The Radiative Heat Transfer Properties of Molten Salts and Their Relevance to the Design of Advanced Reactors

DISSERTATION

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By

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Abstract

Molten salts, such as the fluoride salt eutectic LiF-NaF-KF (FLiNaK) or the transition metal fluoride salt KF-ZrF₄, have been proposed as coolants for numerous advanced reactor concepts. These reactors are designed to operate at high temperatures where radiative heat transfer may play a significant role. If this is the case, the radiative heat transfer properties of the salt coolants are required to be known for heat transfer calculations to be performed accurately. Chapter 1 describes the existing literature and experimental efforts pertaining to radiative heat transfer in molten salts. The physics governing photon absorption by halide salts is discussed first, followed by a more specific description of experimental results pertaining to salts of interest. The phonon absorption edge in LiF-based salts such as FLiNaK is estimated and the technique described for potential use in other salts. A description is given of various spectral measurement techniques which might plausibly be employed in the present effort, as well as an argument for the use of integral techniques. Chapter 2 discusses the mathematical treatments required to approximate and solve for the radiative flux in participating materials. The differential approximation and the exact solutions to the radiative flux are examined, and methods are given to solve radiative and energy equations simultaneously. A coupled solution is used to examine radiative heat transfer to molten salt coolants. A map is generated of pipe diameters, wall temperatures,
and average absorption coefficients where radiative heat transfer will increase expected heat transfer by more than 10% compared to convective methods alone. Chapter 3 presents the design and analysis of the Integral Radiative Absorption Chamber (IRAC). The IRAC employs an integral technique for the measurement of the entire electromagnetic spectrum, negating some of the challenges associated with the methods discussed in Chapter 1 at the loss of spectral information. The IRAC design is validated by modeling the experiment in Fluent which shows that the IRAC should be capable of measuring absorption coefficients within 10%. Chapter 4 contains a parallel effort to experimental techniques, whereby information on absorption in salts is pursued using the Density Functional Theory code VASP. Photon-electron interactions are studied in pure salts such as LiF and are shown to be broadly transparent. Transition metal Fluoride salts such as KF-ZrF$_4$ are shown to be broadly opaque. The addition of small amounts of transition metal impurities is studied by insertion of Chromium into the salt mixtures, which causes otherwise transparent salts to exhibit absorption coefficients significant to heat transfer. The spectral absorption coefficient for FLiNaK with Chromium is presented as is the average absorption coefficient as a function of impurity concentration. Chapter 5 discusses experimental efforts undertaken at The Ohio State University. Challenges with the constructed experimental apparatus are discussed and suggestions for future improvement on the technique are included. Finally, Chapter 6 contains broad conclusions pertaining to radiative transfer in advanced reactors.
Dedication

This document is dedicated to the American taxpayers who have generously funded my research to this point.

It is a debt that I do not take for granted,

and a debt that I intend to repay.
Acknowledgments

While rowing down a river, it’s sometimes easy to lose sight of the current behind you. I want to take this moment to acknowledge and thank the largely unseen forces which helped to ease my progress in life; acknowledge the societal and cultural advantages I earned solely by product of my birth. I am not unaware of how privileged and fortunate my journey has been and continues to be, nor am I unaware of how many others my journey is inaccessible to. That knowledge does not absolve in any way my responsibility or desire to make this a better world for all.

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Publications

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Chapter 1. Introduction and Background

From the earliest days of nuclear power, water has been the primary-side coolant used in the overwhelming majority of nuclear reactors. Its abundance, familiarity, and nuclear moderating properties have made it the coolant of choice during the past six decades of reactor design and construction, going back to the plutonium production reactors at Hanford. However, water has significant downsides in terms of thermal-hydraulics, safety, and corrosion. For the next generation of reactors, there has been growing interest in the use of molten-salts as coolants for nuclear reactors. Molten salt compounds composed of mixtures of alkali-halide salts are chemically stable, have low vapor pressures, high densities and good thermal conductivity. With the right mixture of constituents, they can be designed to thermalize neutrons or be configured for use in fast reactors. Perhaps most importantly, molten salts are single phase throughout a wide range of operating temperatures. Avoiding the instabilities associated with boiling flow and the accumulation of low density vapor presents a powerful safety case for the use of molten salts as coolants in reactors.

Unfortunately, there is limited experience with molten salts, which has hindered their adoption and acceptance. In addition, these materials have not been fully investigated
in terms of their physical properties, and their optical transmission characteristics remain largely unknown. The lack of research in molten-salt radiation heat transfer properties is not without reason, as water-cooled reactors operate at relatively low temperature and so thermal radiation heat transfer is not as important. Proposals for early molten salt cooled reactors do not envision an extremely high operating temperature, and as such radiation heat transfer is often considered insignificant under normal operating conditions. However, without knowing the absorption properties of these materials and how the absorption properties are affected by reactor conditions, it cannot be said with confidence that radiation heat transfer can be ignored. Additionally, the effect of radiation heat transfer under accident conditions could prove to be significant, and corrosion products in the salt may increase absorption to the point where radiation heat transfer does become significant.

Projecting further to an envisioned future class of advanced, very-high temperature reactors, radiation heat transfer will certainly be relevant. Developing a knowledge base into the heat transfer properties of molten salts will thus be important for the development of advanced reactor technology and for accurately modeling and designing advanced reactor components.

Such a reactor design inspired the present research. Specifically, a research program at The Ohio State University, which was funded through the NASA-Steckler Space Research Grant, investigated the potential for molten salt fueled reactors to serve as highly power dense electricity sources for future manned space missions. During the course of
that investigation, it was determined that the absorption coefficient of molten salts strongly
determines the performance of this class of reactor, and the absorption coefficient was
largely unknown. [1] If one reactors design performance was strongly dependent on
characterizing radiation heat transfer, it is possible that this is true for other designs as well.

1.1. Radiation Heat Transfer in Advanced Reactors

Radiation heat transfer has been traditionally ignored in the design of advanced
reactors, partly for lack of data and partly for the lower planned temperatures of first
generation molten salt reactors. The interest in radiation heat transfer is somewhat recent.
In 2002, in a paper on potential advanced reactor concepts, Forsberg [2] discusses the
potential for radiation heat transfer to be a significant factor in the design of advanced
reactors, concluding that molten salt “characteristics imply that above 700°C, radiation
transfer begins to become an important mechanism to enhance heat transfer.”

Several years later, Bardet and Peterson [3] studied the design of experiments for
advanced reactors using helium and molten-salt coolants. They found that “liquid salt
applications involve temperatures where thermal radiation heat transfer has the potential to
be significant. Therefore, in all cases the potential effects of thermal radiation must be
considered in the design of experiments. […] Unfortunately, data and modeling for the
effects of infrared absorption on liquid salt heat transfer are not well developed.”

In 2009, Amborsek et al published a summary on the state of knowledge of heat
transfer in FLiNaK [4]. In order to quantify the effect of radiation heat transfer on the
overall heat transfer coefficient, they performed a simple analysis treating radiation as a zero-dimensional transfer between the walls and a source with a given opacity and thickness. Their model, which is discussed in somewhat more detail in Chapter 2, attempted to map the temperatures and flow regimes for which radiation heat transfer is significant. However, due to a lack of data and a curious choice of heat transfer correlation, it is hard to draw specific conclusions from their study. However, their results indicated that for higher temperatures, larger pipe geometries, and lower Reynolds numbers, radiation heat transfer begins to become a significant mechanism for heat transfer to the fluid. Ambrosek concluded “Radiation heat transfer in high-temperature applications is not negligible as the flow moves to the laminar regime. The exact absorption coefficient of the salt is not known.” Both Peterson and Ambrosek identified uncertainty in the absorption coefficient as worthwhile topic of future research.

1.2. Background Physics of Radiation Attenuation

The first area of interest is the measurement of radiation heat transfer properties, mainly the absorption (extinction) coefficient in molten salts. There is little data available as to the absorption coefficients in proposed coolant salts and there has not been a systematic approach for measuring these coefficients in a manner that is relevant for high-fidelity thermodynamic studies. Unlike liquid metals, which have a consistent and strong absorption coefficient across the electromagnetic spectrum, molten salts are characterized by strong absorption of electromagnetic radiation in some spectral regions and high
transmission in others. Previous studies have investigated a limited subset of regimes and temperatures from which it was determined that radiation heat transfer is not relevant in the cases they were looking at. However, these studies did not have good values for the absorption coefficients in molten salts and so their results are somewhat speculative. By more thoroughly investigating the absorption coefficient of molten salts, radiation heat transfer can be considered without making rough assumptions.

The attenuation coefficient in a participating medium is heuristically defined as the rate at which the intensity of radiation is reduced as it travels along a path. There are two effects that contribute to the attenuation of a ray of energy along a pathline: 1) the energy is absorbed by the material, or 2) it is elastically scattered. The attenuation coefficient accounts for these two effects. For the present research, scattering is expected to be an insignificant factor to energy transfer, and so the attenuation coefficient is assumed to be composed solely of the absorption coefficient. This assumption is justified by the fact that radiation is scattered at high energy by interaction with outer shell electrons, and this process drops off rapidly with wavelength. Scattering also occurs by discrete changes in the index of refraction within a material, but without dissolved or suspended particles, that situation is not present in a molten salt reactor.

1.3. General Behavior of Absorption Coefficients in Halide Salts

Absorption of electromagnetic radiation by halide salts is characterized by three broad phenomenological regions of the electromagnetic spectrum. In the first region, that
of short wavelengths, EM radiation can be captured by promoting electrons from orbitals into higher energy states in the valence band or by promoting electrons into the conduction band. These processes contribute to a high absorption of EM radiation in the high frequency, low wavelength range. This is due to the high band gap energy of most salts. In metals, there is no meaningful band-gap and electrons can be promoted within the conduction band at nearly arbitrary energies. Thus, metals are strongly absorptive and have mean free paths for radiation on the order of angstroms, meaning radiation heat transfer is largely irrelevant for macroscopic quantities of liquid metals. The addition of metal impurities in the salt allows for absorption by electron-photon interactions at lower energies than is available to the pure salt. This will be discussed in Chapter 4.

The second region for pure salts occurs for intermediate energies and is characterized broadly by low absorption, as photons are too low energy to excite electrons across the band gap and too high energy to be captured by processes of low energy absorption. Absorption in this region is dominated by impurity and scattering losses. [5]

The third region occurs for lower energies. In this region, photons can be absorbed by conversion to phonons that are characteristic of vibrational modes in the material. These phonons can be produced by vibrational modes of the long-range lattice or by local vibration and short range ordering. At some wavelength, materials exhibit a strong absorption peak caused by the correspondence of photon energies with characteristic resonant energies available in the material.
Lithium Fluoride, a constituent of proposed coolant salts like FLiBe and FLiNaK, is used in crystalline form as an optical glass. In this form its optical properties have been well documented. The transmission through a 2mm slab of crystalline LiF can be seen in Figure 1. Figure 1 demonstrates the above discussed trends well, with high absorption, or low transmission, up to about 150nm, followed by broad transmission through 7um, followed at lower energies by strong absorption.

![Transmission curve for Lithium Fluoride Glass](image)

**Figure 1. Transmission curve for Lithium Fluoride Glass**

The transmission region for transparent materials exists for a wavelength region that is bounded by four effects. These effects (Urbach absorption, Brillouin scattering, and Raleigh Scatter at short wavelengths and multi-phonon absorption at long wavelengths) contribute to low transmission in the high energy region, tapering off into the transmission region which begins at wavelengths greater than that corresponding to the bandgap for the material (called the band edge). [5] For wavelengths that are greater than the band edge,
attenuation occurs as a consequence of a scattering term with a $\lambda^{-4}$ dependence typically attributed to Rayleigh scattering. Rayleigh Scatter tails off into middle energies. The middle region is labeled impurity-dominated plateau in Figure 2. Multi-phonon absorption starts to contribute to attenuation in the longer wavelength portion of the middle energy region until the phonon absorption peak is reached. This peak is constituted from superposition of the fundamental phonon peaks. This region is the “Intrinsic Lattice Tail” in Figure 2. In the energies between the Urbach and Lattice tails, absorption is primarily from absorption by impurities in the medium, which can have absorption properties different from those of the carrier material.

![Graphical representation of absorption vs. wavelength](image)

**Figure 2. Physical Effects Governing Absorption in Halide Salts**

1.3.1. *Urbach Absorption and Brillouin Scattering*
Urbach Absorption and Brillouin Scattering are two processes that contribute to attenuation of light in halide salts. These processes involve the interaction of photons with the outer shell electrons of atoms within the salt. However, because these effects occur at high photon energies, which are not seen at significant intensities under most conditions, it is not relevant to calculations of heat transfer in reactor applications.

1.3.2. Rayleigh Scattering

Rayleigh Scattering is a phenomenon of elastic scatter of photons traveling through a medium. It contributes to the attenuation coefficient by diverting light from a beam, but since it is an elastic process, it does not directly constitute an energy transfer to the medium. The cross section for Rayleigh scatter typically varies with intensity as the fourth power of wavenumber. Typically, Rayleigh scatter cannot be detected above 1-2 μm. It is difficult to distinguish between absorption and scattering using most experimental techniques, but fortunately the heat transfer in this region is low for most terrestrial reactor considerations.

1.3.3. Multi-phonon Absorption

N-phonon absorption constitutes the major absorption mechanism for binary salt systems in the infra-red portion of the electromagnetic spectrum [5]. It occurs when a vibrational mode in a medium corresponds to the energy of an incoming photon, allowing the entire photon to be absorbed and converted to vibrational energy of a material, which is effectively heat. These vibrational modes are dominated by fundamental vibrations, but lower intensity, high energy modes exist and are typically seen to overlap with the Rayleigh
scattering tail as can be seen in Figure 3 for silica, a representative material which exhibits these general trends.

