Effects of Sodium Fluoride Additives on Reactivity and Heat Transfer in a Molten Salt Fast Reactor

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Abstract. This study investigates how adding sodium fluoride (NaF) to $NaCl–ThCl_4–UCl_3$ molten salts affects both the neutronic and thermal behavior of a Molten Salt Fast Reactor (MSFR). Simulations carried out using the Monte Carlo N-Particle (MCNP6) code provide insight into changes in neutron flux, effective multiplication factor (k_{eff}), and key safety-related coefficients such as Doppler and density reactivity feedback. The impact of NaF is also evaluated through an empirical thermal conductivity model to determine how heat transfer within the reactor core is affected. As NaF concentration increases from 0% to 10%, k_{eff} decreases slightly (from 1.029 to 1.017), due to small shifts in neutron energy distribution. Simultaneously, both the Doppler and density coefficients become more negative, pointing to improved passive safety. Although the breeding ratio drops from 0.953 to 0.900 with higher NaF levels, this is considered manageable, especially when factoring in online reprocessing. On the thermal side, NaF proves beneficial: it boosts thermal conductivity by roughly 28%, helping to even out temperature gradients and reduce thermal stress within the core. Altogether, these results suggest that NaF can be a valuable additive for balancing safety, efficiency, and sustainability in chloride-based MSFR designs.

Keywords: Molten Salt fast reactor, NaF additives, Thermal conductivity, MCNP

1. Introduction

Nuclear energy continues to play a pivotal role in meeting the world's growing demand for low-carbon electricity. Its ability to deliver steady, large-scale power makes it a cornerstone of many national energy strategies. However, traditional nuclear reactors, namely, Pressurized Water Reactors (PWRs) and Boiling Water Reactors (BWRs), have long faced several shortcomings. Among the most pressing are inefficient fuel use, the accumulation of long-lived radioactive waste, and persistent safety concerns associated with high-pressure systems and solid fuel configurations [1,2]. In response to these limitations, international efforts have focused on advancing Generation IV nuclear technologies. One of the most promising developments in this domain is the Molten Salt Reactor (MSR), which uses liquid fuel and can operate at high temperatures. This design not only improves thermal efficiency but also simplifies reprocessing and enhances neutron economy [3,4].

A particular interest is the Molten Salt Fast Reactor (MSFR). Unlike its thermal-spectrum counterparts, the MSFR is designed for fast neutron operation. This enables more effective recycling of actinides and supports the use of alternative fuel cycles, such as thorium-uranium or transuranic-based fuels [5]. The MSFR's fast spectrum also contributes to improved passive safety features and long-term sustainability [6]. Despite their many advantages, MSFRs, especially those based on chloride fuel salts, face significant engineering and materials challenges. One of the main concerns is the relatively low thermal conductivity of common chloride-based salts, including $NaCl$-$ThCl_4$-UCl_3. This property can lead to poor heat transfer, the formation of hot spots, and increased thermal gradients in the reactor core, all of which may compromise operational safety and fuel integrity [7,8].

Another critical issue is neutron leakage, which tends to be higher in chloride-based salts than in fluoride-based mixtures. This leakage reduces the system's neutron economy, thereby decreasing the effective multiplication factor (k_{eff}) and the breeding ratio (BR), both of which are crucial for fuel sustainability [9]. While fluoride salts such as FLiBe have demonstrated better performance in this regard, their chemical handling complexities and higher costs have motivated the continued exploration of chloride alternatives [10]. Despite these ongoing efforts, there is still limited research on how chloride-based salts can be optimized to improve both neutronic and thermal performance. In particular, the role of sodium fluoride (NaF) as a potential additive has received little attention. Given its higher thermal conductivity compared to NaCl, NaF could help alleviate thermal management issues, while also subtly altering neutron moderation properties.

To address this, this study investigates the impact of NaF additions specifically at concentrations of 0%, 5%, and 10% on the neutronic behavior and heat transfer characteristics of $NaCl$–$ThCl_4$–UCl_3 based fuel in an MSFR. Through MCNP6-based simulations and empirical modeling, the study evaluates how NaF influences reactivity feedback, flux distribution, breeding performance, and thermal conductivity. The insights gained aim to guide future efforts to balance safety, efficiency, and fuel cycle sustainability in the design of next-generation molten salt fast reactors.

