EVALUATION OF MOLTEN SALT COOLANT CHARACTERISTICS FOR SMALL MODULAR REACTORS

Authors: Calegario, Mr. Gabriel, Dr. Clarysson Alberto Alberto Mello da Silva, Pereira, Dr. C, Mello da Silva, Dr. Clarysson Alberto Alberto Mello da

Date: 2025-04-19T21:53:34+00:00

Abstract

The concept of the Molten Salt Reactor (MSR) originated in the 1960s, and since then, numerous studies have investigated the utilization of liquid salts as both fuel and coolant in MSRs. Enhanced understanding of these liquid coolant properties could provide significant advantages for technological development in this research domain. This paper presents a literature review of the principal physical and chemical parameters of molten salts, based on prior references. The objective is to evaluate potential candidates for Small Modular Reactors (SMRs) based on density, heat capacity, thermal conductivity, viscosity, and corrosion performance. Among these properties, corrosion performance is particularly critical due to its direct impact on reactor service life. In analyzing the stability of physical and chemical parameters at elevated temperatures, fluoride salts such as LiF-BeF2, LiF-NaF-BeF2, and LiF-NaF-KF consistently exhibit superior performance across studies, establishing them as the focal points of this review. The compiled data provide a reference baseline for applications such as modeling, thereby establishing benchmark values for this field.

Full Text

Preamble

EVALUATION OF MOLTEN SALT COOLANT CHARACTERISTICS FOR SMALL MODULAR REACTORS

Gabriel L. Calegario, Claubia Pereira and Clarysson A. M. Silva
Departamento de Engenharia Nuclear, UFMG (Universidade Federal de Minas Gerais, Av. Antônio Carlos, 6627, Campus UFMG, PCA 1, Bloco 04, Anexo Engenharia, Pampulha, 31270-90 Belo Horizonte, MG, Brazil)
clarysson@nuclear.ufmg.br

Key words: Molten Salt Reactors; Small Modular Reactors; Molten Salts

ABSTRACT

The concept of the Molten Salt Reactor began in the 1960s, and since then, numerous studies have investigated the use of liquid salts in MSRs that can function as both fuel and coolant. A deeper understanding of these liquid coolant properties could provide a significant advantage in advancing this technology. This paper presents a literature review of the main physical and chemical parameters of molten salts, drawing on previous references. The objective is to evaluate potential candidates for Small Modular Reactors based on density, heat capacity, thermal conductivity, viscosity, and corrosion performance. Among these properties, corrosion performance is particularly critical due to its direct impact on reactor lifespan. When analyzing the stability of physical and chemical parameters at high temperatures, fluoride salts such as LiF-BeF_2, LiF-NaF-BeF_2, and LiF-NaF-KF consistently demonstrate the most favorable values, making them the focus of this survey. The compiled data provide a reference point for applications such as modeling, with the aim of establishing benchmark values for the field.

INTRODUCTION

In today' s global context, there is intense demand for energy generation to meet the geopolitical and technological needs of nations. Furthermore, recent global policies and sanctions increasingly mandate the adoption of clean energy sources to minimize CO_2 emissions. Nuclear energy generation aligns perfectly with these objectives. Among the various forms of nuclear power production, SMRs (Small Modular Reactors) have recently gained prominence, as they can expand the reach of energy grids without compromising the delivery of high-output, clean energy. Although promising, SMRs face implementation challenges that the scientific community is actively working to overcome.

One notable candidate for realizing the concept of modularity is the Molten Salt Reactor. Molten Salt Reactors, commonly known as MSRs, began operation in the 1960s [**?**] and were recognized at the time as promising candidates for nuclear energy generation (World Nuclear Association, 2021). A decade later, the project was abandoned due to technological limitations. Now, in the early 21st century, with significant improvements and advances across all fields of nuclear science, the scientific community has returned to MSR research in substantial numbers (MIT Nuclear Reactor Laboratory, 2020).

Compared to other nuclear reactor designs, MSRs possess unique characteristics that make them highly desirable, including their effectiveness and efficiency in generating energy safely. The fundamental principle of an MSR involves the use of nuclear fuel in a medium containing liquid salt at high temperatures, with the salt itself serving as the core coolant. Even among MSRs, multiple core models exist with different configurations regarding fuel cell arrangement, fuel channels, coolant systems, and other aspects.

One of the primary advantages of the MSR design is its ability to operate at low pressures—a constant concern for pressurized water reactors, which require high pressures to prevent water boiling throughout the system. By employing a saline mixture with high melting and boiling points instead of water as a coolant, MSRs can operate at low pressures and high temperatures, thereby offering enhanced safety and efficiency in energy generation.

