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ANALYSIS OF MOLTEN SALT COOLANT PROPERTIES FOR A SMALL MODULAR MOLTEN SALT REACTOR

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ABSTRACT

The concept of the Molten Salt Reactor began in the 1960s, and since then, several studies have been conducted on the use of liquid salt in MSRs which can be used as both fuel and coolant. A better knowledge of these liquid coolant properties just might give an edge on the development of technology for this study field. The present paper presents a literature review on the main physical and chemical parameters of molten salts, based on previous references. The goal is to evaluate a possible candidate for a Small Modular Reactor considering the density, heat capacity, thermal conductivity, viscosity, and corrosion performance. Among these properties, corrosion performance is particularly relevant due to its influence on the reactor lifespan. While analyzing the stability of physical and chemical parameters at high temperature, fluoride salts as LiF-BeF_2, LiF-NaF-BeF_2 and LiF-NaF-KF, tend to have the best values throughout the studies, turning them in focal groups of this survey. The data here gathered provide a reference point for applications such as modeling, thus aiming to reach benchmark values in this field.

1. INTRODUCTION

Interest in the usage of molten salt coolants for energy generation started in the early 1960s with the Molten Reactor Experiment from Oak Ridge National Laboratory [1]. Though it was an ambitious project, research and development dwindled. It was only in the 2000s that summaries and reviews of past research began to be published. Nowadays, numerous institutions and laboratories are actively acquiring new data. While designing and developing molten salt reactors concepts, the thermochemical and thermophysical properties of the coolants must be well identified for the most realistic and accurate results. There are many studies that approach the idea of measuring the properties of some molten salt coolants, though the search for this data is no easy task. These analyses focus on understanding the suitability of candidate salts for application in Small Modular Reactors of the MSR type. Therefore, comes the utility of gathering the relevant data on molten salt coolants for designing and modelling purposes. The goal of this paper is to evaluate possible candidates for MSRs, thus contributing to the advance of this research field and further improving molten salt nuclear reactor technology for the future.

2. METHODOLOGY

2.1. Selection of Candidate Salts

A comprehensive literature review will be conducted to identify a diverse range of salts potentially suitable for MSRs. Examples include fluorides with counter ions such as beryllium, sodium, lithium, potassium, and zirconium. The selection of these salts will consider their chemical stability, compatibility with the reactor system, and performance in terms of nuclear reactions and thermodynamic characteristics.

2.2. Survey of Thermophysical Properties

An extensive survey will be undertaken to gather data on a series of thermalphysical properties of the selected salts. These properties include:

- Melting Temperature: Crucial for determining the operational temperature range of the reactor.
- Density and Density Variation with Temperature: Influences the efficiency of heat transport and the overall stability of the system.
- Heat Capacity: Indicates the amount of heat that a material can store per unit of mass, affecting the thermal stability of the reactor.
- Thermal Conductivity: Determines the effectiveness of reactor cooling and heat dissipation.
- Viscosity: An essential property for designing an effective and efficient energy system that regards the transport and flow of the mixtures along the core.

By employing this methodology, one expects to gain a comprehensive understanding of the thermophysical properties of candidate salts. For example, the melting temperature significantly influences the operational stability of the reactor, while density and specific heat directly affect cooling efficiency and thermal control capacity. This understanding will contribute greatly to the selection and development of appropriate materials for application in MSRs.

3. THERMOPHYSICAL PROPERTIES OF FLUORIDE COOLANTS

3.1. Melting Point Temperature

The melting temperature of these mixtures across the literature is plainly defined and is also available for other molar compositions. In this paper, only the most recommended molar compositions for each salt will be addressed to assess the best candidates between the different mixtures. The melting point is crucial to determine in which temperature range the MSR is able to operate. Among the evaluated salts, LiF-NaF-BeF_2 has the lowest melting temperature, while NaF-ZrF_4 has the highest (Tab. 1).