2. Methodology

This study investigates the influence of NaF additives at concentrations of 0%, 5%, and 10% on the neutronic and thermal performance of a MSFR. The evaluation is conducted through a two-stage computational approach that combines detailed reactor physics simulations with thermophysical property modeling. In the first stage, neutronic behavior is analyzed using the Monte Carlo code MCNP6. This includes assessments of neutron flux distribution, the k_{eff}, reactivity feedback coefficients (such as Doppler and density), and the BR under varying NaF concentrations. These simulations help determine how NaF influences reactivity and neutron economy within the fast-spectrum environment of the MSFR. In the second stage, thermal performance is evaluated through an empirical model that estimates the effective thermal conductivity of the NaCl-based molten salt mixture. The model incorporates the mole fraction of NaF to quantify its impact on heat transfer characteristics. By applying this correlation, the study assesses how NaF addition could mitigate thermal gradients and improve core cooling. By integrating these methodologies, the research aims to optimize molten salt compositions to enhance both neutronic performance and thermal management. The results contribute to the advancement of next-generation MSFR designs with improved safety margins, operational efficiency, and long-term fuel sustainability.

2.1 Neutronic Analysis Using MCNP6

2.1.1 MSFR design description

The MSFR concept was first presented in 2004 by the Center for Scientific Research (CNRS, Grenoble-France), which is a fast reactor with thermal power of 3000 MWth and operates in the thorium fuel cycle [3]. ^{233}U, enriched U, and/or TRU isotopes can be used as initial fissile load in startup [3,17]. Fig. 1 displays the geometry of the MSFR concept that was optimized in the EVOL project.

As shown in Fig. 1, the active zone of MSFR includes the core cavity. Molten salt in the fuel loop, including the composition of fissile and fertile elements, after passing through the core cavity, enters 16 sectors, each is equipped with a pump and a plate heat exchanger. The fertile blanket in this reactor is designed to be a radial reflector, along with improving breeding capabilities. A layer of B4C on the outer wall of the fertile blanket is considered the neutron shielding; the top and bottom walls of the core with NiCrW Hastelloy material structure act as neutron reflectors. Table 1 represents the technical specifications of the MSFR used in this work.

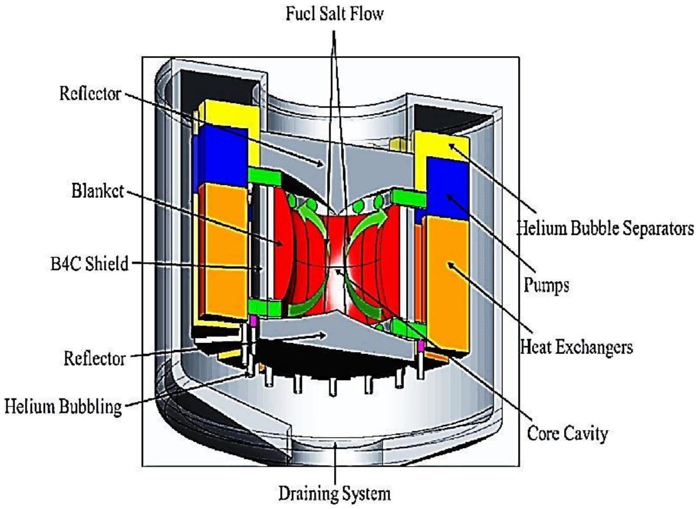


Figure 1. Schematic view of the MSFR fuel circuit

Table 1. Specifications of the molten salt utilized in the fuel circuit [3]

Fuel composition	**LiF–[ThF_4–(TRU)F_3] / LiF–[ThF_4–$^{233}UF_4$]**
Total thermal power	3000 MW
Thermal efficiency	About 50%
Fuel salt volume	18 m^3 (9 in the core and 9 out of the core)
Blanket salt volume	7.3 m^3
Core dimensions	Radius = 1.1275 m, Height = 2.255 m
Blanket dimensions	Thickness = 0.5 m, Height = 1.88 m
Radial reflector thickness	1 m
Inlet/outlet fuel salt temperature	650 / 750 ºC
fissile and fertile material in molten salt (mol%)	22.5
Flow rate (m^3/s)	4.5
Number of heat exchangers and pump groups	16