The key factor enabled by low-pressure operation is modularity, leading to the proposal of the SM-MSR (Small Modular Molten Salt Reactor). This unique feature could revolutionize the scale at which nuclear energy contributes to the power grid, expanding the generational reach of this technology. Currently, numerous institutions, companies, and startups are pursuing research on SM-MSRs in an effort to transform the nuclear energy industry.

However, developing this type of nuclear system requires studies across various fields of knowledge, and the present work is part of this broader effort. The aim of this paper is to evaluate potential candidates for MSR salts, thereby advancing this research field and enhancing molten salt nuclear reactor technology for the future.

2.1. Selection of Candidate Salts

A comprehensive literature review was conducted to identify a diverse range of salts potentially suitable for MSRs. The examples examined are fluorides, due to their ability to maintain stable properties across a wide temperature range. This study analyzes the following salts: LiF-BeF_2, LiF-NaF-KF, NaF-ZrF_4, LiF-NaF-ZrF_4, LiF-NaF-BeF_2, Li-KF, Li-RbF, and LiF-NaF-RbF. The selection of these salts considered their chemical stability, compatibility with reactor systems, and performance in terms of nuclear reactions and thermodynamic characteristics.

2.2. Survey of Thermophysical Properties

An extensive survey was undertaken to gather data on key thermophysical 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 overall system stability.
- **Heat Capacity:** Indicates the amount of heat a material can store per unit mass, affecting reactor thermal stability.
- **Thermal Conductivity:** Determines the effectiveness of reactor cooling and heat dissipation.
- **Viscosity:** An essential property for designing efficient energy systems regarding the transport and flow of mixtures through the core.

- **Graphite Corrosion:** A subject of extreme importance that defines the lifespan of the reactor core.

Through this methodology, we expect to gain a comprehensive understanding of the thermophysical properties of candidate salts and how they relate to one another. For example, melting temperature significantly influences operational stability while also enabling more efficient energy utilization when combined with high heat capacity values. Additionally, higher thermal conductivity provides better energy and heat transfer. Understanding these correlations will greatly contribute to the selection and development of appropriate materials for MSR applications.

3.1. Melting Point Temperature

The melting temperatures of these mixtures are well-documented in the literature for various molar compositions. This paper focuses on the most recommended molar compositions for each salt to identify the most promising candidates. Determining the melting point is essential for defining the operational temperature of the MSR. Among the evaluated salts, LiF-NaF-BeF_2 has the lowest melting temperature of 588 K, while NaF-ZrF_4 has the highest at 773 K (Table 1).

Tab. 1. Salt Melting Temperature

Molar Composition (mol%)	Melting Temperature (K)

References

[7] [12] [8] [12] LiF-BeF_2 LiF-NaF-KF NaF-ZrF_4 LiF-NaF-ZrF_4 LiF-NaF-BeF_2 Li-KF Li-RbF LiF-NaF-RbF

3.2. Density

Among the properties discussed in this paper, density data are particularly abundant and reliable, characterized by relatively small uncertainties. Most density data are expressed as functions of temperature, correlated through the Archimedes Method—a technique widely used for both liquids and solids [**?**]. Table 2 provides density equations as a function of salt temperature T (in Kelvin).

Tab. 2. Salt Density Correlations

Salt	Molar Composition (mol%)	Density Equation (kg/m^3)
LiF-BeF_2		$2413.0 -0.49 \cdot T$ (K)
LiF-NaF-KF		$2579.3 -0.62 \cdot T$ (K)
NaF-ZrF_4		$3827.0 -0.89 \cdot T$ (K)
LiF-NaF-ZrF_4		$3533.0 -0.87 \cdot T$ (K)
LiF-NaF-BeF_2		$2313.0 -0.45 \cdot T$ (K)
Li-KF		$2460.0 -0.68 \cdot T$ (K)
Li-RbF		$3300.0 -0.96 \cdot T$ (K)
LiF-NaF-RbF		$3261.0 -0.81 \cdot T$ (K)

At the typical operating temperature of coolant salts in a Molten Salt Reactor (873 K), NaF-ZrF_4 exhibits the highest density, while Li-KF has the lowest. In MSRs, higher density offers benefits such as greater heat capacity, improved neutron moderation, and enhanced structural stability. However, it also presents challenges, including the need for more powerful pumps and increased wear on reactor components such as pipes and pumps, potentially shortening their lifespan. Conversely, low density facilitates easier salt circulation and reduces structural stress but suffers from lower heat capacity and reduced neutron moderation effectiveness. Therefore, moderate density is often ideal, balancing the advantages of both high and low density.