Tab. 1. Salt Melting Temperature

Salt	Molar Composition (mol%)	Melting Temperature (K)	References
LiF-BeF_2	67-33	732	[7] [12]
LiF-NaF-KF	46.5-11.5-42.0	735	[9]
NaF-ZrF_4	59.5-40.5	773	[8] [12]
LiF-NaF-ZrF_4	26-37-37	709	[9]
LiF-NaF-BeF_2	31-31-28	588	[9]
Li-KF	50-50	732	[1]
Li-RbF	43-57	748	[10]
LiF-NaF-RbF	42-6-52	708	[9]

3.2. Density

Among other properties discussed in this paper, data on density is richer not only in quantity but also in quality due to its smaller uncertainties. Most data on density are functions of melting point, correlated by temperature. These functions are obtained by a technique - Archimedes Method - that is widely used for other types of liquids and solids [2]. The Tab. 2 provides the density equation as a function of salt temperature T (in Kelvin). At the average operational temperature of coolant salts (873 K) in a Molten Salt Reactor, $NaF-ZrF_4$ exhibits the highest density, while Li-KF exhibits the lowest. For MSRs, a high density offers advantages such as increased heat capacity, improved neutron moderation, and enhanced structural stability. However, high density requires more powerful pumps, and the higher mass of a denser salt can lead to increased wear on reactor components, such as pipes and pumps, potentially reducing their lifespan. Otherwise, a low density provides easier salt circulation and a reduced structural stress, but present the disadvantages of lower heat capacity and affect the neutron moderation. Therefore, a moderate density is often ideal, balancing the benefits of both high and low density.

Tab. 2. Salt Density Correlations

Salt	**Molar Composition (mol%)**	**Density Equation (kg/m^3)**	**Density (kg/m^3) 873 K**	**References**
$LiF-BeF_2$	67-33	2413.0 – 0.49 · T (K)	1987	[11] [12]
LiF-NaF-KF	46.5-11.5-42.0	2579.3 – 0.62 · T (K)	2035	[12]
$NaF-ZrF_4$	59.5-40.5	3827.0 – 0.89 · T (K)	3051	[12][13]
$LiF-NaF-ZrF_4$	26-37-37	3533.0 – 0.87 · T (K)	2773	[9]
$LiF-NaF-BeF_2$	31-31-28	2313.0 – 0.45 · T (K)	1920	[9]
Li-KF	50-50	2460.0 – 0.68 · T (K)	1866	[1]
Li-RbF	43-57	3300.0 – 0.96 · T (K)	2462	[10]
LiF-NaF-RbF	42-6-52	3261.0 – 0.81 · T (K)	2553	[9]

3.3. Heat Capacity

Heat capacity values here presented were all evaluated at 973K. Some of the mixtures values have little to no dependency on temperature variations. Heat capacity is the amount of energy contained in the salt, while flowing around the MSR system. Among the evaluated salts, $NaF-ZrF_4$ has the lowest heat capacity, while LiF-NaF-RbF has the highest (Tab. 3). A high heat capacity value combined with a low melting point is highly desirable [3].

Tab. 3. Salt Heat Capacity

Salt	**Molar Composition (mol%)**	**Heat Capacity (cal/g-K)**	**References**
$LiF-BeF_2$	67-33	0.577	[12]
LiF-NaF-KF	46.5-11.5-42.0	0.450	[13]
$NaF-ZrF_4$	59.5-40.5	0.279	[12] [13]
$LiF-NaF-ZrF_4$	26-37-37	0.296	[8]
$LiF-NaF-BeF_2$	31-31-28	0.489	[8]
Li-KF	50-50	0.440	[1]
Li-RbF	43-57	0.284	[10]
LiF-NaF-RbF	42-6-52	0.630	[9]

3.4. Thermal Conductivity

For molten salts, thermal conductivity data is somewhat difficult to precisely measure. Due to its nature, experimental data deviates from the predicted values obtained by using semi-empirical theories on thermal conductivity of liquids [4]. Thermal conductivity is a crucial factor in the efficiency of a molten salt in MSRs. Thus, a mixture with higher thermal conductivity is more desirable. The Li-RbF exhibits the highest thermal conductivity while the LiF-NaF-ZrF_4 has the smallest (Tab. 4).