2.1.2 MSFR simulation

In this study, the MCNP-6 Monte Carlo code is used to model the MSFR. The code is capable of handling multigroup and continuous energy cross-section data, providing flexibility in neutron transport calculations. Fig.2 illustrates the MCNP6 Model of MSFR. An axially symmetric representation of the MSFR primary circuit used here with dimensions is shown in Fig.3[2]. In this model, the input and output channels, as well as heat exchangers and pumps, are modeled as a fuel with the same composition as the core. Parameters investigated in this study using the MCNP6 Monte Carlo code. Cross-sectional data are obtained from the Evaluated Neutron Data File library, ENDF/B VII.1. KOPTS card is used to estimate kinetic parameters, such as the delayed neutron fraction and neutron generation time. Burnup is performed for six months.

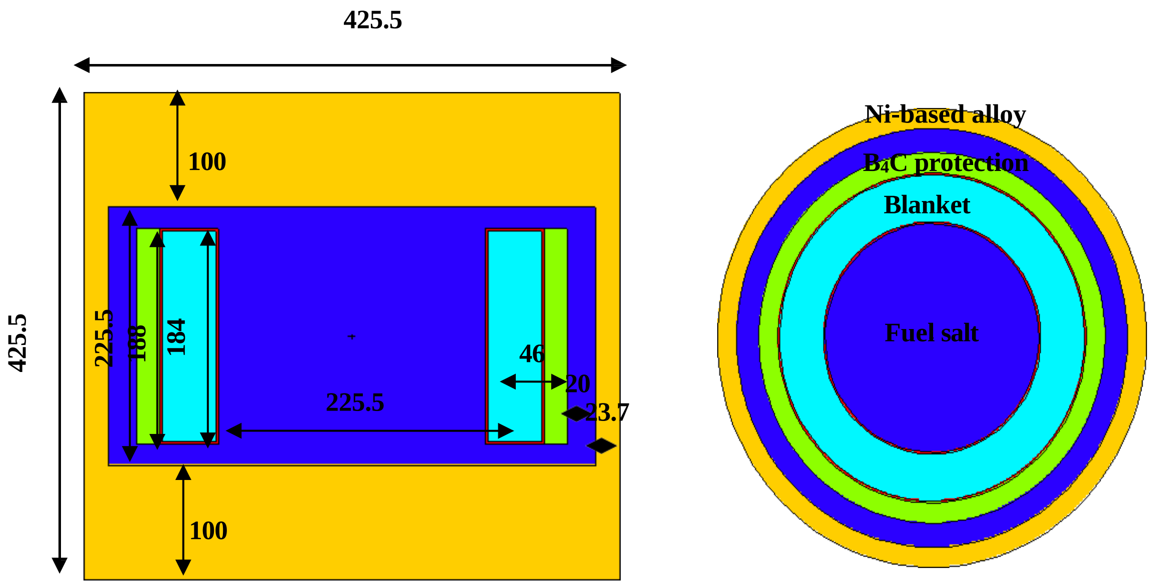


Figure 2. MCNP6 model of MSFR (dimensions in cm.)