3.3. Heat Capacity

All heat capacity values presented here were evaluated at 973 K. Some mixture values show little to no temperature dependency. Heat capacity represents the amount of energy the salt can store as it circulates through the MSR system. Among the evaluated salts, NaF-ZrF_4 has the lowest heat capacity, while LiF-NaF-RbF has the highest (Table 3). A high heat capacity combined with a low melting point is highly desirable [?].

Tab. 3. Salt Heat Capacity

Salt	Molar Composition (mol%)	Heat Capacity (cal/g-K)

References

[12] [13]

3.4. Thermal Conductivity

Thermal conductivity data for molten salts are somewhat difficult to measure precisely. Due to their nature, experimental data often deviate from predicted values obtained using semi-empirical theories on liquid thermal conductivity [?]. Thermal conductivity is a key factor in the efficiency of molten salts in MSRs, making mixtures with higher thermal conductivity more desirable. Li-RbF exhibits the highest thermal conductivity, while LiF-NaF-ZrF_4 has the lowest (Table 4).

Tab. 4. Salt Thermal Conductivity

Salt	Molar Composition (mol%)	Thermal Conductivity (W/m-K)
LiF-BeF_2		0.91 (at 973 K)

References

[12] [14] 0.71 (at 1150K) LiF-BeF_2 LiF-NaF-KF NaF-ZrF_4 LiF-NaF- LiF-NaF-Li-KF Li-RbF LiF-NaF-

3.5. Viscosity

Due to their Newtonian liquid nature, the viscosity of molten salts is a temperature-dependent property. This suggests that the provided data primarily correlate with salt temperature, except where data quality is poor or uncertain. Viscosity determines how easily the molten salt flows through the MSR system; lower viscosity reduces the energy required for pumping the fluid.

Tab. 5. Salt Viscosity

Salt	Molar Composition (mol%)	Viscosity (cp)
LiF-BeF$_2$		0.116 exp [3755 / T(K)]
LiF-NaF-KF		0.040 exp [4170 / T(K)]
NaF-ZrF$_4$		0.077 exp [3997 / T(K)]
LiF-NaF-ZrF$_4$		0.021 exp [4678 / T(K)]

References

[11] [12]

3.6. Thermophysical Comparison

Undoubtedly, the most suitable salts must possess a combination of advantageous thermophysical properties. A specific set of properties has been identified as most desirable. Figure 1 [Figure 1: see original paper] plots heat capacity versus thermal conductivity based on values from Tables 3 and 4. Higher heat capacity combined with high thermal conductivity is essential for more efficient energy transfer, making the most desirable values fall toward the upper right region of the graph.

Fig. 1. Heat Capacity versus Thermal Conductivity.

Figure 2 [Figure 2: see original paper] depicts heat capacity versus melting temperature based on values from Tables 3 and 1. Lower melting temperatures combined with higher heat capacity enable more efficient energy utilization in MSRs, positioning the most desirable values toward the lower right region of the graph.

Fig. 2. Heat Capacity versus Melting Temperature.

Furthermore, Figure 3 [Figure 3: see original paper] shows heat capacity versus salt density using values from Table 2 for density at 873 K. Moderate density combined with high heat capacity makes salts more suitable, with the most desirable values falling toward the middle-right region of the figure.

Fig. 3. Heat Capacity versus Density

Based on these analyses, the most desirable salts identified are LiF-BeF$_2$, LiF-NaF-BeF$_2$, and LiF-NaF-KF, although the other salts remain suitable for MSR applications.

4. GRAPHITE CORROSION AND INFILTRATION

Protecting graphite from corrosion by molten salt and its gases is critically important for ensuring reactor longevity. With molten fluoride salts, graphite corrosion occurs through the dissolution of alloying elements in the mixture when their Gibbs free energies of fluoride formation are more negative, meaning the reaction is spontaneous. Salt and gas permeation into graphite pores can affect its microstructural properties, facilitating the diffusion and retention of fission products and tritium [**?**]. To prevent corrosion, seal coats can be applied to graphite to reduce open porosity, or different types of graphite can be developed to circumvent these issues. The literature contains extensive reports on the corrosion behavior of various salts.

4.1. Corrosion Study

For the most desirable salts selected, no direct comparative data were found for LiF-NaF-BeF_2, though LiF-BeF_2 and LiF-NaF-KF were examined in a detailed report that considered various materials, their mass changes, and corrosion rates [**?**].