![Figure 3. Absorption Effects in Silica Glass](image)

Figure 3. Absorption Effects in Silica Glass

The dominant vibrational modes are typically clustered in a range of energies; therefore the region of multi-phonon absorption is typically referred to as an absorption plateau or absorption band, despite being composed of finite and discrete peaks.

For a linear diatomic molecule of masses $m_1$ and $m_2$, the fundamental vibrational frequency $\omega_0$ is defined by the Szigeti relation, Equation (1.1), where $f$ is the force constant, and $\mu$ is the reduced mass. [2]

$$\omega_0 = \sqrt{\frac{f}{\mu}} \quad (1.1)$$

here
The reduced mass is easy to calculate, but the force constant is a product of the exact lattice structure and valence state of the constituent atoms. Previous investigation [6] of the lattice absorption edge in molten LiF found it to be at a wavelength of roughly 5.9 μm, which corresponds closely to that of solid LiF glass. Working backwards to estimate the force constant, and then using that to calculate the absorption edge for NaF and KF, predicts that the absorption edges will be at approximately 9μm and 12μm, respectively. Although the force constant will be different for the different atoms, Bendow [5] indicates that as a general trend, \( f \) will be smaller for heavier atoms, making the likely absorption edges for NaF and KF at even lower energy, (i.e. longer wavelength). It is plausible that different fundamental vibrational modes could exist for multi-component ionic melts than for single component systems due to the possibility of vibrations existing between the various cations in the melt. Typically, however, the lightest component of multi-component melts determines the structure of the absorption edge. [7] As such, it is likely that the absorption edge for FLiNaK will be dominated by LiF.

Experimentation and theory with multiple salts has shown that there is a temperature dependence for the absorption edge. Higher temperature of the medium shifts the absorption edge into higher energy regions. However, that shift is small and more importantly, it has been shown to be minimally affected by the transition from liquid to
solid medium after accounting for change in number density caused by melting. This was first demonstrated by AJ Barker and is demonstrated in Figure 4 for LiF. [8]

**Figure 4. Phonon-Edge Absorption Coefficient for Lithium Fluoride, Melting Temperature 1115K.**

1.4. **Estimating the Absorption Edge in LiF-based salts**

Although there exist some data for absorption coefficients in salts or salt constituents, reliable data performed with heat transfer in mind are nearly nonexistent. In order to perform initial simulations to estimate the effect of radiation heat transfer, the available literature was examined. Fortunately, the same halide salts that compose
candidate salts for advanced reactors have been studied as optical materials for high intensity laser systems with energy ranges within the infrared. This has led to occasional research on the spectral absorption coefficients of some candidate salts. H. H. Li [7] performed a wide ranging study of available literature and generated a fitting function and coefficients for the phonon absorption edges for various halide salts, including LiF and NaF. The reported correlation from Li is given below as Equation (1.3).

\[
\kappa(\lambda, T) = \kappa_0 \exp \left[ -A \left( \frac{C}{\lambda} + B \right) \left( C - \log(T) \right) \right]
\]

(1.3)

where \( \lambda \) is the wavelength in centimeters and \( T \) is the temperature in Kelvin. For LiF, the coefficients reported were

\[
\kappa_0 = 10^{4.512} \text{ cm}^{-1}; \ A = 0.00224 \text{ cm}; \ B = 44.1 \text{ cm}^{-1}; \ C = 5.434
\]

For NaF

\[
\kappa_0 = 10^{5.480} \text{ cm}^{-1}; \ A = 0.00437 \text{ cm}; \ B = 108.4 \text{ cm}^{-1}; \ C = 5.434
\]

The two absorption curves for the salt are plotted below for a temperature of 800K, a temperature just above the melting point of the salt and a proxy for the lowest operating temperature of an advanced reactor.
Figure 5. Phonon Absorption Edge for pure Lithium Fluoride and Sodium Fluoride at 800K, Li Correlation

Although data is not available to determine coefficients for KF, the third component of FLiNaK, it is reasonable to assume that its form will be similar to the form for LiF and NaF. All three are halide salts with a Fluorine cation and so KF should not exhibit radically different behavior, as the physics governing the absorption edge are the same for the different salts. Examination of Equation (1.1) and (1.2) make it clear that the absorption edge for KF will occur at a longer wavelength than that for LiF or NaF, likely occurring at a wavelength greater than 12µm. Even without accurate knowledge of the absorption coefficient of KF, by taking into account the information that is relevant for heat transfer
properties, the absorption data that is available is enough to make a reasonable estimate of the absorption coefficient for FLiNaK, which follows.

From a heat transfer perspective, when the non-dimensional product of absorption coefficient and a relevant length scale (the product is referred to as optical thickness) exceeds a certain value, the actual value becomes somewhat irrelevant. For example, optical thicknesses of 100 and 1000 result in nearly identical heat flux and temperature distributions if all else is held constant. [9] Radiation heat transfer in wavelength regimes where the optical thickness exceeds 100 can be treated as effectively opaque and the absorption coefficient can be capped at a somewhat arbitrary value. Additionally, the intensity of thermal energy decreases at very long wavelengths and is not significant for heat transfer calculations. From all the above, it can be more confidently stated that the intrinsic absorption of thermal radiation in FLiNaK will be dominated by phonon absorption by its least massive constituent (i.e. LiF); however, the additional constituents will still play a role in that their presences decreases the number density of Li-F bonds in the salt.

To properly account for the presence of the other salts, a mixture averaging methods is that the individual anion-cation bond vibrations are the highest energy phonon. The probability of a photon interacting with one of these bonds is proportional the number density of bonds present in a material. Therefore, the mixture absorption coefficient is
calculated by number density weighting the individual absorption curves. The weighting is specifically defined as follows,

\[ \kappa_m = \sum_x \frac{N_x^m}{N_T^m} \frac{\rho_m}{\rho_x} \frac{M_x}{M_m} \kappa_x \]  

(1.4)

where the ratio \( \frac{N_x^m}{N_T^m} \) is the molar fraction of salt \( x \) in the FLiNaK mixture \( m \), \( \frac{\rho_m}{\rho_x} \), is the ratio of the mass density of FLiNaK to salt \( x \) and \( \frac{M_x}{M_m} \) is the ratio of the molar mass of salt \( x \) to FLiNaK. \( \alpha_x \) is the absorption coefficient of salt \( x \). Although data is lacking for KF, the absorption coefficient for KF was assumed to be zero, because as discussed above, the multi-phonon absorption edge for KF occurs at a longer wavelength than for LiF or NaF. The FLiNaK densities were taken from the Engineering Database of Liquid Salt Thermophysical and Thermochemical Properties [10] and absorption coefficients for LiF and NaF from Li [7]. Plotting the results of equation (1.4) gives the absorption coefficient for multi-phonon absorption for pure FLiNaK.
Figure 6. Phonon Absorption Edge for FLiNaK at 800K

With a plausible estimate of the absorption coefficient for multi-phonon absorption in FLiNaK, in hand it is possible to generate the inputs for computational heat transfer codes. The tail of the peak is broad enough that it is not acceptable to use a two-region model, with a transparent region at shorter wavelengths and an opaque region at longer. The salt curve must be approximated, as the bulk of heat transfer occurs within the spectral region where the salt is neither opaque nor transparent. Computations involving radiative heat transfer are usually performed by dividing the spectral energy distribution into various
energy bands within which spectral properties are kept constant. To do this, one can define an average absorption coefficient for the spectral region $n$.

$$\bar{\kappa}_n = \frac{\int_{\lambda_n}^{\lambda'_n} \kappa'(\lambda) I_{b\lambda} d\lambda}{\int_{\lambda_n}^{\lambda'_n} I_{b\lambda} d\lambda}$$ (1.5)

Here $\bar{\kappa}_n$ is the absorption coefficient in energy region $n$, $\kappa'(\lambda)$ is the spectrally varying absorption distribution, while $\lambda_n$ and $\lambda_{n+1}$ are the wavelength at which the $n$th and $(n+1)$th energy regions begin. $I_{b\lambda}$ is the blackbody energy distribution at a reference temperature. Performing the averaging using a reference blackbody at 800K, and for example, using 4 gray energy bins is shown in Figure 7. Averaging of FLiNaK Absorption Edge into Four Absorption Bands Figure 7.

**Figure 7. Averaging of FLiNaK Absorption Edge into Four Absorption Bands**
In the extrinsically dominated absorption region, the region from roughly 1μm to 5μm, the absorption coefficient will be dominated by impurities. As has been discussed, extrinsic absorption will likely represent a significant effect on the heat transfer properties of the salt, but without data on extrinsic absorption, the minimum value of \( \kappa' (\lambda) = 1 \text{m}^{-1} \) is used as an absorption coefficient based on previous estimates. Additionally, the maximum value of \( \kappa' (\lambda) \) is set at 1000\text{m}^{-1} based on experimentation as a value which is high enough to capture the effects of opaque radiation heat transfer, especially considering that for wavelengths much greater than those corresponding to the multi-phonon absorption edge of FLiNaK, energy emitted in the region is small.

1.5. Previous Estimates of Absorption Coefficient

One bounding value for the absorption coefficient comes from an industrial data for pure LiF glass. Accounting for reflective losses, the measured absorption coefficient is found to be 5.9×10^{-5} \text{m}^{-1}, or a mean free path on the order of kilometers. Given the lack of other data, many people have treated the absorption coefficient for FLiNaK and other halide salt melts as purely transparent. However, this is the minimum absorption coefficient anywhere in the spectrum, occurring only at the wavelength of 4.3μm. This value is the wavelength of minimum absorption in ultra-pure LiF glass and is not directly relevant to heat transfer calculations. The average absorption coefficient would be significantly larger, depending on the wavelength interval it is averaged over. Additionally, the absorption coefficient for molten salt mixtures will be higher if heavier elements such as impurities
are in the salt. As discussed previously, absorption in the spectral region between the photo-electron and photo-phonon region is dominated by impurities.

In a paper on heat transfer in inorganic compounds, Ewing [11] estimated the value of the absorption coefficient in FLiNaK by indirect methods and determined the value was between 6 m\(^{-1}\) and 20 m\(^{-1}\), or a mean free path between 5 cm and 16 cm. The method employed to estimate the absorption coefficient contained considerable sources of potential error, but serves as an argument that the actual value of the absorption coefficient in FLiNaK is in a relevant range. Ewing’s experiment was performed to determine the molecular thermal conductivities of the salts, which at that time were largely unknown. Ewing’s experiment consisted of a heated Inconel rod with a central axial filling tube descending from a reservoir into a 1.62 inch internal diameter by 1 inch length sample chamber. The sample chamber was situated above an Inconel rod, with the bottom of the rod cooled by an external heat sink. The upper Inconel bar was heated, while salt was in the chamber and the thermal gradient on the lower rod was measured to determine the total heat flow through the sample. Compensating heaters were used in order to flatten the radial thermal gradients. The experiments were performed at a range of temperatures, which were high enough that radiation heat transfer between the boundaries couldn’t be ignored. Ewing assumed that blackbody energy emitted by the upper wall would be weakly attenuated by the salt, and that the heat flow from the upper plate to the lower plate could be reasonably approximated by
\[ q_{1 \rightarrow 2} = \varepsilon_1 A_1 \sigma T_1^4 e^{-\kappa(z_1 - z_2)} \] (1.6)

where the last term in Equation (1.6) is the optically thin approximation for the radiation heat flux. Similarly, the heat flow from the lower plate to the upper plate could be approximated by

\[ q_{2 \rightarrow 1} = \varepsilon_2 A_2 \sigma T_2^4 e^{-\kappa(z_2 - z_1)} \] (1.7)

Additionally, heat is transferred by molecular conduction through the salt, which at steady state in the absence of radiation to distort the temperature profile is given by

\[ q_m = k_m A \frac{T_1 - T_2}{z_1 - z_2} = k_m A \frac{\Delta T}{\Delta z} \] (1.8)

The total heat transfer rate, measured by the calibrated lower rod, can be decomposed into a portion that is transferred by molecular conduction and a portion that is transferred by radiation.

\[ q_t = q_m + q_{r, 1 \rightarrow 2} - q_{r, 2 \rightarrow 1} \] (1.9)

Dividing through by area and thermal gradient converts the total heat transfer into an effective thermal conductivity. If the upper and lower surfaces are assumed to be black, giving an upper estimate for the amount of radiation heat transfer, then the previous expressions can be combined to determine an effective conductivity.

\[ k_e = \frac{q_e \Delta z}{A \Delta T} \]
\[ = k_m + e^{-\kappa \Delta z} \frac{\Delta z \sigma(T_1^4 - T_2^4)}{\Delta T} \] (1.10)
Plotting the measured data for $\hat{k}_e$ against the fractional term on the right hand side of Equation (1.10) should yield a straight line with the intercept equal to the molecular conductivity, the value of which Ewing was after. However, useful to the present experimental effort, is that the slope of that line would be directly related to the optical thickness of the chamber, from which the absorption coefficient of FLiNaK could be estimated.

Based on Ewing’s experimental data, it seems likely that the value of $\overline{K}$ for clean salt is closer to $6m^{-1}$ than $20m^{-1}$, and probably is lower than that. Each time Ewing attempted to measure the attenuation coefficient, the value increased; it is likely that this was caused by increased corrosion on the transfer surfaces leaching metallic impurities into the salt.

![Figure 8. Experimental Results from Ewing Calibration](image-url)
In Figure 8 above, the three different correlations denote three consecutive experimental runs. Ewing made no claims that what had been measured was actually the radiation absorption coefficient in the salt; rather, the results was used to correct conductivity data. Despite this, Ewing’s results were used as estimates of the gray model absorption coefficient by Ambrosek, et al in a paper estimating different modes of heat transfer in molten salts. [4] Additionally, by measuring the absorption coefficient by correlation, what is measured is the average absorption coefficient, rather than the spectrally varying absorption coefficient. This assumes constant spectral values for all properties, but in reality is an integral average absorption coefficient.