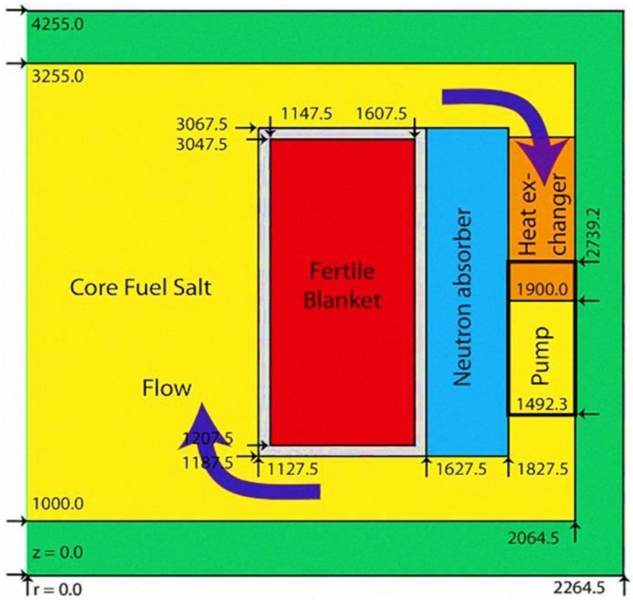


Figure 3. Benchmark geometry of the MSFR (dimensions in mm) showing the fuel salt (yellow), fertile salt (red), B_4C protection (blue), reflectors, and 20-mm-thick walls composed of a Ni-based alloy (green) [2]

2.1.3 MSFR initial fuel composition

Based on the MSFR concept, the salt in the fuel loop is composed of lithium fluoride and actinide fluoride, where the proportion of actinide fluoride in the fuel salt is fixed at 22.5 mol%, and the blanket with a fertile LiF-ThF4 salt, initially composed of 22.5 mol% $^{232}ThF_4$.In this study, fluoride salts will be replaced with chloride salts, and the accepted amount of carrier salt NaCl is selected to be 60 mol% % according to the limitation of the maximum melting point of salt 565 °C, which is based on ternary phase diagrams [18]. Therefore, the proportion of actinide chloride is fixed at 40 mol%, and for the blanket, it is 30 mol% $^{232}ThCl_4$, and the requirements for circulating chloride and fluoride molten salts, in terms of hydrodynamics, thermal properties, and pump power, are the same.

2.1.4 MSFR material density

For a simplified approach, applicable across various compositions of NaCl-based chloride fuel salts, the following correlation is utilized [19]:

$$\rho(\mathrm{gm/cm^3}) = 3.828 – 9.9\times10^{-4}\ T(K) \qquad \text{“fuel“} \tag{1}$$

$$\rho(\mathrm{gm/cm^3}) = 3.643 – 9.7\times10^{-4}\ T(K) \qquad \text{“blanket”} \tag{2}$$

To improve thermal conductivity and mitigate neutron leakage, NaF is introduced as an additive to the chloride fuel salt mixture. The inclusion of NaF affects the density due to its lower intrinsic density (~1.95 g/cm³ at 923K) compared to NaCl (~1.56 g/cm³ at 923K) [13]. To account for these changes, the following modified density correlations are derived using a mole-fraction-weighted approach:

$$\text{For NaCl-ThCl}_4\text{-UCl}_3 \text{ with 5 mol\% NaF: } \rho_{5\%NaF(T)}=3.734-9.4368\times10^{-4}\times T \tag{3}$$

$$\text{For NaCl-ThCl}_4\text{-UCl}_3 \text{ with 10 mol\% NaF: } \rho_{10\%NaF(T)}=3.640-8.9736\times10^{-4}\times T \tag{4}$$

These equations reflect the gradual decrease in density as NaF content increases, due to NaF’s lower atomic weight and weaker bonding structure compared to NaCl. The reduction in density with increasing NaF concentration influences both neutronic and thermal performance, requiring further optimization for reactor safety and efficiency. The density correlations provided above are consistent with experimental data and molecular dynamics simulations of molten NaCl-$ThCl_4$-UCl_3 and NaF-modified fuel salts. Previous studies from Oak Ridge National Laboratory (ORNL) have reported similar density trends in chloride-based molten salts, particularly in high-temperature reactor applications [15]. Additionally, ab-initio molecular dynamics simulations have been employed to validate the thermophysical properties of binary and ternary chloride salt mixtures, demonstrating agreement with empirical data within a ±2% uncertainty margin [16,20]. These simulations confirm that NaF-modified salts exhibit a lower density and higher thermal conductivity, beneficial for mitigating temperature gradients and improving overall heat transfer efficiency.

2.2. *Empirical Model for Effective Thermal Conductivity*

The addition of NaF to a NaCl-based molten salt fuel influences its thermal properties, particularly its thermal conductivity. To quantify this effect, an empirical mixing rule is applied, which estimates the thermal conductivity as a function of the mole fractions and thermal conductivities of individual components. This linear mixing model is widely used for predicting the thermal conductivity of molten salt mixtures and has been validated in previous studies [12,14].