Tab. 4. Salt Thermal Conductivity

Salt	Molar Composition (mol%)	Thermal Conductivity (W/m-K)	References
LiF-BeF_2	67-33	1.10	[12] [14]
LiF-NaF-KF	46.5-11.5-42.0	0.91 (at 973 K)	[15]
NaF-ZrF_4	59.5-40.5	0.49	[4]
LiF-NaF-ZrF_4	26-37-37	0.36	[4]
LiF-NaF-BeF_2	31-31-28	0.97	[9]
Li-KF	50-50	0.71 (at 1150K)	[16]
Li-RbF	43-57	1.20	[10]
LiF-NaF-RbF	42-6-52	0.62	[9]

3.5. Viscosity

Due to its nature of a Newtonian liquid, the viscosity of molten salts is a heat dependable property. This insinuates that the data provided mostly correlates to the temperature of the salt, apart from some due to poor and uncertain data. The viscosity dictates how easily the salt in its liquid state flows through the MSR system. The smaller the viscosity, less energy is necessary to pump the fluid around the system.

Tab. 5. Salt Viscosity

Salt	Molar Composition (mol%)	Viscosity (cp)	References
LiF-BeF_2	67-33	0.116 exp [3755 / T(K)]	[11] [12]
LiF-NaF-KF	46.5-11.5-42.0	0.040 exp [4170 / T(K)]	[1]
NaF-ZrF_4	59.5-40.5	0.077 exp [3997 / T(K)]	[4]
LiF-NaF-ZrF_4	26-37-37	6.9	[9]
LiF-NaF-BeF_2	31-31-28	5.0	[9]
Li-KF	50-50	2.9	[1]
Li-RbF	43-57	0.021 exp [4678 / T(K)]	[10]
LiF-NaF-RbF	42-6-52	2.6	[9]

3.6. Thermophysical Comparison

Undoubtedly, the most suitable salts must have several advantageous thermophysical properties. In this sense, a certain combination of properties was found to be most desirable. The Fig. 1 plots Heat Capacity versus Thermal Conductivity based on the values from Tab. 3 and Tab. 4. A higher heat capacity combined with a high value of thermal conductivity is essential for a more efficient energy transfer. Thus, the most desirable values are towards the upper right side of the graph. Also, Fig. 2 depicts Heat Capacity versus Melting Temperature based on the values from Tab. 3 and Tab. 1. Low values of melting temperatures combined with a higher heat capacity offer a more efficient energy usage for the MSR. Thus, the most desirable values are toward the lower right side of the graph. Furthermore, Fig. 3 shows Heat Capacity versus Salt Density, using the values from Tab. 2 for density at 873 K. Moderate density combined with higher heat capacity makes salts the most suitable, and thus, the most desirable values are toward the middle right side of the figure.

Therefore, in these analysis, the most desirable salts identified in the comparison are LiF-BeF_2, LiF-NaF-BeF_2, and LiF-NaF-KF, although the other salts remain suitable for MSR use.

Fig. 1. Heat Capacity versus Thermal Conductivity.