The only published literature that has been found that attempted to directly measure spectral attenuation coefficients in molten salts measured salts for solar storage [12]. That investigation found that the attenuation coefficient in the transmission region for KNO$_3$. NaNO$_3$ (40-60 wt%) was on the order of $1m^{-1}$. Additionally, because the investigation was focused on salts for solar storage, the experimental setup was only able to measure transmission in a fairly narrow range, that of solar radiation, and not extending into the mid or near infra-red where the bulk of thermal radiation heat transfer takes place.

No other attempt to classify molten salts for heat transfer applications in terms of spectral absorption coefficient has been found, and there is no research that has directly measured the absorption coefficient in the molten salts proposed as coolants in nuclear reactors.
1.6. Spectral Methods for Measurement of Absorption Coefficient

Experimentally measuring the spectral linear absorption coefficient of liquids presents significant challenge, more so under conditions of high temperature and potential corrosion. For this reason, there have only been limited studies that have attempted to measure high temperature liquids in the wavelength range of interest, especially in semi-transparent, as opposed to highly absorbing, materials.

The standard assumption made when measuring the absorption coefficient is to measure the extinction coefficient and assume that scattering is negligible. Measuring attenuation is simple in theory but has some difficulties to overcome in terms of practical execution, especially with the present materials considered.

For solid samples, the technique is somewhat simpler than for liquid samples. The specimen of interest is held in the beam path of a light and the spectral intensity is measured with a spectrometer. With knowledge of the thickness of the material, the absorption coefficient can be simply measured by applying the Beer-Lambert law, Equation (1.11), to the data.

\[ I(\tau) = I(0)e^{-\tau} \]  

(1.11)

This simple setup can only be used if there is precise knowledge of the reflection and other losses in the system. One way to account for this is to measure two nearly identical samples of different thicknesses. The reflection and other non-absorptive losses in the system should be nearly identical in the two samples, and so any difference in the
resulting spectra would be the result of increased attenuation along the path line in the sample. If the change in thickness is known, then the attenuation coefficient can be calculated from the ratio of the intensity of the spectra.

A number of techniques have been used to measure the absorption spectra in liquids, since it is difficult to contain the sample in a test chamber and difficult to measure the exact thickness of a liquid. Aside from the method previously described, another common technique involves measuring reflection on the surface of a sample of material, and applying correlations that exist between the complex index of refraction and the absorption coefficient. However, these techniques include significant sources of experimental error that are difficult to eliminate. [9] Additionally, liquids pose a challenge for these techniques because they are so dependent on the surface conditions, which are hard to quantify or guarantee consistency for liquids due to unknown surface tension effects.

Another class of techniques is known as submerged mirror techniques. As shown in Figure 9, the sample is held in a vertical orientation and light is reflected down through the sample to a mirror. A technique similar to this was used by Barker. The depth of the material was measured with a heated probe that sensed the different conductivities of the free surface and the mirror in order to take a precise depth measurement.
This technique has the advantage of removing any lenses from the material but has the shortcoming that it cannot be used with large thicknesses of material. As such it is not suitable for measuring the transmission coefficient of a largely transparent material since the change in intensity across the sample would be too small to measure. In order to try a similar technique with a larger sample would require a prohibitively large setup given the instrumentation available. It also requires a significant amount of extra equipment to properly align the mirrors and construct a furnace capable of keeping the sample at temperature during measurement compared to transmission techniques.

The method employed by Passerini to measure salt samples for solar ponds used a variation on the varying thickness technique. In that technique, the molten salt sample was
contained in a silica crucible and melted. A second, smaller crucible was inserted coaxially from the top with an apparatus to raise or lower it a precise amount. A collimated light beam was directed through the center axis and down through the top crucible, salt and bottom crucible. The light was collected with an integrating sphere to attempt to capture as much light as possible.

![Experimental Setup Diagram](image)

**Figure 10. Experimental Setup for Measurement of Spectral Absorption Coefficient, method of Passerini**

While this setup worked somewhat for the measurement performed, the technique is not directly applicable to the present research for a number of reasons. First, background radiation from the furnace overwhelms the signal in the near and mid-infrared. This was not a problem for the Passerini setup because they were investigating visible light. Second, all of the components in this setup use silica or quartz as a window or transmission medium.
Silica is cheap and exceptionally clear in the visible range, but it does not transmit light over 2µm. Experimentation of this kind is not often performed and so there are limited or no components available that will function in the 1-6 micron range of interest that are compatible with a similar setup. Third, even if components with transmission in the relevant range could be found, molten salts can attack the surfaces of glasses rendering them opaque to radiation.

In order to generate and analyze the spectrum required to generate linear absorption coefficients in molten salts, a Fourier Transform Infrared Spectrometer (FTIR) would be required. This poses new challenges for the experimental setup, since FTIR are stand-alone units, where the alignment and spacing of the components is critical to operation. Additionally, generating the temperatures required to keep the salt volume molten while encasing it in inert, transparent materials also poses significant problems. Finally, the background signal generated by the salt emits a powerful background signal which may render experimental data that it would be possible to discern the light source signal from the blackbody background generated from heating the salt.

Due to the complexities associated with measuring a liquid sample, the simplest experimental technique to produce usable spectral data is simple transmission with a solid glass sample. Doing so is predicated on the assumption that the absorption characteristics do not change significantly with temperature and that the molten and solid forms will exhibit very similar absorption behavior. However, this assumption has two shortcomings,
first in that although the phonon absorption edge does shift dramatically with melting, the absorption does shift appreciably. A second effort would be required to characterize this shift for all materials of interest. Second, for appreciable salt thicknesses, it may prove challenging to produce glass samples that do not form grain boundaries upon cooling. And equipment would be required to form and polish the solid salt, since surface conditions and internal grain boundaries would present strongly variable surface and internal reflections, introducing significant internal error. High temperature liquids present some of the most significant challenges to measuring broad spectrum linear absorption coefficients. [9] For these reasons, it was decided to pursue an integral heat transfer method, where the entire spectrum is measured at once, at the loss of specific knowledge of spectral structure. However, in return, integral techniques give information on all physics at all wavelengths relevant for heat transfer. Since heat transfer is the desired goal of the present measurement, integral techniques may be the only and best option for obtaining reliable data.
Chapter 2. Radiation Heat Transfer in Participating Media

Solution of the energy equation coupled with radiation is an additional complexity to performing thermal-hydraulic analysis that is typically avoided if at all possible. The present research obviously requires the computation of radiative fluxes. This chapter describes the models used for one dimensional heat transfer in planar and radial geometry and discusses the coupled solutions with the general energy equation. The effects of radiation heat transfer on typical reactor geometries are discussed and an examination of the regimes where radiation heat transfer is significant is conducted.

2.1. General Formulations for Radiation Heat Transfer

Any material at temperatures above absolute zero emits energy as thermal radiation randomly and in all directions depending on the temperature of the material and other properties. A “black” body is one that emits absorbs that the theoretical maximum amount of radiant energy at all wavelengths. The spectral distribution of this energy was first calculated by Planck in 1901, where he defined the emissive power density of a blackbody per unit wavelength as a function of wavelength and temperature.

\[ E_{\text{bb}}(T, \lambda) = \frac{2\pi h c_0^2}{n^2 \lambda^5 \left( e^{hc_0/\lambda kT} - 1 \right)} \]  

(2.1)
where \( h \) is the Planck constant, \( c_0 \) is the speed of light in a vacuum, \( n \) is the index of refraction, \( k \) is the Boltzmann constant and \( T \) is the temperature of the material. Integrating over all wavelengths and directions, the emissive power of a blackbody in power per unit area is given by the Stefan-Boltzmann law

\[
E_b(T) = \sigma T^4
\]  

(2.2)

When performing calculations with participating media, it is more convenient to determine energy balances in terms of the spectral radiative intensity, \( I_\lambda \), defined as the energy flow per unit solid angle per unit area per unit wavelength across a surface with a surface normal in the direction of the ray. The emissive power is related to the intensity in that the emissive power emanating from a differential area is equal to the intensity dotted with the surface normal integrated over all solid angles,

\[
E_\lambda(r) = \int \int_{0}^{2\pi} I_\lambda(r, \theta, \varphi) \cos \theta \sin \theta d\theta d\varphi
\]

(2.3)

where \( r \) is the position vector, \( \theta \) is the angle between the outward normal to the surface and direction of motion of the ray, and \( \varphi \) is the azimuthal angle.

The total radiative intensity, \( I_t \), is defined by integrating the spectral intensity over all wavelengths.

\[
I(r, \theta, \varphi) = \int_{0}^{\infty} I_\lambda(r, \theta, \varphi) d\lambda
\]

(2.4)
In the following sections, where equations are valid spectrally, the dependence on wavelength has been noted either as a subscript or as a dependent variable. In a material that attenuates radiant energy, but does not scatter it, the rate of decrease of intensity has been found by experimentation to be proportional to the magnitude of the intensity. [9] The equation of transfer is given by

$$\hat{s} \cdot \nabla I_\lambda = \frac{dI_\lambda}{ds} = \varepsilon_\lambda I_{\lambda k} - \kappa_\lambda I_\lambda$$

(2.5)

Along a path, s, the intensity of light decreases proportional to a coefficient $\kappa$, known as the attenuation coefficient, and increases due to the emission of radiant energy based on the local blackbody spectrum and emissivity coefficient, $\varepsilon$. Due to the high speed of light and the relatively small dimensions for all but celestial calculations, a transient term proportional to $1/c$ is traditionally ignored. Kirchhoff’s law and subsequent experimentation determined that local emissivity must be equal to absorptivity for a material in thermodynamic equilibrium, in other words, $\varepsilon = \kappa$. The physical basis for this relationship is that allowable energy transitions define what energies can be absorbed, and these transitions in the opposite direction govern what energies can be emitted.

The non-dimensional optical thickness is defined in Equation (2.6)

$$\tau_\lambda = \int_0^s \kappa_\lambda ds$$

(2.6)

Combining Kirchhoff’s law and Equation (2.6), Equation (2.5) can be rewritten
\[
\frac{dI_\lambda}{dt} + I_\lambda = I_{b\lambda} \tag{2.7}
\]

Though a relatively simple equation on its face, solution of the intensity relation is complicated by the fact that knowledge of the entire temperature distribution within the region of interest is required.

In terms of heat transfer calculations, the two quantities of interest will be the incident radiation and the radiation heat flux. The incident radiation, also known as the *irradiance*, is the integral over all solid angles of the intensity into a point and represents the energy flow into a control volume from all other sources of radiant energy.

\[
G_\lambda(\tau) = \int I_\lambda(\tau, \hat{s})d\Omega \tag{2.8}
\]

where \( G \) will then have units of energy transferred per unit time per unit area.

The second quantity of interest is the total radiative heat flux, \( q \). The heat flux is similar to the irradiance, but is only the energy flow normal to a unit of surface area, where positive flux is defined relative to the normal for a surface element.

\[
q_\lambda = \hat{q}_\lambda \cdot \hat{n} = \int I_\lambda(\hat{s})\hat{n} \cdot \hat{s}d\Omega = \int I_\lambda(\hat{s})\cos \theta d\Omega \tag{2.9}
\]

Expanding solid angle and introducing the direction cosine, \( \mu = \cos \theta \), \( G \) and \( q \) are rewritten
The determination of the radiative heat flux and irradiance are important because they are required to determine the interface of radiation in the general energy conservation equation. The general form of the energy equation is

\[ \rho \left( \frac{\partial \vec{u}}{\partial t} + \vec{v} \cdot \nabla \vec{u} \right) = -\nabla \cdot \vec{q} - p\nabla \cdot \vec{v} + \mu \Phi + \dot{Q} \]  

(2.12)

where the quantity \( q \) is the heat flux with contributions from both radiation and molecular diffusion or conduction. Most physical processes depend only on the properties of immediately neighboring regions, while radiation depends inherently on the instantaneous value of every other point in the domain. As such, the radiation term in (2.12) is often included as a source to the general energy equation and is solved separately in an iterative manner. In this formulation, the source has the value

\[ \dot{Q}_r = -\nabla \cdot \vec{q}_r \]  

(2.13)
Note that this quantity is only relevant to the overall energy equation when the radiative flux is integrated over all wavelengths. We now define the divergence of the radiation heat flux based on the quantities already defined. Integrating equation (2.5) over all solid angles yields

$$\int_{4\pi} \hat{\mathbf{s}} \cdot \nabla I_\lambda d\Omega = \kappa_{\lambda}(\int_{4\pi} I_{\text{b\lambda}} d\Omega - \kappa_{\lambda}(\int_{4\pi} I_\lambda (\hat{s}) d\Omega)$$

(2.14)

Since the divergence and directional coordinates are independent, the divergence operator can be taken out of the integral. What is left inside the integral is equal to the definition given previously of the radiation heat flux in (2.11). The last term in equation (2.14) is identical to the irradiance as given in (2.10). Thus, incorporating the above identity and integrating over all wavelengths, the divergence of the heat flux is defined

$$\nabla \cdot q_r = \int_0^{\infty} \kappa_{\lambda}(4\pi I_{\text{b\lambda}} - G_{\lambda}) d\lambda$$

(2.15)

Thus the challenge is left to calculate the local irradiance, which is a function of the geometry and temperature distribution in the situation of interest. From this, the total energy equation be solved with this source term, and the two solutions can be iterated between until convergence is reached.

2.2. Equations for One Dimensional Transfer with Gray Medium

2.2.1. Planar Geometry

The solution of the radiation transfer equation is sought for a one dimensional planar geometry. This geometry is relevant for nuclear reactors using plate type fuel, such
as the AHTR, [13] and also as a convenient geometry for the design of a test chamber. For a one-dimensional plane parallel medium, several simplifications can be made. With black walls and without scattering, any radiation emitted from one plane will be absorbed by the facing plane or by the participating material. Additionally, due to the assumption of plane parallel geometry, radiation can only be emitted in the hemisphere facing out from the surface. Thus there are essentially only two intensity functions, one emanating from the top wall and directed downward, and one emanating from the bottom wall directed upward.