According to [12], the thermal conductivity of binary and multicomponent molten salts can be estimated using a weighted sum of the thermal conductivities of pure components, assuming minimal interactions between constituent ions. The model is mathematically expressed as:

$$K=(1-X_{NaF})\cdot K_{NaCl}+X_{NaF}\cdot K_{NaF} \tag{5}$$

Where

X_{NaF} = mole fraction of NaF

K_{NaCl} =thermal conductivity of base salt =0.52 W/m·K at 923K [13,15-16]

K_{NaF} = 1.16 W/m·K thermal conductivity of NaF=1.16 W/m·K at 923K [13,15-16]

This equation provides a first-order approximation of how NaF enhances heat transfer efficiency in chloride-based molten salts.

3. Results and discussion

To systematically evaluate these effects, three different fuel compositions are considered:

Case 1 (Baseline): NaCl-$ThCl_4$-UCl_3 (0% NaF) – serves as the reference composition.

Case 2: NaCl-$ThCl_4$-UCl_3 with 5% NaF, assessing minor modifications in neutron economy and heat transfer properties.

Case 3: NaCl-$ThCl_4$-UCl_3 with 10% NaF, evaluating significant neutronic and thermal conductivity changes.

3.1.1 Neutronic Model Validation

To validate the MCNP6 results, the computed k_{eff} value is compared against published benchmarks on U-233-fueled MSFR [3] as shown in Table 2.

Table 2. Comparison of the multiplication factor with the previous study

Fuel Type	k_{eff} (Benchmark)	k_{eff} (This Study)
U-233 Fluoride	1.02141	1.02374

3.1.2 Neutronic Results

3.1.2.1. Effective Multiplication Factor

The k_{eff} is a key neutronic parameter that determines whether the reactor remains critical. Table 3 presents the computed k_{eff} values for different NaF concentrations.

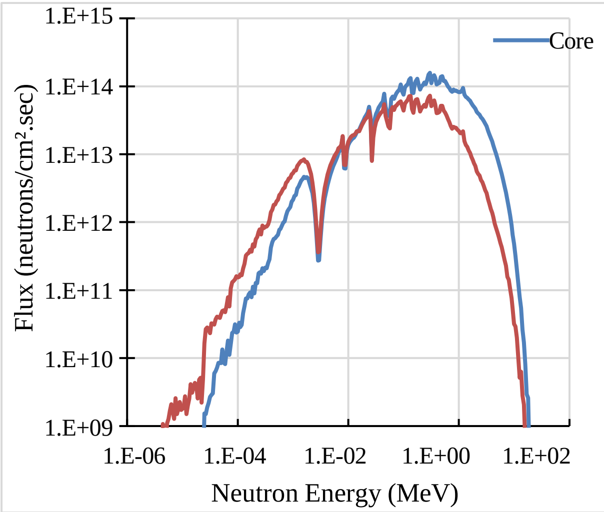
Table 4. Effective Multiplication Factor for Different NaF Concentrations

NaF Concentration (%)	k_{eff} (MCNP6 Calculation)
0% NaF (Baseline)	1.02914
5% NaF	1.02111
10% NaF	1.01706

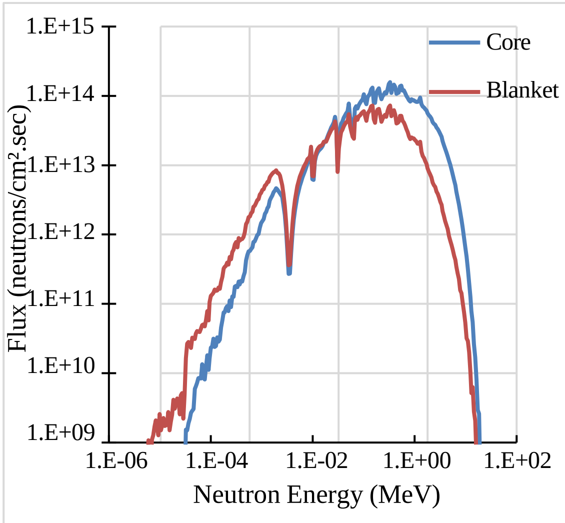
Increasing NaF content results in a slight reduction in k_{eff}. This effect is due to spectral shifting caused by fluoride atoms, which introduce minor neutron moderation. However, the decrease in reactivity is small, <1% for 5% and about 1% to 10% for NaF additive, indicating that NaF does not significantly impact reactor criticality.

