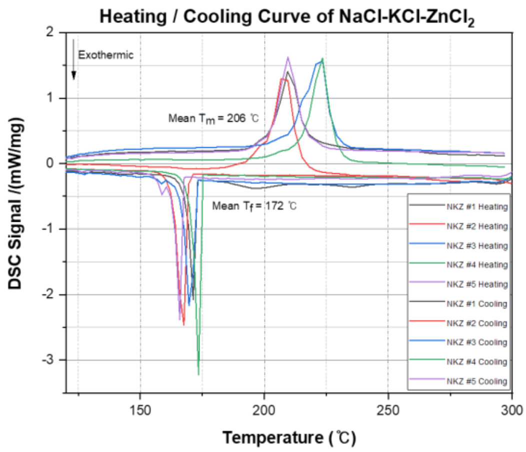

Fig. 5. DSC melting curves of NaCl-KCl-$ZnCl_2$

Table I: Comparison of Predicted and Measured Melting Points for NaCl-$MgCl_2$ Mixtures

Mole Fraction [%.mol]	Predicted Melting Point [℃]	Measured Melting Point [℃]	ΔT [℃]
52.4-47.6	464.81	439.24	25.57
55.6-44.4	462.44	436.29	26.15
57.9-42.1 (Eutectic Point)	**459.13**	**432.59**	**26.54**
59.6-40.4	467.04	437.25	29.79
61.9-38.1	471.63	442.52	29.11

Table II: Comparison of Melting Points Data for NaCl-KCl-$MgCl_2$ Mixtures

Mole Fraction [mol.%]	Predicted Eutectic Point [℃]	Reported Eutectic Point [℃]	Measured Eutectic Point [℃]
30.2-22.7-47.1	385.4	388.55 ± 0.07	399
30-20-50	396	390.5	384.45
18.6-21.9-59.5 (Eutectic Point)	**383**	404.9	**383.85**

Table III: Comparison of Predicted and Measured Melting Points NaCl-KCl-$ZnCl_2$ Mixtures

Mole Fraction [mol.%]	Theoretical Melting Point [°C]	Reported Melting Point [°C]	Measured Melting Point [°C]
13.8-41.9-44.3	229	199.4	201.06
18.6-21.9-59.5 (Eutectic Point)	**213**	**198.7**	**199.79**
13.4-33.7-52.9	204	210.3	211.55
16.2-28.2-55.6	-	-	214.87
13.8-38.0-48.2	-	-	202.05

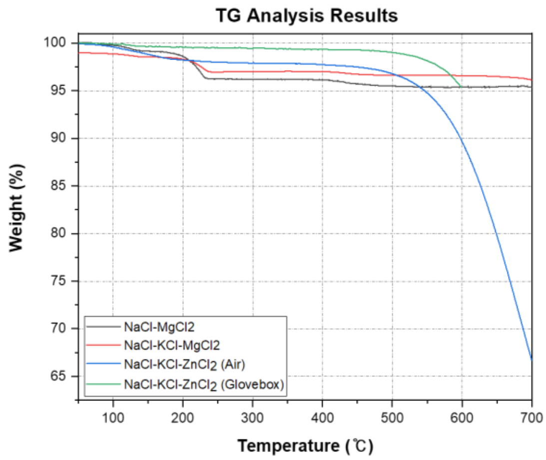

Fig. 6. Thermal Stability Analysis Result of chloride salts

5. Summary and Further Works

This study investigates the thermal stability and melting point sensitivity of chloride-based coolant salts for Molten Salt Fast Reactors (MSFRs) with a fast neutron spectrum. Chloride salts are appealing due to their low neutron absorption, low melting points, and reduced corrosivity compared to fluoride salts.

Experimental analyses using Differential Scanning Calorimetry (DSC) and Thermo-Gravimetric Analysis (TGA) were performed to evaluate the thermal stability and melting points of NaCl-KCl-$ZnCl_2$, NaCl-KCl-$MgCl_2$, and KCl-$MgCl_2$. The DSC results showed that NaCl-KCl-$MgCl_2$ exhibited high thermal stability with decomposition occurring above 700 ˚C, and an acceptable average melting point suitable for MSFR operation. NaCl-KCl-$ZnCl_2$, while having the lowest average melting point in the low 200 ˚C range, was deemed unsuitable as a high-temperature coolant due to its high hygroscopicity and significant decomposition above 500 °C.

The TGA results demonstrated that NaCl-KCl-$MgCl_2$ and NaCl-$MgCl_2$, which both contain $MgCl_2$, exhibited excellent thermal stability, with cumulative weight loss remaining within 3-5% even at 700 °C. In contrast, NaCl-KCl-$ZnCl_2$ showed severe degradation under the same conditions.

When comparing measured melting points to predictions by the CALPHAD method, the experimental results indicated lower melting points for NaCl-$MgCl_2$, suggesting limitations of the CALPHAD method in accurately predicting exact melting points despite its usefulness in understanding general trends.

Comparison with FLiBe indicated that chloride salts have lower sensitivity to composition changes in melting points. While FLiBe exhibits significant melting point variation with composition, all tested chloride salts demonstrated more stable melting points. Among the tested salts, NaCl-KCl-$MgCl_2$ was identified as the most promising coolant due to its low melting point and high thermal stability. Future research should focus on confirming the applicability of NaCl-KCl-$MgCl_2$ to actual MSFR systems and exploring other chloride salt mixtures for enhanced performance.

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