In order to account for thermal radiation in a system, it is desired to solve for the radiative heat flux in a system with a given temperature distribution, such as one found by solving the continuum energy equation. The exact solution for the radiative heat flux in plane parallel geometry is given by Modest. [9]

\[
q(\tau) = 2\sigma T^4(0)E_3(\tau) - 2\sigma T^4(\tau_L)E_3(\tau_L - \tau) \\
+ 2\int_0^{\tau_L} \sigma T^4(\tau') E_2(\tau - \tau')d\tau' - 2\int_{\tau}^{\tau_L} \sigma T^4(\tau') E_2(\tau' - \tau)d\tau'
\]  

(2.16)

Where the functions \( E_n(x) \) are given by

\[
E_n(x) = \int_0^1 \mu^{n-2} e^{-x/\mu} d\mu
\]

(2.17)

Thus the radiative transport equation in the absence of scattering can be seen to be composed of two terms: Intensity emitted from boundaries, and intensity emitted by the continuous medium. The exact solution requires multiple integrations to compute the value at each point and each integration is of highly non-linear functions. Unfortunately, this
means that the exact solution is computationally expensive to compute, even for simple geometries.

The radiative transfer equation in participating media is often also solved by transforming the integro-differential equations into a series of coupled differential equations. One method to do so is the Method of Spherical Harmonics, the first order approximation is known as the $P_1$ method. Following the formation of Wang and Tien [14], this results in the following transformations of equation (2.16)

$$\frac{d^2G}{d\tau^2} + 3(4\sigma T(\tau)^4 - G) = 0 \quad (2.18)$$

Subject to the boundary conditions

$$\tau = 0: \quad \frac{dG}{d\tau} + \frac{3}{2}(4\sigma T(0)^4 - G) = 0$$

$$\tau = \tau_L: \quad \frac{dG}{d\tau} - \frac{3}{2}(4\sigma T(\tau_L)^4 - G) = 0 \quad (2.19)$$

Equations (2.18) and (2.19) solve for the irradiance, $G$, of a given temperature distribution. From this, the total flux and flux gradient can be calculated, assuming the temperature distribution is known from another solution method, such as the continuum energy equation.

For cases where the combined radiation and conduction equation are desired to be solved, an iterative method is employed. The energy equation is solved with the gradient of the radiative flux as a source term. Solution of the energy equation leads to a temperature
distribution, which can then be used to solve for the radiative flux and from this to update the source term. This is done until the residual of the energy equation reaches zero.

To verify that the radiation and conduction heat fluxes could be solved correctly, the total flux was compared to an alternate method known as the additive method. The additive method is a simple approximation for the calculation of radiation and conduction fluxes between surfaces and is commonly employed to generally estimate the effects of radiation heat transfer [4]. For the case of black plates separated by a radiatively participating, conducting medium the approximation for the radiative flux is given by

$$q_r = e^{-\tau} (\sigma T_1^4 - \sigma T_2^4) \quad (2.20)$$

And the conductive flux is given by

$$q_c = -k \frac{\Delta T}{\Delta x} \quad (2.21)$$

The additive flux is then found by adding the two together.

The total flux between two plates was calculated by iteratively solving the energy equation with the flux computed using the $P_1$ approximation over a range of conductivities and optical thicknesses. The additive flux was also calculated under identical conditions. The fluxes were plotted against the non-dimensional radiation-to-conduction parameter, $N$, where $N$ is defined:

$$N = \frac{k \kappa}{\sigma T_1^3} \quad (2.22)$$
The resulting curves were compared to data published in [9] which it reproduced exactly and is shown below in Figure 11.

![Figure 11 Comparison of Additive and P1 Solutions for coupled radiation and conduction heat transfer](image)

2.2.2. Radial Geometry

Heat transfer in circular cross section piping is of obvious interest from a reactor design perspective. Thus, we will examine the solution of the radiative transport equation in circular pipes with gray, absorbing, non-scattering media with black walls. The equation of transfer for radial geometry is similar to that for a one dimensional case, with the added
complication that the cylindrical geometry adds a geometric attenuation to the transport equation. The exact solution for one-dimensional radiative transfer in a non-scattering medium is given by Azad [15]

\[
q(\tau) = \int_{0}^{\tau} 4 \frac{d(\sigma T(\tau')^{4})}{d\tau} F(\tau', \tau) \tau' d\tau' + \int_{\tau}^{2} 4 \frac{d(\sigma T(\tau')^{4})}{d\tau} F(\tau, \tau') d\tau'
\]

Here the function \( F \) is a geometric function that accounts for the effects of the cylindrical coordinate system.

\[
F(\tau, \tau') = -\frac{1}{\pi} \int_{0}^{\pi/2} \int_{0}^{1} e^{\frac{-\tau}{\sin \theta}} \left( \sqrt{\frac{\tau'}{\tau}} \sin \psi \right) d\theta d\psi
\]

While the function \( F \) is cumbersome to calculate, since it is only a geometric function, it can be calculated once for a range of values and stored. Still though, the analytical solution is time consuming and cumbersome to calculate, so a reasonable differential approximation is sought.

It is possible to apply the same approximations to radial geometry there were used in planar geometry. In cylindrical coordinates, the governing second order differential equation for \( q_r \) in a gray medium is given by Equation (2.25)

\[
\frac{d^2q_r}{d\tau^2} + \frac{1}{\tau} \frac{dq_r}{d\tau} - \frac{1}{\tau^2} q_r - 3q_r = 4\pi \frac{d(I_0)}{d\tau}
\]
where $\tau = \kappa r$ is the optical coordinate and $I_b = \sigma T^4 / \pi$ is the total blackbody intensity.

In a pipe flow, the inner boundary satisfies a symmetry boundary condition. The outer boundary satisfies Equation (2.26)

$$\frac{1}{\tau} \frac{d(\tau q_r)}{d\tau} \bigg|_{\tau_0} + 2 \frac{(2 - \varepsilon)}{\varepsilon} q_r(\tau_0) = 4\pi (I_b(\tau_0) - I_{b,w})$$  \hspace{1cm} (2.26)

where $\tau_0 = \kappa R$, where $R$ is the radius of the pipe, $\varepsilon$ is the wall emissivity, and $I_{b,w}$ is the blackbody intensity of the wall, which may be different from the blackbody intensity of the salt at the wall if there is a temperature discontinuity at the interface of the wall and salt. All walls are assumed to be black in the present analysis.

Figure 12 shows a comparison of the non-dimensional radiative heat flux in radial geometry generated from solving the exact and P1 approximation with a representative temperature distribution with low optical thickness. The results show good agreement between the P1 and exact solutions.
2.3. Generating an impurity-averaged absorption coefficient

Based on the intrinsic absorption curve developed in Section 1.4 and knowledge of the impurity absorption peaks, it was desired to use the above-developed equations to determine a gray (single-wavelength, band-averaged absorption coefficient), $\bar{\kappa}$, with which the total heat transfer to a participating medium can be accurately calculated. A gray medium is assumed to have no variation in $\kappa$ with wavelength. The methodological method is to calculate the heat transfer for a given absorption spectrum and determine the gray absorption coefficient which would produce the same total energy transfer.
The methods described above for determining the heat flux have been valid as both spectral and integral properties. Where a blackbody intensity is included in the computation, it is equally valid to say that the flux within a given wavelength range is a function of the intensity emitted in that range. Mathematically, the total flux emitted in a given spectral range is

\[ q_{\lambda} = \int_{\lambda_{1}}^{\lambda_{2}} q_{\lambda} d\lambda \]  

(2.27)

Since the only parameter in the present analysis that has a spectral variation is the absorption coefficient, and the absorption coefficient can be reasonably approximated as constant within an appropriately sized energy bin, the total flux entered in the energy equation is the fraction of energy emitted in an energy bin times the total blackbody flux. The fraction of energy emitted in each bin is computed as

\[ w_{j} = \int_{\lambda_{j-1}}^{\lambda_{j}} I_{b,\lambda}(T_{ref})d\lambda / \int_{0}^{\infty} I_{b,\lambda}(T_{ref})d\lambda \]  

(2.28)

The reference temperature, \( T_{ref} \), is the fourth power, volume-weighted, mean temperature of the radial temperature distribution.

As an example of the energy binning strategy used, two energy bins can be used, one for energies above a certain cutoff wavelength and one for energies below. To avoid significant added complexity, the energy weighting was accomplished using a blackbody temperature equal to the fourth power average of temperature points in the domain.
\[ I_{\text{ref}} = I_{b,\lambda} \left( \frac{1}{N} \sum T_i^4 \right) \]  

(2.29)

The same fractional deposition weighting is applied throughout the domain, regardless of the temperature at each location, which simplified the computation considerably at minimal compromise of accuracy. Considering that the variation in bin width is small over the temperature ranges within relevant cases, the simplification is justifiable. With two energy bins and a cutoff wavelength equal to 7µm, the weight of each bin was calculated for a range of reference temperature and is shown below in Figure 13.

![Fractional energy deposition graph](image)

**Figure 13.** Variation in fractional energy deposition for a cutoff wavelength of 7µm over a range of reference temperatures

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The $\kappa(\lambda)$ for FLiNaK shown in Figure 6 was divided into discrete bands ($j$), with a constant $\kappa_j$ over each band taken at the midpoint of each band interval. The $q_{r,j}$ for each band was calculated with $\overline{\kappa}$ equal to $\kappa_j$. Integrating the divergence of $q_{r,j}$ over the cross section of the pipe yields the power transferred to the pipe, $Q_{r,j}$ as shown in Equation (2.30):

$$Q_{r,j} = \int \nabla \cdot q_{r,j} dV$$

(2.30)

The total power transferred to the pipe was calculated by weighting and summing $Q_{r,j}$ using Equation (2.31):

$$\overline{Q}_r = \sum_j w_j Q_{r,j}$$

(2.31)

An “impurity” band, $j=i$, was generated between the wavelengths of 0.15 $\mu$m and 3 $\mu$m. Though slightly larger than the 0.4 $\mu$m and 2 $\mu$m wavelength region identified by Young and White, [16] this range was chosen because it yields an upper estimate for the effects of impurities and impurity effects in the region are suggested by the work in Chapter 4. To determine $\overline{\kappa}$ as a function of $\kappa_i$, all $\kappa_j$ were kept constant while varying $\kappa_i$. Calculating energy transfer using Equations (2.25) through (2.31), values of $\overline{\kappa}$ which produced the same $\overline{Q}_r$ as by the method above is the impurity averaged absorption
coefficient, denoted henceforth as $\langle \kappa \rangle$. The averaging conditions were chosen as a 2-cm pipe with 1150 K walls, using a parabolic temperature distribution within the salt, the results are shown in Figure 14 as a graph of $\langle \kappa \rangle$ versus $\kappa_i$.

Figure 14. Impurity-dependent equivalent absorption coefficient for FLiNaK.

The resulting values of $\langle \kappa \rangle$ are only weakly sensitive to the choice of averaging conditions within the subset of wall temperatures and pipe diameters relevant to advanced reactor design. Although it would be more valuable to know the impurity concentrations that result in a certain $\kappa_i$, the data with which to support correlation is not yet known, though an attempt to estimate this is conducted in Chapter 4. Regardless, it is evident that

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\( \langle \kappa \rangle \) for FLiNaK is approximately bounded by \( \langle \kappa \rangle = 5 \, \text{m}^{-1} \) for clean salt and \( \langle \kappa \rangle = 25 \, \text{m}^{-1} \) for salt with a high concentration of metal impurities. It is encouraging that these values are very similar to the estimates of \( \langle \kappa \rangle \) based on the data of Ewing, which indicated clean salt had \( \langle \kappa \rangle \) of 6 \, \text{m}^{-1} \) increasing to 20 \, \text{m}^{-1} as impurities increased.

2.4. Radiation Heat Transfer Effects in Reactor Geometries

With the models developed in the previous two sections, and with preliminary data and estimates from existing experimental information, an examination of reactor geometries was undertaken with the goal of more realistically estimating the effects of radiation heat transfer in advanced reactors.

2.4.1. Radiation Heat Transfer in Planar Geometries

From (2.12), the steady state energy equation with constant thermal conductivity and specific heat in Cartesian coordinates is as follows:

\[
\rho c_p \vec{v} \cdot \nabla T = -\nabla \cdot \vec{q}_c - p \nabla \cdot \vec{v} + \mu \nabla \Phi - \nabla \cdot \vec{q}_r \tag{2.32}
\]

The geometry for which the energy equation is to be solved is shown below in Figure 15.
Figure 15. Geometry Definitions for Planar Flow

If variation in the density is assumed to be small in the region of interest, then it can be assumed that the velocity profile is not affected by the temperature distribution and the velocity can be taken from a solution of the momentum equation. If axial conduction is neglected, viscous affects ignored and pressure drop is small, then the energy equation for flow between flat plates in the laminar region is:

\[ \rho c_p (v_i(y) \frac{dT}{dx}) - k \left[ \frac{d^2 T}{dy^2} \right] = -\nabla \cdot \vec{q}, \]  

(2.33)

The heat flux is assumed not to vary significantly in the axial direction, so that the axial flux gradient is small. This assumption is obviously inaccurate near the inlet, but further downstream is somewhat justifiable for the same arguments from which axial conduction is neglected, with the additional argument that wall-to-wall transfer is zero based on the constant wall temperature boundary conditions. For constant heat flux conditions, radiation will have the effect of flattening the temperature profile and ignoring
axial gradients is not as valid an assumption. Axial gradients are still likely to have a small effect, as self-view factors down high aspect-ratio tubes are minimal. Discretizing the energy equation using finite central differencing for the spatial derivative, and the axial gradient term treated with upwind forward differencing, the discretized equation is as follows.

\[
\rho c_p v_j \frac{T_{i,j} - T_{i-1,j}}{\Delta x} - k \left[ \frac{T_{i,j+1} - 2T_{i,j} + T_{i,j-1}}{\Delta y^2} \right] = \dot{Q}^w
\]  

(2.34)

The volumetric energy source is computed from the radiative transport equation

\[
\dot{Q}^w = -\sum_i w_i \nabla \cdot q_{r,i}
\]  

(2.35)

The boundary conditions were solved at constant temperature. The boundary condition set for constant temperature is

\[
\begin{align*}
y = 0 : & \quad T(x,0) = T_{wall} \\
y = D : & \quad T(x,D) = T_{wall} \\
x = 0 : & \quad T(0,y) = T_{in}
\end{align*}
\]  

(2.36)

The full solution to these equations is not presented here, as radial geometry is a more interesting case for reactor design. Planar geometry in advanced reactors does exists for primary coolants used in conjunction with plate type fuel. However, for these cases, the expected coolant channel thickness is so small that radiation heat transfer will be negligible for most reasonable reactor designs.