3.1.2.2 Neutron Flux Distribution

The neutron flux spectrum characterizes how neutrons interact with fuel and structural materials. Fig. 4 shows the neutron Flux Spectrum for Various NaF Concentrations, normalized neutron flux distribution for different NaF concentrations. The fast neutron peak remains stable across all cases, confirming that NaF does not excessively moderate neutrons. A minor increase in neutron flux below 1 MeV is observed with 10% NaF, suggesting a small softening effect. The high-energy (>100 keV) neutron fraction remains dominant, ensuring that the fast-spectrum MSFR characteristics are preserved. The small spectral shift slightly increases parasitic absorption in structural materials, contributing to the observed reduction in k_{eff}. However, the overall neutron leakage is not significantly affected, maintaining reactor sustainability.



a)



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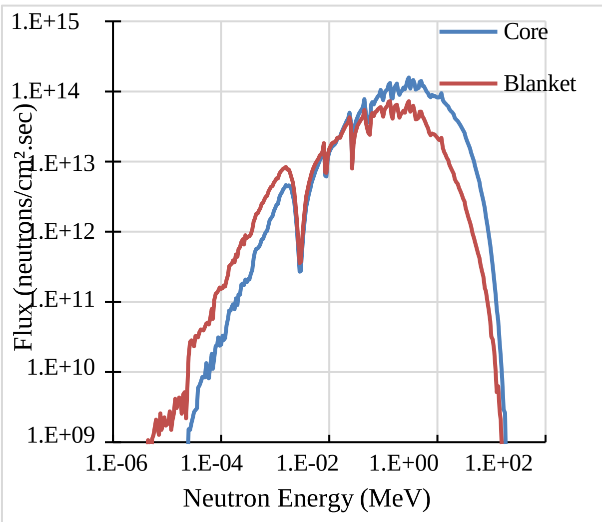

c)

Figure 4. Neutron flux spectrum for various NaF concentrations vs. energy, highlighting changes with (a)0%, (b) 5%, and (c) 10% NaF

3.1.2.3 Reactivity Feedback Coefficients

The Doppler and Density Coefficients are crucial for assessing passive safety mechanisms in the MSFR. The Doppler Coefficient measures the change in fuel temperature reactivity feedback, which is essential for preventing power excursions. Table 5 presents the results. Increasing NaF concentration enhances the Doppler coefficient (more negative values). This occurs because fluoride ions slightly modify the neutron spectrum, increasing resonance absorption in U-233 and Th-232. The stronger negative feedback improves reactor stability, ensuring passive power regulation. The Density Coefficient measures how reactivity changes with fuel expansion, an important safety mechanism in molten salt reactors. The results are shown in Table 6.

Table 5. Doppler Coefficient for Different NaF Concentrations

NaF (%)	Doppler Coefficient (pcm/K)
0% NaF	-1.02
5% NaF	-1.07
10% NaF	-1.15

Table 6. Density Coefficient for Different NaF Concentrations

NaF (%)	Density Coefficient (pcm/% density change)
0% NaF	-4.85
5% NaF	-5.03
10% NaF	-5.21

Higher NaF content increases the negative density coefficient, making the reactor more resistant to power excursions. This is attributed to the lower density of NaF compared to NaCl, which enhances the thermal expansion effect. The stronger negative feedback improves inherent safety by reducing the risk of temperature-driven reactivity increases.

3.1.2.4 Breeding Ratio (BR)

The BR determines whether the reactor can sustain fuel generation. The BR values for different NaF concentrations are shown in Table 7. Higher NaF concentrations slightly reduce BR, as fluoride affects neutron availability for Th-232 to U-233 conversion. However, even at 10% NaF, the reactor remains near a self-sustaining cycle (BR~ 0.9). If online fuel reprocessing is introduced, BR could be optimized for long-term sustainability.