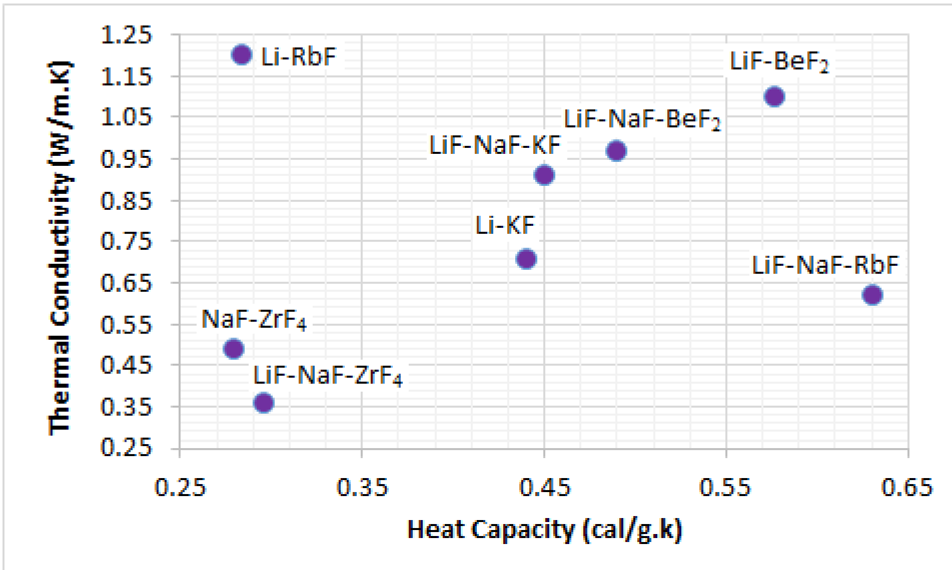


Fig. 2. Heat Capacity versus Melting Temperature.

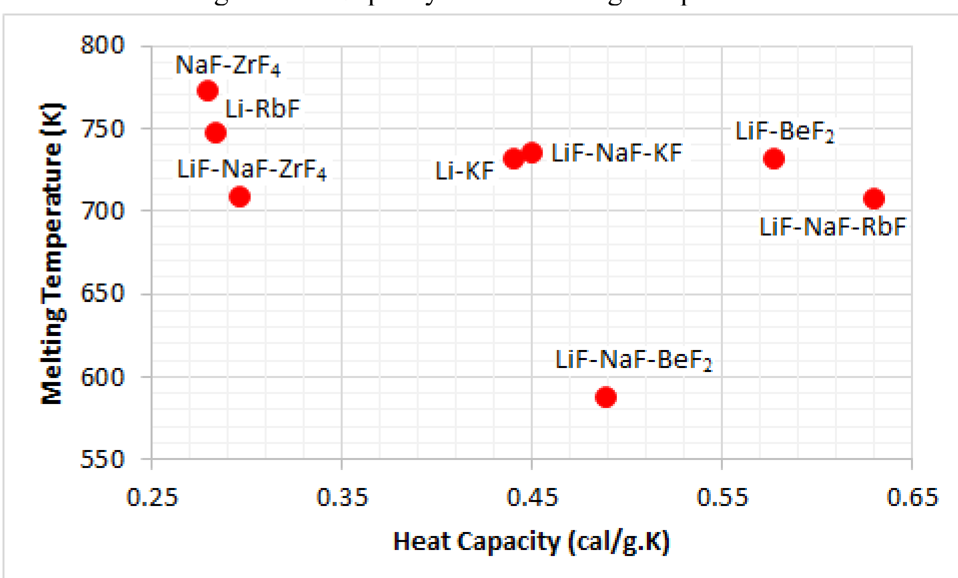
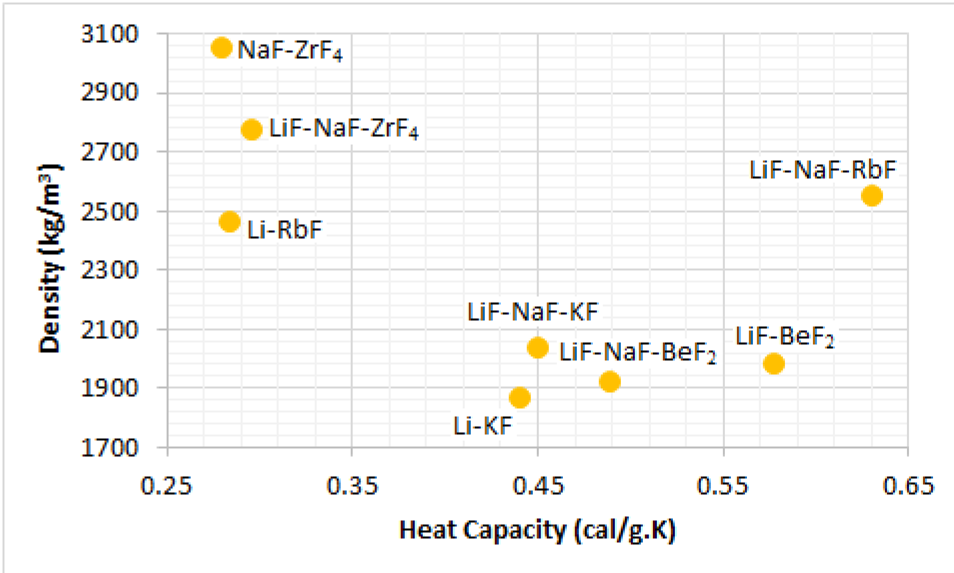