2.4.2. Radiation Heat Transfer in Cylindrical Geometries
To capture the effect of RHT and its interaction with temperature field, the energy equation was solved for a flowing salt in a cylindrical pipe with a radiation energy emitted by walls and absorbed within the salt, effectively constituting a volumetric energy source. The geometry under consideration is shown in Figure 16.

The relevant energy equation is

\[
\rho c_p u_x(r) \frac{\partial T}{\partial \xi} - \frac{1}{r} \frac{\partial (r q_r)}{\partial r} = \nabla \cdot q_r
\]  

(2.37)

where \( \rho \) is the salt density, \( c_p \) is the salt specific heat capacity, \( u_x(r) \) is the axial velocity, and \( q_r \) is the conduction heat flux. The wall temperature is constant azimuthally and axially. The salt temperature at the inlet is radially constant. Axial conduction has been neglected, and the velocity field was set to be that of fully developed laminar flow. Additionally, to simplify the calculations, only the radial variation of \( q_r \) has been considered. This approach is similar to that of Kim, [17] who demonstrated that
this treatment is accurate for axially constant wall temperature. Axial energy transport may be worth considering in the design of heat exchangers and in cases of constant heat flux, but in terms of examining heat transfer to the salt, the present assumptions accurately capture the local effects of RHT and so should prove instructive.

Equation (2.37) was discretized using a finite volume formulation. Fourier’s law was used to calculate $q_c$ with the thermal conductivity held constant. The radiation heat flux was calculated using the differential approximation as discussed in by Equations (2.25) through (2.31). First-order upwind differencing was used for the flow term. All salt properties were taken from “Engineering Database of Liquid Salt Thermophysical and Thermochemical Properties.” [10]

The solution methodology was as follows: the wall temperature and inlet temperature were specified. Equation (2.37) was solved at $x = x_1$ with $\nabla \cdot q_r$ set to zero. The radiation flux was calculated using Equations (2.25) and (2.26) based on this temperature distribution, and a new radiative source term was calculated. The radial temperature distribution was solved with the new source term. This process was iterated using linear under-relaxation of the temperatures until the residual of Equation (2.37) had decreased by six orders of magnitude. Once the temperature field was converged, the solution was calculated at the next downstream location. Once the solution had progressed a specified length down the pipe, the simulation terminated.
The Nusselt number for convection, $Nu_{\text{conv}}$, was calculated at each axial location as

$$Nu_{\text{conv}} \equiv D q_{r w} / k(T_w - T_m)$$  \hspace{1cm} (2.38)

where $D$ is the pipe diameter, $k$ is thermal conductivity and of the salt, and $T_m$ is the mixing cup mean temperature. The equivalent radiation wall heat flux is computed as

$$q_{r w} = \frac{\bar{Q}_r}{(2\pi R dx)}$$  \hspace{1cm} (2.39)

The Nusselt number for radiation, $Nu_{\text{rad}}$, was then calculated in a similar manner as to Equation (2.38)

$$Nu_{\text{rad}} \equiv D q_{r w} / k(T_w - T_m)$$  \hspace{1cm} (2.40)

As a validation, the simulation was run without radiation at a range of $T_w$ and $D$. The computed Nusselt number was compared to the expected value for laminar flow and was found to agree within 1% for all cases. As additional validation, the solution was compared to computation done using the commercial software ANSYS Fluent [18].

The Fluent model was constructed with axisymmetric symmetry on a 2cm diameter pipe with 10m length. Mapped face meshing was used with 4000 axial nodes and 40 radial nodes, giving a nodal aspect ratio of 10. Radiation was calculated using Discrete Ordinates method. Without radiation, the axial heat flux was computed with the MatLab model and Fluent in a pipe with $T_w = 1073K$, $D = 2$-cm.
Figure 17. Comparison of computed heat flux between MatLab and Fluent in a pipe with are \( T_w = 1073K \), \( D = 2\)-cm, no radiation

The results can be seen in Figure 17, and show good agreement between FLUENT and the MatLab model.

Using the MatLab model, the fraction of energy transferred by radiation was calculated by computing the Nusselt number for radiation divided by the total Nusselt number. An example of the results for a single case are shown in Figure 18, where the simulation conditions are \( T_w = 1073K \), \( D = 2\)-cm, and \( \langle \kappa \rangle = 5 \text{ m}^1 \).
Figure 18. Nusselt number development for $T_w = 1073$K, $D = 2$-cm, and $\langle \kappa \rangle = 5$ m$^1$.

As can be seen from Fig. 4., $Nu_{conv}$ is more strongly dependent on the radial temperature profile than is $Nu_{rad}$. As the salt progresses down the pipe, the ratio $f_{Nu}$, defined in Equation (2.41)

$$f_{Nu} = \frac{Nu_{rad}}{(Nu_{rad} + Nu_{conv})}$$  \hspace{1cm} (2.41)

asymptotically approaches a maximum value. The final value of this ratio is independent of the Reynolds number, provided the flow is laminar. This final value of the ratio is also independent of the temperature at the inlet. For validation, a simulation was generated using MatLab, and the percentage increase in wall heat flux as a function of axial position
was computed for a case with radiation divided by a case without. An identical simulation was performed using the commercial software Fluent. The results for both can be seen in Figure 19.

![Figure 19](image)

**Figure 19.** Increase in Wall Heat Flux as a function of axial position calculated with Fluent and MatLab for $T_w = 1073K$, $D = 2$-cm, and $\langle \bar{r} \rangle = 5$ m$^{-1}$.

Near the inlet, the simulation conditions are slightly different, so it is not surprising that the results differ slightly. Two effects cause the apparent difference. First, Fluent solves the coupled momentum and energy equations, whereas the MatLab solver treats the
velocity profile as fully developed. Additionally, the MatLab code also does not account for the axial gradient in radiation heat flux, which is relevant close to the inlet. For these two reasons, the FLUENT results lags slightly behind the MatLab results and is slightly lower overall. However, the asymptotic values calculated by both methods are very close. For the conditions shown in Figure 19, the result from Fluent predict a 9.35% increase compared to 9.5% increase calculated with MatLab. Thus, the MatLab solution is sufficiently accurate to estimate the effects of radiation heat transfer.

Several thousand coupled solutions were performed, varying absorption coefficient, pipe diameter, and wall temperature for each. At each simulated value of the pipe diameter, the MatLab code was used to calculate the $T_w$ for which radiation heat transfer constituted a 10% increase compared to convection. Together the points form a map, as shown in Figure 20, which indicates the circumstances under which RHT will be significant for varies values of the average absorption coefficient.
Figure 20. Conditions under which RHT becomes significant for various $\langle \kappa \rangle$.

For points to the right and above curves for a certain $\langle \kappa \rangle$, RHT will contribute more than 10% of the total heat transfer to the salt. FLiNaK with a low concentration of impurities is expected to behave as having a $\langle \kappa \rangle$ of 5 m$^{-1}$ as discussed previously. Thus, if clean FLiNaK is used as the coolant in a heated channel with 2-cm diameter coolant passages and a wall temperature of 1073 K, then radiation heat transfer would represent 10% of heat transfer to the salt.

A similar map with curves for various percentages of RHT for $\kappa$ of 5 m$^{-1}$ is presented in Figure 21.
Figure 21. Conditions of $T_w$ and $D$ under which RHT is responsible for various fractions of energy transferred to the salt.

From the preceding figures, several things are important to consider. In all cases, RHT augments heat transfer to the salt. More importantly, the presence of RHT is not shown to significantly affect the amount of energy transferred by convection. This is explained by Figure 22, which shows the ratio of the fully developed temperature profile for a representative case with RHT to an identical case without. Also plotted is the source term of radiation power absorbed by the salt per unit volume.
Figure 22. Distortion of temperature profile from radiation energy deposition.

As can be seen from Figure 22, the inclusion of the radiation source term only marginally distorts the fully-developed temperature profile in the salt, since the bulk of radiative power is absorbed far from the walls. Since convective heat transfer is driven by the wall temperature gradient, $N_{t_{\text{conv}}}$ is essentially unchanged between the radiative and non-radiative calculations. This is convenient for the heat transfer engineer, since it suggests that RHT can accurately be calculated independently from, rather than coupled with, heat transfer from convection.
As an aid to the reader, the results presented in Figure 20 can be estimated using Equation (2.42). Equation (2.42) accurately reproduces values of $f_{Nu}$ for $0.5 \text{ cm} < D < 4 \text{ cm}$, and $T_w < 1400 \text{ K}$, for a salt with $\langle \kappa \rangle = 5 \text{ m}^{-1}$.

$$f_{Nu} = 0.0002625 e^{-28.37D} \times (D \times T_w)^{2.147}$$

(2.42)

here $D$ is the pipe diameter in meters and $T_w$ is the wall temperature in Kelvin. Equations of similar form to Equation (2.42) accurately reproduce the importance maps for other values of $\kappa$ but are not presented here.

For this study, the focus has been on low Reynolds flow. It is apparent that for turbulent and developing flow, the importance of RHT will be diminished, because the magnitude of the temperature gradient near the wall is greater for turbulent flows.

Turbulence flattens the temperature profile near the centerline and increases the temperature gradient near the walls. A turbulent simulation was not run, but the effect of turbulence on radiation heat transfer is demonstrated by sampling temperature profiles from various axial positions in a simulation. For turbulent flow, the volume-weighted mean temperature, $T_M$, is closer to the center-line temperature, $T_{CL}$. Temperature profiles with the same $T_w$ and $T_{CL}$, with varying wall gradients, result in different mean temperatures. The effect of increasing turbulence is demonstrated in Figure 23. In Fig. 8, larger wall gradients have smaller values of the abscissa. The insets show representative temperature profiles. The ordinate of Fig. 8 is the fraction of energy transmitted to the salt by radiation.
in a turbulent flow relative to the fraction of energy transmitted to the salt by radiation in a laminar flow.

Figure 23. Turbulent profile effect on radiation heat transfer fraction. Insets show representative temperature profiles.

Increasing the wall temperature gradient decreases the relative contribution of RHT. This is due to the fact that RHT is not very sensitive to the radial temperature distribution compared to heat transfer from convection. Figure 23 can be understood as the radiation heat flux remaining constant while the convective heat flux decreases as the value of the abscissa increases.
Smoothly polished metal walls will decrease the wall emissivity and reflect incident radiation, such that with perfect mirror walls, RHT is effectively zero. The use of graphite surfaces, or the presence of corrosive scale or surface roughness inside pipes will increase the emissivity, and thus increase radiation heat transfer. The scaling of radiation heat transfer with emissivity is show in Figure 24 where energy transfer for cases with gray walls is plotted relative to energy transfer with black walls, leaving all other factors constant.

![Figure 24. Scaling of radiation heat transfer with emissivity.](image)

Due to the non-linear effect of emissivity, for all but highly polished and clean surfaces, the effects of non-black emissivity will not significantly affect the results presented here.
One final point that must be discussed is absorption coefficients for significantly opaque materials. Pure FLiNaK has a relatively low absorption coefficient, and low concentrations of metal impurities will raise the effective optical thickness from much less than unity to small values that are still significantly less than unity. However, for transition metal fluoride salts or fuel-in-salt reactors, the average absorption coefficient may well be several orders of magnitude higher, as the metal fluorides may retain their metal character in solution and possess strong absorption. This will result in optical thicknesses orders of magnitude greater than unity. To a first order approximation, the total amount of heat transfer is maximized for an optical thickness of approximately unity, but this decreases for both increasing and decreasing thickness. To demonstrate this point, and obtain a general sense of what values of optical thickness will lead to significant heat transfer from radiation, the total heat transferred by radiation to a molten salt flowing in a 1cm radius tube was calculated for a wide range of absorption coefficients. The data is plotted below in Figure 25.
Figure 25. Radiative Power Deposition as a function of Optical Thickness for a representative heat transfer case.

For clean FLiNaK in a 1cm radius tube, the likely values of the absorption coefficient will result in optical thickness approximately equal to 1E-3. Due to the symmetrical distribution of energy deposition about $\tau = 1$ as seen in Figure 25, radiation heat transfer is likely to be relevant for optical thicknesses between 1E-3 and 1E3. Outside of this range, the radiative power distribution is too small to significantly affect the total heat transfer rate. For very thin cases, $\tau < 10^{-3}$ insufficient energy in absorbed by the salt
to significantly affect total heat transfer. For highly opaque cases, \( \tau > 10^3 \) the length scale for radiation is shorter than that for conduction, and conduction will dominate local heat transfer. For materials and geometries which result in an integral average optical thickness near unity, radiation heat transfer will be maximized.