Table 6 presents an experimental corrosion study in which a graphite capsule is filled with solid salt and sealed in an inert atmosphere to ensure maximum impurity control. The capsule is then heated in a furnace to 973 K. Variations in exposure duration for each salt result in different overall mass changes of the graphite. However, by comparing corrosion rate values, it is possible to assess which salt exhibits a more severe corrosion profile. The results show similar corrosion patterns for both salts, with LiF-BeF_2 exhibiting a lower corrosion rate.

Tab. 6. Corrosion Study

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

4.2. Graphite Protection

Regarding graphite protection, another study conducted a series of tests involving different coating methods applied to nuclear-grade graphite to reduce open porosity and improve resistance to salt permeation. One method in particular, the CVD PyC seal, proved to be the most viable option for protecting moderator graphite.

4.2.1. PyC Coating

The application of PyC to seal core graphite in MSRs has been a known technique since early demonstrations and remains one of the most effective methods. A PyC coating was deposited on IG-110 via CVD [**?**]. Both uncoated and coated samples were exposed to 650°C in FLiNaK for 12 hours at 1, 3, and 5 atm. For the CVD PyC-coated IG-110, the infiltrated amount was 0.0047 ml/g, compared to 0.1089 ml/g for the uncoated IG-110, representing a reduction in salt permeability of over 95%. It was also observed that pore diameters on the coated IG-110 were more scattered and dispersed than on the uncoated material, likely due to coating defects that could eventually cause infiltration.

4.2.2. Glassy Carbon Coating

Glassy carbon seal coating protection was studied in FLiNaK salt. Possessing both glassy and ceramic properties along with the thermal advantages of graphite, glassy carbon offers benefits such as increased hardness and impermeability to gases and liquids [?]. The sample underwent a 2-day heat treatment at 500°C before and after filler impregnation [?]. An adhesion issue was found between the glassy carbon and graphite, possibly due to different dimensional changes caused by neutron irradiation. The results showed graphite expansion and glassy carbon layer shrinkage; this difference in irradiation-induced dimensional changes can lead to material cracking.

4.2.3. SiC Coating

SiC is well-regarded for its temperature resistance, low activation, and neutron transparency. SiC coatings have been utilized in nuclear applications with positive results. The test involved exposing modified IG-110 (M-IG-110) to FLiNaK for 24 hours at 650°C and 5 atm [?]. The weight change from salt permeation decreased from 14.8 wt% in IG-110 to 1.1 wt% in M-IG-110, showing modest improvement. It is worth noting that the chemical stability of SiC has not been determined for molten fluoride mixture applications, and salt purity appears crucial for achieving elevated performance [?].

Tab. 7. Coating Infiltration Decrease

Coating	Grade	Salt	Infiltration Decrease (%)	Reference
Glassy Carbon	IG-110	LiF-NaF-KF		
PyC	IG-110	LiF-NaF-KF		
SiC	M-IG-110	LiF-NaF-KF		

Fig. 4 [Figure 4: see original paper]. Comparative Decrease in Salt Infiltration for PyC Coated IG-110 and Uncoated IG-110

When designing different MSRs, studying graphite corrosion caused by the selected salt mixtures must be a key factor in development. This critical consideration will significantly contribute to reactor lifespan and help maintain lower maintenance costs.

5. CONCLUSION

This study conducted an analysis of various salts potentially applicable in Molten Salt Reactors (MSRs) using a methodology that involved careful salt selection, bibliographic survey of physical, chemical, and thermal properties, and comparative analysis of collected data. The results revealed that all salts share similar chemical compositions as fluorides with alkali metal counter ions. The melting temperature range of the salts proved adequate for MSR operation, remaining below the working temperature range of the reactors.

Furthermore, the density and heat capacity of the salts varied within ranges indicating potential for efficient heat transfer and stable reactor operation. Based on these findings, the analyzed salts exhibit promising characteristics for MSR applications, offering a viable alternative for safe, efficient, and sustainable nuclear energy generation.

However, detailed property analysis identified LiF-BeF_2 (67-33), LiF-NaF-BeF_2 (31-31-38), and LiF-NaF-KF (46.5-11.5-42.0) as the most desirable salts among those initially selected.

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

ACKNOWLEDGEMENTS

The authors gratefully acknowledge CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior), CNEN (Comissão Nacional de Energia Nuclear), CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico), FAPEMIG (Fundação de Amparo à Pesquisa do Estado de Minas Gerais), and other funding agencies for their financial support. The authors also thank the Departamento de Engenharia Nuclear for infrastructure and intellectual support, and the Universidade Federal de Minas Gerais for maintaining the Graduate Program in Nuclear Sciences and Techniques and the Department of Nuclear Engineering.

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