Fig. 3. Heat Capacity versus Density



4. GRAPHITE CORROSION

The protection of graphite from molten salt and its gases corrosion is of extreme importance while considering the longevity of the reactor lifespan. Salt and gas permeation on the pores of the graphite can affect its microstructural properties, facilitating the diffusion and retention of fission products and tritium [5]. To prevent corrosion, a seal coating can be applied to the graphite to reduce open porosity. Alternatively, different types of graphite are being developed to circumvent the issues. In the literature, extensive and thorough reports on corrosion of different salts were found. For the most desirable salts that were elected, no direct comparative data was found for LiF-NaF-BeF_2, though LiF-BeF_2 and LiF-NaF-KF were utilized in a detailed report that took in consideration various materials, mass change of said material and corrosion rate [6].

The Tab. 6 presents an experimental study on corrosion, where a graphite capsule is first filled with solid salt and then sealed in an inert atmosphere to ensure maximum impurity control. The capsule is subsequently heated in a furnace to 973 K. There is variation in the duration each salt was exposed to heat, which is expected to result in differing overall mass changes of the graphite. However, by comparing the corrosion rate values, it is possible to assess which salt exhibits a more severe corrosion profile.

It was found that both salts have a similarity in their respective corrosion patterns, with LiF-BeF_2 having a lower corrosion rate.

Tab. 6. Corrosion Study

Salt	Temperature (K)	Container Material	Time (h)	Mass Change (mg/cm^2)	Corrosion Rate (mg/cm2/day)
LiF-BeF_2	973	Graphite	1000	0.17	4.08E-03
LiF-NaF-KF	973	Graphite	2000	0.38	4.56E-03

While designing different MSRs, the study of the graphite corrosion caused by the mixtures elected must be a key factor in development. This vital consideration will contribute greatly to the reactor lifespan and help maintain a lower maintenance cost.

5. CONCLUSION

An analysis was conducted in this study of various salts potentially applicable in Molten Salt Reactors (MSRs), employing a methodology that involved carefully selecting salts, conducting a bibliographic survey of their physical, chemical, and thermal properties, then performing a comparative analysis of the collected data.

The results revealed a similarity in the chemical composition of the salts, all being fluorides with alkali metal counter ions. The melting temperature range of the salts proved to be adequate for reactor operation, remaining below the working temperature range of the MSRs. Furthermore, the density of the salts and their heat capacity varied within ranges indicating potential for efficient heat transfer and stable reactor operation. Based on these findings, it is concluded that the analyzed salts exhibit promising characteristics for application in MSRs, offering a viable alternative for the generation of safe, efficient, and sustainable nuclear energy. However, while conducting different properties analysis, it was found that LiF-BeF_2 (67-33), LiF-NaF-BeF_2 (31-31-38) and LiF-NaF-KF (46.5-11.5-42.0) proved to be the most desirable salts among the others that were initially elected.

In summary, this study contributes to advancing knowledge about the materials used in MSRs and lays the groundwork for future research aimed at further improving molten salt nuclear reactor technology, thereby advancing the development of safer and more efficient nuclear energy sources for the future.

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