2.5. Conclusion

Enough data exists in the literature to make a reasonable estimate of the absorption coefficient of the molten salt coolant FLiNaK. The effective absorption coefficient ranges from approximately 5 m\(^{-1}\) for clean salt to 25 m\(^{-1}\) for salt with a high concentration of metal impurities. The effect of RHT in general is to increase the quantity of energy transferred to the salt by the pipe walls. The amount with which total heat transfer will increase depends primarily on the pipe diameter and wall temperature. The emissivity of the walls and the Reynolds number of the flow are also factors worth considering. In general, it is valid to treat radiation by considering it as an additional energy transfer mechanism without considering how it affects conduction and convection at a given axial location. Radiation heat transfer has historically been ignored because the effect was assumed to be small. This is unfortunate, as incorporating radiation heat transfer in the design of reactor components will allow the heat transfer engineer to leverage the increases in heat transfer associated with RHT. Though RHT will not represent a tremendous effect, even small increases in the efficiencies of multi-billion dollar reactors translate to substantial economic benefits.
Chapter 3. Design and Construction of Integral Radiation Absorption Chamber (IRAC)

Chapter 2 demonstrated that radiation heat transfer may play a significant role in heat transfer to molten salts. However, the current state of research leaves the absorption coefficients for most salts unknown. In order to resolve this shortcoming, an experimental apparatus was designed which was capable of containing, heating and measuring the heat flux on a sample of molten salt in order to measure the integral absorption coefficient of the salts. Based on the availability of resources and equipment at OSU, spectral measurement of the absorption coefficient were deemed infeasible and subject to unquantifiable errors. An integral test, where the integral heat flux was measured in addition to the thermal conductivity, was designed that would yield acceptable accuracy while eliminating the potential for systematic errors. The design of the experiment was inspired largely by the work of Ewing, [11] with changes to focus on radiation heat transfer as opposed to conduction. The fundamental theory behind the design of the IRAC is that the energy transfer between two surfaces that are at steady state separated by a conducting, participating medium are functions of the radiative and conductive heat fluxes, which are themselves functions of the boundary temperatures and constituent materials.
Temperatures and heat fluxes can be measured, and so the temperature dependence of the fluxes can be determined. The radiative fluxes are fundamentally governed by the absorption coefficient, and so careful examination of the total heat flux should reveal information about the absorption coefficient of the salt.

3.1. Mathematical Basis of IRAC

The mathematical basis for the IRAC apparatus was first described by Ewing as a method for measuring thermal conductivity at high temperatures in optically thin materials. Although more complex analysis is possible, with a high degree of uncertainty, it was preferred to keep the number of variables low and minimize the number of assumptions required. This tactic of course comes at the expense of accuracy, but for a relatively novel technique with few means to validate results, a simplified analysis should provide more confidence in whatever results are obtained.

At low fluxes with an optically thin medium, that is a medium that does not strongly absorb radiation, the radiation and conductive heat fluxes can be assumed to be independent. Although this is not exactly the case for the proposed experiment, it is a reasonable approximation from which to discuss the basis of the technique.

Plane-parallel geometry with a participating medium separating two plates, shown in Figure 26, represents the simplest mathematical case and will be the basis of the experimental technique. Two plates are assumed located at positions \( z_1 \) and \( z_2 \) with temperatures \( T_1 \) and \( T_2 \).
The steady state heat transfer for this case by molecular conduction, $q_m$, in the absence of radiation, is given by

$$q_m = A_m k_m(T) \frac{\Delta T}{\Delta z}$$

(3.1)

where $k_m$ is the molecular thermal conductivity, which may be temperature dependent, and $A_m$ is the projected area of the medium normal to the planes, $\Delta T$ is the difference between $T_1$ and $T_2$.

For radiation passing through a medium which absorbs, but does not emit, the radiative flux decreases proportional to the intensity of the flux as energy propagates through a medium. This results in an exponential decrease of the flux with distance. The heat flux as a function of position $z$, assuming no reflection, is given by
\[ q_1(z) = A_1 \varepsilon_1 \sigma T_1^4 e^{-\kappa z} \]  \hspace{1cm} (3.2)

where \( \varepsilon_1 \) is the emissivity of plate 1 and \( \sigma \) is the Steffan-Boltzmann constant. The absorption coefficient, \( \kappa \), is the linear absorption coefficient of the medium, with units of inverse length. The spectral character of the salt cannot be directly measured by this technique, thus, in this chapter all radiative quantities are to be interpreted as integral over all wavelengths.

The heat energy emitting from a second plate to the first is similarly

\[ q_2(z) = A_2 \varepsilon_2 \sigma T_2^4 e^{-\kappa z} \]  \hspace{1cm} (3.3)

If both surfaces are assumed to be black surfaces with \( \varepsilon_{1,2} = 1 \), then combining the previous 3 equations, the net heat flux from conduction and radiation between two plates separated by a distance of \( \Delta z \) is, if the terms are assumed independent,

\[ q_{tr} = q_{con} + q_{rad} \]  \hspace{1cm} (3.4)

or

\[ q_{tr} = A_m k_m \frac{\Delta T}{\Delta z} + A_m e^{-\tau} \sigma (T_1^4 - T_2^4) \]  \hspace{1cm} (3.5)

where the optical thickness is defined as

\[ \tau = \kappa \Delta z \]  \hspace{1cm} (3.6)

Since the thermal conductivity of the salt is at least reasonably well known for many salts, it would be theoretically possible to measure the heat flux through a sample and
attempt to isolate the radiative component after accounting for all other heat transfer pathways, by attempting to isolate $\tau$ in equation (3.5) or a coupled heat transfer solution. However, if this measurement were attempted, a 1% error in $q_{tr}$ could lead to a 100% error in measurement of $\kappa$, as the change in $q_{tr}$ with $\kappa$ is relatively small compared to other terms. There are many sources of potential error, such as inaccuracy in the knowledge of the thermal conductivity of the salt, or the presence of small convective cells in the fluid, that could lead to an error of 1% or more. As such, a more robust method of examining the experiment was desired.

Dividing through by the linear temperature gradient and $A_m$, the heat flux in Equation (3.5) can be written as an effective thermal conductivity, $k_e$, that is normalized to the cross sectional area of the radiative surface normal to the boundary planes. This quantity is defined

$$k_e = \frac{q_{tr}}{A_m \Delta T} = k_m + e^{-z} \frac{\sigma(T_1^4 - T_2^4)\Delta z}{\Delta T}$$

(3.7)

Using Equation (3.7), Equation (3.5) is rewritten as

$$k_e = k_m + e^{-z} \frac{\sigma(T_1^4 - T_2^4)\Delta z}{\Delta T}$$

(3.8)

Without radiation heat transfer, $k_e$ would be equal to the molecular conductivity of the medium. Conversely, any change in the value of $k_e$ will be dominated by changes in radiation heat transfer. Measurement errors in $k_e$ that are constant, oscillate randomly
around a constant, or scale with the linear temperature gradient, will cancel out and not affect the final results, greatly decreasing the measurement sensitivity to errors.

The radiation term, denoted as \( X \), is defined as

\[
X = \frac{\sigma(T_1^4 - T_2^4)\Delta z}{\Delta T}
\]

which has units of \( W/m-K \) and is the ratio of the emissive powers to the linear temperature gradient. Equation (3.7) can be rewritten in terms of \( X \)

\[
k_e = k_m + e^{-\tau}X
\]

The utility of Equation (3.10) is that it allows experimental data to be decomposed into a radiative term and a conduction term.

Temporarily ignoring the temperature dependence of the thermal conductivity from Equation (3.10), the derivative of \( k_e \) with respect to \( X \) will be a function of the geometric conditions as they pertain to radiation. For the approximation derived thus far, the derivative of \( k_e \) with respect to \( X \) is simply

\[
\frac{dk_e}{dX} = e^{-\tau}
\]

This function can easily be manipulated to recover the absorption coefficient if the effective thermal conductivity and \( X \) are known by experimental measurement; i.e.

\[
\kappa = -\frac{1}{\Delta z} \ln \left| \frac{dk_e}{dX} \right|
\]
For a less simplified model of radiation energy transfer, the relationship defined in Equation (3.11) fails to accurately capture the spatial character of radiation transfer. In reality, the salt both emits and absorbs radiation, so the decrease in flux is not strictly exponential. It is a well-established assumption in radiation transfer that for most cases, the emissivity of a medium is identical to the absorptivity. [9] Using that assumption, the P1 approximation for planar media, discussed in Chapter 2, can be derived, and can be solved for a planar case with a conducting medium, yielding the following relation for steady state radiative transfer

\[
q_{\text{rad}} = A_m \frac{1}{1 + \frac{3}{4} \tau} \sigma (T_1^4 - T_2^4)
\]

where the exponential term in Equation (3.8) has been replaced with the term emanating from the P1 approximation.

Using the P1 approximation for the radiative heat flux, Equation (3.4) can be determined with the radiative flux shown in Equation (3.13). A reasonable estimate of the heat transfer rate, \(q_{tr}\), for the geometry shown in Figure 26 is given by Equation (3.14)

\[
q_{tr} = \frac{\Delta T}{\Delta z} A_m k_m(T) + A_m \frac{1}{1 + \frac{3}{4} \tau} \sigma (T_1^4 - T_2^4)
\]

Although this simple equation does not capture all of the physics of radiation heat transfer, it is useful as it allows complex physical interactions to be compared across a
range of scenarios and has a minimal number of variables. The $P_1$ solution is not perfectly accurate, but it is sufficiently rigorous to serve as an analytical tool.

Thus, the task is to define this relationship for a specific physical case and construct an apparatus that can be used to generate usable data. Due to space constraints, it is impossible to construct a measurement apparatus consisting of infinite planes. The geometry shown in Figure 27 represents a more physically realizable experimental setup. A cylindrical sample is contained within mirror reflective walls. Mirror reflective walls mean that all radiation emitted from one end plate reaches the other plate, regardless of emission angle, mimicking infinite planar geometry. The presence of walls means that some energy will transfer through the walls by conduction and that the walls will be radiatively in communication with the ambient background. This creates a path for energy to “leave” the system, as it participates with an energy sink not strictly in contact with $T_1$ or $T_2$ or a measurement of heat flux. Additionally, the presence of walls will cause the temperature profile of the salt to exhibit radial, as well as axial variation. This model envisions an experiment surrounded by a vacuum, which does not obstruct radiation but does prohibit conduction.
Figure 27. Geometry description for more complex experimental geometry.

Since radiative loss to the environment will be significant, a modification is introduced to Equation (3.14) to account for some level of radiative loss from the chamber walls, assumed to be at the average of the plate temperatures, to the environment at ambient temperature. A term is also added to account for transfer through the walls of the chamber, which necessarily surrounds the salt. The notation has been updated to include a subscript $s$, for the salt and a subscript $w$, for the walls. For the emissive portion of the calculation, the walls are assumed to be at a uniform, average temperature, $T_{\text{avg}} = 0.5(T_1 + T_2)$, with external area approximately $A_{\text{ext}}$. 

\[ T_{\text{avg}} = 0.5(T_1 + T_2) \]
This equation will be referred to as the additive approximation, because it is used to calculate the total heat transfer assuming all energy transfer methods are de-coupled and that their contributions to \( q_{tr} \) are added together. The first term in Equation (3.15) accounts for conductive heat transfer through the walls and body of the chamber. The second term accounts for radiative exchange between black surfaces with a participating medium using the \( P_1 \) approximation, and the final term accounts for radiative losses to the environment. A set of tunable parameters are introduced to account for the non-linearity and non-uniformity of the exact solution. Two parameters, \( B_1 \) and \( B_2 \) are set to unity as initial guesses, while \( B_3 \), is set to 0.1, as the metal wall of the external surface will be a low emissivity surface. The numbering of terms in Equation (3.15) is in order of their magnitude: conduction will dominate, followed by radiative transfer, followed by external losses.

Equation (3.15) can be re-written in terms of the radiation parameter \( X \) by substituting in Equation (3.9)
\[
k_e = B_1 \left[ k_s(T) + \frac{A_s}{A_x} k_u(T) \right] \\
+ B_2 \times \frac{1}{1 + \frac{3}{4} \tau} X \\
- B_3 \times \frac{A_{ext}}{A_s} \frac{(T_{avg}^4 - T_{amb}^4)}{T_1^4 - T_2^4} X
\]  \tag{3.16}

The derivative with respect to \(X\) of Equation (3.16) is as follows

\[
\frac{dk_e}{dX} = \frac{d}{dX} \left[ B_1 \left[ k_s(T) + \frac{A_s}{A_x} k_u(T) \right] \right] \\
+ B_2 \times \frac{1}{1 + \frac{3}{4} \tau} - B_3 \times \frac{A_{ext}}{A_s} \frac{(T_{avg}^4 - T_{amb}^4)}{T_1^4 - T_2^4} \\
- \frac{d}{dX} \left( \frac{(T_{avg}^4 - T_{amb}^4)}{T_1^4 - T_2^4} \right)
\]  \tag{3.17}

The first and last terms on the right-hand side of Equation (3.17) are not strictly zero. The first term will vary with \(X\) if the thermal conductivity is non-constant. The last term can vary with \(X\) if the numerator and denominator do not scale exactly proportionally. However, both of these terms are, in practice, small relative to the middle terms, especially if the experimental data is acquired at similar temperatures. Assuming both of these terms are zero yields the following, simpler, relation

\[
\frac{dk_e}{dX} = B_2 \times \frac{1}{1 + \frac{3}{4} \tau} - B_3 \times \frac{A_{ext}}{A_s} \frac{(T_{avg}^4 - T_{amb}^4)}{T_1^4 - T_2^4}
\]  \tag{3.18}
If the two fitting parameters and areas are known, and temperatures are recorded, then the optical thickness can in this way be recovered from measurements of the heat flux through a sample chamber by algebraic manipulation of Equation (3.18). In practice, this will be done computationally in order to average over multiple data points with various temperatures.