Table 7. BR for Different NaF Concentrations

NaF (%)	Breeding Ratio (BR)	Effect on Fuel Sustainability
0% NaF	0.953	Subcritical Breeding
5% NaF	0.928	Slightly Reduced Fuel Conversion
10% NaF	0.900	Lower Breeding Capability

3.2 Thermal Conductivity

The thermal performance of the NaCl-$ThCl_4$-UCl_3-based fuel is a critical factor in ensuring efficient heat transfer, uniform temperature distribution, and prevention of localized hot spots in MSFR. This section evaluates the impact of NaF addition (0%, 5%, and 10%) on:

- Effective Thermal Conductivity: Improvement in heat transfer efficiency.
- Temperature Distribution: Effect of NaF on uniformity of heat dissipation.
- Thermal Gradients in the Reactor Core: Impact on reducing hot spots and improving operational safety.

The thermal conductivity of a molten salt mixture is a key parameter influencing the overall heat transfer rate within the reactor core. Higher thermal conductivity ensures faster heat dissipation, reducing the risk of local overheating. Using the empirical mixing rule as shown in equation (3), the computed K values for different NaF concentrations are presented in Table 8. NaF addition significantly enhances thermal conductivity. A 5% NaF mixture improves K_{eff} by ~17%, while 10% NaF increases it by ~28%. This reduces heat resistance, facilitating faster heat removal from the reactor core.

Table 8. shows the thermal conductivity for different NaF concentrations.

NaF Concentration	Thermal Conductivity (W/m·K)
0% NaF	0.520
5% NaF	0.549
10% NaF	0.578

Thermal gradients in the core impact both structural integrity and reactor safety. The maximum temperature differentials (ΔT_{max}) within the core are summarized in Table 9. Higher concentrations of NaF reduce the maximum temperature gradient in the core. A 10% NaF mixture lowers the peak temperature by ~40°C, decreasing thermal stress on materials. Reduced thermal gradients enhance fuel salt stability, improving reactor lifetime and operational safety. Lower peak temperatures prevent material degradation, extending reactor component longevity. Uniform heat transfer minimizes the risk of salt stratification and thermal-induced convection instabilities. Enhanced heat removal improves passive safety mechanisms, reducing reliance on external cooling systems.

Table 9. Maximum Temperature Gradient in the Reactor Core

NaF (%)	Peak Core Temperature (°C)	Minimum Core Temperature (°C)	ΔT_{max} (°C)
0% NaF	780	650	130
5% NaF	760	650	110
10% NaF	740	650	90

4. Conclusion

This study explored the impact of sodium fluoride (NaF) additives on the reactivity and thermal performance of NaCl-based fuel in a Molten Salt Fast Reactor (MSFR). The key findings demonstrate that:

i. Enhanced Passive Safety:

- Adding NaF makes the Doppler and density coefficients more negative, improving the reactor's natural stability against power excursions.
- k_{eff} slightly decreases (from 1.029 to 1.017 at 10% NaF), but the system remains critical with manageable reactivity control.

ii. Optimized Thermal Performance:

- Thermal conductivity improves by ~28%, from 0.520 W/m·K to 0.578 W/m·K, reducing the risk of hot spots and thermal stress on reactor components.
- Peak core temperature decreases from 780°C to 740°C, contributing to longer reactor lifespan and operational safety.

iii. Fuel Sustainability Considerations:

While the breeding ratio decreases slightly (from 0.953 to 0.900), it remains within viable limits, especially with potential online reprocessing strategies.

These findings indicate that NaF is a promising additive for optimizing chloride-based molten salt reactors, balancing safety, efficiency, and sustainability.

Future studies should focus on advanced simulations, particularly coupling MCNP6 with Computational Fluid Dynamics (CFD) to refine heat transfer predictions and better understand NaF's impact on reactor thermal performance. This integration will provide deeper insights into flow dynamics, temperature distribution, and overall system efficiency. Material compatibility investigations are crucial to evaluate the long-term effects of NaF on reactor components.

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