3.2. Experimental Method

Based on the mathematical foundations, it is possible to determine a series of measurements that would yield viable experimental data. A sample volume is to be contained in a chemically inert chamber between two graphite plates. Thermocouples will be used to measure the temperature near the graphite plates, while a heat flux sensor is employed to measure the total heat energy transferred through the sample and the nickel walls. By measuring the heat flux at various temperatures, a relationship can be determined for the effective thermal conductivity of the sample chamber as a function of the radiation parameter, $X$. Analysis of the derivative of $k_e$ with respect to $X$ will reveal the optical thickness of the sample chamber, and thus the absorption coefficient of the salt.

The experiment will be performed inside a vacuum bell jar, protecting the graphite plates from oxidation and limiting conductive losses to the environment. If proper values are obtained for the three fitting parameters, then the additive model should behave similarly to the experimental model. If this can be achieved, it is straightforward to determine the optical thickness of the chamber by examination of the model.
By performing two calibration tests with known absorption coefficients, zero and infinity, the parameters $B_2$ and $B_3$ can be experimentally determined. For the first calibration, the sample chamber is filled with a radiatively opaque insulation, effectively an absorption coefficient of infinity. In practice, this will be accomplished by layering silica thermal insulation between round pieces of sheet metal to block both radiative and conductive energy transfer. This setup renders the second term in Equation (3.18) equal to zero, and only the radiative loss term remains, as seen below

$$\frac{dk}{dX} = B_2 \times 0 - B_3 \times \frac{A_{\text{ext}}}{A_y} \frac{T_{avg}^4 - T_{amb}^4}{T_1^4 - T_2^4}$$

By fitting $B_3$ to calibration data generated in this manner, the behavior of the external radiation can be captured, including such effects as the effective emissivity and area of the external surface.

Next, the insulation is removed and the sample chamber is left empty and exposed to the vacuum through a filling port. This results in unobstructed radiation heat transfer between the two plates. Since the radiative loss term is already determined, the radiative transfer correction term, $B_2$, can be fitted to match the variation with $X$, as seen below

$$\frac{dk}{dX} = B_2 \times \frac{1}{1 + \frac{3}{4} \times 0} - B_3 \times \frac{A_{\text{ext}}}{A_y} \frac{T_{avg}^4 - T_{amb}^4}{T_1^4 - T_2^4}$$

(3.20)
By fitting $B_2$ to this data, information about the radial variation in heat flux and temperature, gray surfaces, and other terms that should scale the radiative properties, can be accounted for.

It would be difficult to directly calibrate $B_1$, because doing so would require the sample chamber be filled with a substance fully opaque or clear to radiation, but with identical thermal conductivity to the candidate salt. This material simply does not exist. However, the exact value of $B_1$ does not affect the determination of absorption coefficient, so it does not affect results if the fitting of $B_1$ is less rigorous, or not performed at all. $B_1$ can be fit by matching the constant term, that is the term that does not vary as $X$, in the data from either initial calibration.

Once the calibration terms are known, an experiment can be performed with the material under investigation in the sample chamber. The value of $\kappa$ which, for the same boundary temperatures, produces the same value of $dk_c/dX$ should closely approximate the physical value for the salt.

3.3. Computational Evaluation

In order to evaluate the potential experimental model, the proposed experiment was simulated using the computational code ANSYS Fluent. [19] First, a simplified model was analyzed to show an idealized version of the experiment. After this validation, a full model was simulated, in order to evaluate the technique using a more representative simulation.
3.3.1. Simplified Fluent Model

The additive model is obviously not accurate enough on its own to be useful. Implemented without properly tuned fitting parameters, it simply serves to capture the functional behavior of various physics, but not their relative total contributions. Numerous complexities will need to be incorporated through the fitting parameters in order to cause the additive model to reflect physical data. A simplified experimental model was generated in Fluent in order to examine the ability of the additive model to do this. The simulated geometry is shown in Figure 28.

![Diagram of simplified experimental geometry modeled in Fluent](image)

**Figure 28. Simplified experimental geometry as modeled in Fluent**

Two circular plates, representing graphite coated Inconel, with constant thermal conductivity $k_g$, have one external edge insulated and one edge at a fixed temperature. In between the plates, a volume is modeled as a radiatively participating salt with thermal conductivity $k_s$. 

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conductivity $k_s$, and a conductive wall with thermal conductivity $k_w$, representing a nickel crucible. The interface between the end plates and the salt is treated as black, while the interface between the salt and crucible wall is treated as a mirror wall. The outer wall of the crucible is modeled as having a low emissivity ($\varepsilon = 0.1$) and being in radiative communication with a black body at 300K, but subject to no conductive losses, to model the vacuum enclosure.

The 2D simulation was performed on the mesh geometry that is shown in Figure 29. The minimum orthogonal quality of the mesh is 0.917 out of 1, and the maximum aspect ratio is 6.3.
Radiation was treated using discrete ordinates with a gray radiation approximation, meaning that radiative properties are integrated over the entire electromagnetic spectrum. All thermal conductivities were kept constant as a function of temperature. External radiation was treated with a radiation boundary condition in Fluent, and an interface temperature of 300K. The salt-crucible interface is modeled as fully reflective with diffuse radiation, while salt-graphite interface is modeled as black.

3.3.2. Simplified Fluent Results
The first calibration test involves the sample chamber filled with an opaque material, such that radiation cannot transfer through the sample chamber, similar to the situation described by Equation (3.19). This was simulated by turning off the radiation solver in the salt region. A series of temperature points were simulated by fixing the upper and lower boundary temperatures, resulting in values of \( X \) between 2 and 4. The resulting effective thermal conductivity was calculated, for the additive model using Equation (3.15) or in Fluent by computing effective conductivity using the surface integral heat flux and the definition of effective conductivity,

\[
k_e = \frac{q_u \Delta z}{A_s \Delta T}
\]  

(3.21)

A script was written in MatLab to determine the value of \( B_3 \) which caused \( dk_e / dX \) for the additive model to match the data from Fluent as closely as possible. A value of \( B_3 = 0.0523 \) results in a match between the slopes of the additive model and the Fluent results. Figure 30 shows the result of the simplified experiment and the additive model after fitting \( B_3 \),

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Figure 30. Calibration data from the Additive model and from Fluent for a calibration with an opaque media in the sample chamber

where the $B_3$ fitting parameter for the experiment is estimated using Equation (3.19). Examination of the additive model shows that $B_3$ is an effective emissivity which relates the 0-D temperature averaged term to the 2D calculation. The derivative of $k_e$ with respect to $X$ is negative, as radiative losses increase with $X$ while the conduction terms do not, and no increased radiation is seen through the chamber, since it is filled with an opaque material. This results in a decreasing effective conductivity of the salt with increasing radiation.
Next, a simulation was performed with a non-conducting, non-absorbing material in the sample chamber, simulating vacuum conditions. The same temperature points were simulated, and Figure 31 shows the results of the data after calibration of $B_2$.

**Figure 31. Calibration data from the Additive model and from Fluent for a calibration with vacuum in the sample chamber**

where the $B_2$ fitting parameter for the experiment is estimated using Equation (3.20). The slope of the relationship is positive, as the increase in radiative transfer through the empty chamber is of a greater magnitude than increased emission to the environment, such that total heat transfer increases with $X$. As expected, the vacuum chamber has a significantly higher effective conductivity compared to a chamber filled with insulation, as noted by the
increased value of $k_e$ at each value of $X$ compared to the insulated case. A value of $B_2 = 0.797$ results in a match in the slopes of the additive model and Fluent results.

The parameter $B_1$ does not need to be fit to perform the analysis, as such, the process is omitted.

3.3.3. Analysis of Simplified Model

Once the coefficients are known for the experimental setup, an experiment can be performed with a conductive, participating salt in the chamber. From this, the additive model can be used to generate a function that relates $dk_e/dX$ and $\kappa$. With this relationship, the optical thickness of the chamber, and thus, $\kappa$, can be determined from an experimental determination of $dk_e/dX$.

The utility of using Fluent is that the exact absorption coefficient is known beforehand. The additive model can be generated for the same temperature points as the Fluent model, and compared to the Fluent results. For example, the results of the tuned additive model and simplified Fluent results with an absorption coefficient of $5\text{m}^{-1}$ is shown in Figure 32.
Using the “experimentally determined” fitting parameters, the effective conductivity can be predicted for a given case over a range of absorption coefficients, $\kappa_i$.

\[
k_e(i) = 0.64 \left[ k_s + \frac{A_w}{A} k_w \right] + 0.797 \times \frac{1}{1 + \frac{3}{4} (\kappa_i \Delta z)} X \\
-0.0523 \times \frac{A_{ext}}{A_\Delta} \left( \frac{T_{avg}^4 - T_{amb}^4}{T_1^4 - T_2^4} \right) X \tag{3.22}
\]

Using the simplified Fluent model, various absorption coefficients were simulated, covering a range of absorption coefficients that molten salts might exhibit, with optical thicknesses from zero to unity. The value of $dk_e/dX$ was determined for each case simulated in Fluent. The curve relating $dk_e/dX$ to $\kappa$ was generated for the additive
model. That curve, as well as for the individual data points generated in Fluent is shown in Figure 33.

Figure 33. Effective conductivity “measured” from Fluent compared to prediction based on additive model.

The absorption coefficient which produced the same value of $\frac{dk_e}{dX}$ in the additive model was determined, and compared to the value input to Fluent. The result of this method of analysis is shown in Figure 34, which shows the value which would have been measured by this method compared to the known input value.
Figure 34. Expected measured absorption coefficient compared to input

3.3.4. Conclusions of Simplified Model

The results are generally in good agreement with the input, especially in the likely value of the absorption coefficient, between $5\text{m}^{-1}$ and $20\text{m}^{-1}$. Based on the results of Chapter 2, it is noted that a high degree of accuracy in knowledge of $\kappa$ is not necessary to perform useful heat transfer calculations, and the accuracy indicated by Figure 34 would be sufficient at improving knowledge of the heat transfer properties of molten salt, especially considering the high degree of uncertainty at present.

Additionally, there are a number of ways that the analysis could have been improved to improve accuracy, but these were not done. Specifically, after performing this analysis, it was noticed that the diffuse fraction of reflected energy at the wall boundary
was set to 1 in Fluent, instead of the correct value of zero, or close to zero. This partially explains why the predicted values are low for low optical thickness and higher for large optical thickness. This oversight was not corrected, as the purpose of performing the simplified simulation was simply to demonstrate the potential utility of the method. The correct wall diffuse fraction, as well as efforts to improve the accuracy of the analysis, were implemented on the more complex physical model, discussed below.

3.3.5. Complex Fluent Model

A higher fidelity Fluent simulation was performed in order to examine how well the corrected additive model is able to produce results given a more accurate treatment of radiation loss, complex geometry, and non-constant thermal conductivity. To better understand the complex model, the physical experimental design must be briefly described.

Table 1 describes the components shown in Figure 35. The experiment consists of a heater, (A) which heats one face of a nickel crucible (D) in which sits a sample of molten salt (E). The heat flux through the chamber is measured by a High-Temperature HT-50 heat flux sensor (H). The entire setup rests atop a stainless steel rod which serves to provide thermal inertia to the system and to increase the temperature gradient between the crucible and the outer test chamber. It was desired to increase the thermal inertia of the system in order to provide a consistent contact flux for the heat flux sensor while damping any variation in system temperature. The steel rod sits on top of a thin plate of high temperature
The entire setup is supported by a water-cooled vacuum base, not shown.

Table 1 shows the components of the IRAC in the order of heat flow.

<table>
<thead>
<tr>
<th>Component</th>
<th>Function</th>
<th>Material</th>
<th>Label</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heater</td>
<td>Set hot-side temperature</td>
<td>Multiple</td>
<td>A</td>
</tr>
<tr>
<td>Upper Flange</td>
<td>Interface with heater</td>
<td>Inconel 618</td>
<td>B</td>
</tr>
<tr>
<td>Graphite Flange</td>
<td>Blackbody Surface and gasket</td>
<td>Graphite</td>
<td>C</td>
</tr>
<tr>
<td>Crucible Walls</td>
<td>Contain sample</td>
<td>Ni 203</td>
<td>D</td>
</tr>
<tr>
<td>Molten Salt</td>
<td>Test Sample</td>
<td>FLiNaK</td>
<td>E</td>
</tr>
<tr>
<td>Graphite Flange</td>
<td>Blackbody surface and gasket</td>
<td>Graphite</td>
<td>F</td>
</tr>
<tr>
<td>Lower Flange</td>
<td>Structural support for graphite</td>
<td>Ni 203</td>
<td>G</td>
</tr>
<tr>
<td>Heat Flux Transducer (HFT)</td>
<td>Measure heat flux</td>
<td>Multiple</td>
<td>H</td>
</tr>
<tr>
<td>Cold Finger</td>
<td>Create thermal inertia and improve contact for HFT</td>
<td>SS316</td>
<td>I</td>
</tr>
<tr>
<td>Insulation</td>
<td>Allow larger temperature gradient</td>
<td>AlSi</td>
<td>J</td>
</tr>
<tr>
<td>Baseplate</td>
<td>Maintain vacuum and cooling</td>
<td>Al 6061</td>
<td>K</td>
</tr>
</tbody>
</table>

Table 1. IRAC Thermal Components and their Function
As opposed to the simplified model, for a more complex analysis, the experiment was modeled to include the heater, flanges, ultimate heat sink, and vacuum enclosure using 2-D axisymmetric geometry. A view of the computational mesh is shown in Figure 36. The mesh is fairly dense inside the salt, in order to capture the more complex physics of conduction and radiation occurring within the salt. The minimum orthogonal quality of the mesh is 0.319, and the maximum aspect ratio is 5.69. The domain representing the salt is modeled with mapped face meshing with 1,200 elements. The meshing is relatively
coarse overall, as the model would have to be run a significant number of times in order to generate the necessary data, and computational speed was preferred over accuracy.

Figure 36. Results of Multi-Component meshing For the Complex Model

Convection was not modeled, as attempting to model convection coupled with radiation caused convergence issues. However, convective additions to the heat flux will
scale linearly with $\Delta T$, and should therefore be a small effect, if any, on the measurements of the absorption coefficient. Additionally, because the temperature gradient is aligned with gravity, convective cell formation should be minimal. If present, any convective effects should be encapsulated within the conduction terms of the approximation and should not greatly affect the radiative results.

The boundary conditions were modeled as follows. The temperature of the Inconel heater was set at a fixed, uniform temperature. The boundaries of the base plate were also set, as it will be water-cooled by a chilled water system. The outer boundary of the vacuum was modeled as an adiabatic boundary with emissivity of 0.1 at 300K, as the experiment will be surrounded by a sheet metal radiation shield inside a vacuum enclosure. The emissive surfaces of the crucible that interact with the environment were also give emissivities of 0.1, as an attempt to estimate the emissivity of the metal surface of the nickel. The graphite plates were modeled as black. The internal wall of the crucible, which has been hand polished, were modeled as having an emissivity of 0.05, with a specular fraction of reflected light of 0.95.

Non-constant thermal conductivities were input in Fluent as linear functions of temperature. Modeling non-constant thermal conductivity is important, as the variation in thermal conductivity with temperature means the first term in equation (3.17) will not be zero. However, since conduction through the walls is significantly greater than conduction through the salt, the effect of increasing conductivity in the nickel walls should be captured
within the fitting parameter for radiation losses, as this term also works to capture effects which vary with $X$.

The conductivity of the nickel walls was modeled as

$$k_n(T) = 0.0235 \times T + 46.441$$  \hspace{1cm} (3.23)

and is taken from [20]. The salt conductivity was modeled as

$$k_s(T) = 5 \times 10^{-4} \times T + 0.43482$$  \hspace{1cm} (3.24)

and is taken from Allen [21].

Upon initial examination of temperature distributions within the domain, it was clear that there was a larger than expected difference between the temperature where a thermocouple could be located, and the graphite surface temperature. The graphite surface temperature should be used as the boundary temperature in the additive model, but it cannot be directly measured. Due to the flanges, which provide a large surface for radiation losses, there is significant temperature drop between the temperatures at the location of the thermocouple, and the average temperature of the radiating surface. This effect was not present in the simplified model, due to the use of adiabatic outer boundary conditions and the lack of flanges. The temperature recorded for the heat flux transducer (HFT) is the average internal temperature of the domain which represents the device, while the heater temperature recorded was the boundary condition, which is modeled at the height of the thermocouple within the heater assembly. Compared to a one-dimensional analysis, or a simplified analysis with insulated flanges, there is a significant temperature difference.
between the measurement points and the surface temperatures of the graphite for both the upper (C) and lower (F) graphite flanges. The centerline temperature versus vertical position for a representative simulation is shown in Figure 37.

![Figure 37. Centerline Temperature for representative simulation.](image)

The radiating surface of the upper graphite is located at 9.2cm, represented by the rightmost dashed line, and is the temperature which should be used in the additive model. The heater thermocouple is located at 9.8cm, and for the simulation in Figure 37, it can be seen that the heater is approximately 18K hotter than the centerline temperature of the upper graphite. Similarly, the thermocouple in the HFT reads approximately 15K cooler than the centerline temperature at the face of the lower graphite. If this temperature difference were known, the graphite face temperature could be estimated from the measured thermocouple temperature.
Using the data from each of the Fluent simulations performed, the temperature difference between the heater set-point temperature and the area-averaged upper graphite surface temperature was calculated. The area averaged temperatures are different from the centerline temperature differences due to radial variation. The temperature difference for the upper surface fit well as a function of heater temperature. Figure 38 shows the temperature difference between the heater thermocouple and the upper graphite surface temperature from the Fluent model.

![Figure 38. Temperature correction for hot-side experimental temperature](image)

For the hot side, the temperature correction, that is the amount by which the heater thermocouple should be adjusted to match the graphite surface temperature, was observed to have significant curvature, such that a second order polynomial correction was used.
\[ T_{\text{hot}}' = T_{\text{hot}} - 0.0001T_{\text{hot}}^2 + 0.032T_{\text{hot}} - 8.797 \] \hspace{1cm} (3.25)

where \( T_{\text{hot}}' \) is the estimate of the upper graphite surface temperature and \( T_{\text{hot}} \) is the heater thermocouple sensor temperature.

Using the data from each of the Fluent simulations performed, the temperature difference between the thermocouple temperature from within the HFT and the area-averaged lower graphite surface temperature was calculated. The temperatures fit well as a function of HFT temperature. Figure 39 shows the temperature difference between the HFT and the lower graphite surface temperature from the Fluent model.

Figure 39. Temperature correction for cold-side experimental temperature
The correction to the cold-side temperatures, that is the amount by which the HFT thermocouple reading should be adjusted to match the lower graphite surface temperature, was observed to be linear and applied as

\[ T'_{\text{cold}} = T_{\text{cold}} + 0.0701 T_{\text{cold}} - 23.7566 \]  \hspace{1cm} (3.26)

where \( T'_{\text{cold}} \) is the estimate of the lower graphite surface temperature and \( T_{\text{cold}} \) is the HFT thermocouple sensor temperature.

It was investigated whether a-priori knowledge of the temperature dependent thermal conductivities of the salt and nickel walls could be leveraged to improve the accuracy of the overall analysis. This is indeed the case, and can be applied in the additive model by updating \( k_s(T) \) and \( k_w(T) \) at \( T_{\text{avg}} \) for each calculation. Unfortunately, attempting to improve the overall accuracy in this manner is counterproductive, as the resulting measurement of \( \kappa \) becomes highly sensitive to the value generated by Equations (3.25) and (3.26). This is due to the fact that such a large fraction of energy is transferred by conduction. If the temperature correction is exactly right, then a small improvement in accuracy is gained. However, if the temperature corrections are off by even a very small amount, the average temperature would be wrong, and the thermal conductivity will vary with \( X \), not as it physically does, but as the error in the correction. Allowing the thermal conductivity to change in this manner dominates the changes due to optical thickness and thus significantly degrade the experimental accuracy. Since confidence in the temperature
correction is low, it was decided to not include temperature dependent thermal conductivities in the additive model used for analysis.

### 3.3.6. Complex Fluent Results

A series of simulations were performed in Fluent with various values of the gray absorption coefficient for the salt. The derivative of effective thermal conductivity with respect to \( X \) was calculated for each value of \( \kappa \), and is shown in Figure 40.

![Figure 40. Temperature corrected relation between optical thickness and slope.](image)

For each of the data points simulated in Fluent, the additive model, as given by Equation (3.15), was used to determine the optical thickness of the chamber, and thus, the absorption coefficient of the salt. The output of the additive model was compared to the
known value input to the Fluent simulation. The ratio of the predicted $K$ output from the analysis to the simulated values of $K$ input to Fluent, was calculated and is shown in Figure 41.

![Figure 41. Ratio of predicted absorption coefficient to simulated absorption coefficient.](image)

Figure 41 indicates that the measurement of the absorption coefficient may be off by as much as 25% from the actual value. It was desired to see if any further improvement to the analysis could be undertaken to improve the accuracy of the present analysis.

Investigation of the Fluent results as compared to the additive model, indicates that the variation in $dk_c/dX$ varies less strongly with optical thickness than would be predicted by the $P_1$ approximation. This can be seen in Figure 42, which plots the curve
relating $dk_e/dX$ to the chamber absorption coefficient for the additive model as well as the same curve generated from the Fluent simulations.

![Comparison of Additive model with P1 Approximation and Fluent Results](image)

**Figure 42. Comparison of Additive model with P1 Approximation and Fluent**

**Results**

As the absorption coefficient increases, the additive model predicts $dk_e/dX$ will decrease more than the Fluent results indicate. By reducing the coefficient of $\tau$ in Equation (3.13), and thus flattening the curve of $dk_e/dX$, the accuracy of the technique can be improved. However, it would be inadvisable to adjust the relation arbitrarily in order to agree with the Fluent results; the results in Fluent may be the result of some computational or user error which should not be propagated forward to experimental results.
In order to determine a more accurate relation for use in the additive model, the exact equations for combined radiative and conductive heat transfer in a planar medium were solved for the conditions of interest. While generally accurate, the $P_1$ approximation may not exactly capture the effects of combined radiation and temperature dependent conduction especially for relatively thin geometries. Based on an exact solution of combined heat transfer for a participating medium with the properties of FLiNaK, the relation shown in Equation (3.13) can be updated based on the exact solution. This analysis is described in Appendix A. The new relation is shown to be

$$ q_{rad} = A_m \frac{1.028}{1 + 0.649 \times \tau} \sigma(T_1^4 - T_2^4) \quad (3.27) $$

The relation defined by Equation (3.27) can be used as the functional relationship built into the additive model, instead of Equation (3.13). Doing so, the Fluent results can be re-analyzed.

Using the updated additive model, the value of the absorption coefficient can be predicted based on heat transfer experiments simulated in Fluent. The output of the analysis compared to the absorption coefficient input to Fluent is shown in Figure 43.
Figure 43. Expected measured absorption coefficient compared to input for the Complex Model

The ratio of predicted to simulated values is shown in Figure 44.
The preceding analysis predicts that measured value of the absorption coefficient for a candidate salt can be reasonably expected to be within approximately 10% of the actual value, an accuracy that should provide useful data to inform heat transfer calculations. The additive model can be used to determine absorption coefficients within acceptable accuracy for heat transfer purposes. Next, the experimental apparatus was constructed.

3.4. Construction

Based on the prior analysis, and within material constraints, the integral radiation absorption facility was constructed at The Ohio State University. The components
enumerated in Table 1 are identified in Figure 35, which shows a cross section of a Computer Assisted Design (CAD) model of the experimental setup.

FLiNaK in powdered form is significantly less dense than liquid form. Therefore, the sample chamber is designed to be filled in a vertical orientation inside an inert glove box by attaching the end of the filling port to a stainless steel chamber. The filling and operational procedures will be described in more detail in Chapter 5, which discusses the results of experimentation.

A photograph of the assembled test chamber before calibration is shown below.
Temperatures are measured by K-Type thermocouples embedded in the heater body and the heat flux sensor. The heat flux sensor is a custom build, solid-state HFT constructed by iTi technologies. It uses a DC thermopile and a high sensitivity DC voltage sensor to determine heat flux. The graphite gaskets, used as black surfaces and sealing surfaces, are Garlock pure graphite gaskets. All fasteners are Monel fasteners in order to withstand the
high temperature of operation. The heater is a BlueWave scientific 1.6” Inconel substrate heater powered by a 300W BlueWave power supply and temperature controller.

3.5. Conclusion

High temperature advanced reactors cooled with molten salts will encounter conditions where radiation heat transfer may be significant. It is currently difficult to account for radiation heat transfer, as there is no reliable data for absorption coefficients in molten salts. In order to address that deficiency, a facility has been designed and constructed at the Ohio State University in order to measure the absorption coefficients in molten salts. An additive method for evaluating the heat flux data and determining absorption coefficients has been determined. The experiment was simulated with computational heat transfer software, and the analysis indicates that the apparatus should be capable of resolving a relevant range of integral absorption coefficients within 10% of their actual value.
Chapter 4. Ab-Initio Estimation of Photon Absorption in Molten Salts

As discussed in Chapter 1, photon-phonon effects are a large source of photon absorption relevant to heat transfer in pure molten salts. Since most pure salts are composed of relatively large band-gap materials, only high energy photons can excite electrons and consequently be absorbed. However, upon the introduction of impurities in a salt, the band structure changes, allowing for different photon absorption energy ranges.

Prior research has suggested that the presence of transition metals will substantially increase absorption coefficients in molten salts [11] and allow the absorption of much lower-energy photons than would be allowable in a pure molten salt. To date, the exact manner and magnitude of this effect has not been systematically investigated. The presence of transition metals in the mixture can create additional energy states, facilitating photon-electron interactions at energies relevant for heat transfer. They can also shrink the bandgap by increasing bond lengths. Whether these elements are present due to being constituents of the salt, such as in KF-ZrF4, or are present as impurities in the mixture, such as Chromium leached from stainless steel, the effect they may have on absorption coefficients can be investigated using ab-initio methods.
There are two processes that govern inelastic photon absorption in molten salts. The first, inelastic phonon scattering and absorption, could be, in principle, modeled from first principles [22]. However, doing so would be a major undertaking with potentially little payoff, since sufficient experimental data exist on photon-phonon interactions in candidate salts that allow generating a reasonable-quality estimate of these effects, as discussed in Chapters 1 and 2. The second, photon-electron interactions, can also be modeled from first principles, and should especially capture the effect of metal ions in the salt, for which the experimental situation is much less clear with little quantitative data. This is especially cumbersome since the experimental capabilities required to directly measure photon-electron interactions are not available within the scope of this project. Therefore, research efforts were focused on computational methods to understand the specific effect of transition metals on the electronic structure and the resulting change in absorption coefficients from electron-photon processes in halide salts.

4.1. Background

The goal of the present effort is to calculate linear absorption coefficients in the liquid structures of molten salts. The absorption coefficient has been defined as the exponential decrease in photon intensity as the photons pass through a material along a path-line. This attenuation is mathematically defined

\[ \frac{I_x(r)}{I_x(0)} = e^{-\kappa_x r} \]  

(4.1)
where $I$ is the photon intensity, $r$ is the distance of travel along a path-line with units of length, and $\kappa$ is the absorption coefficient with units of inverse length. The subscript $\lambda$ denotes that the quantity has a spectral dependence. The dimensional linear absorption coefficient $\kappa_\lambda$ is the formulation employed in radiative heat transfer calculations. The absorption coefficient can be related to the imaginary portion of the complex index of refraction, often referred as the absorptive index and herein denoted as $k_{\text{abs}}$. This relation is accomplished by examination of the Poynting Vector, [23] which shows that an electromagnetic field will decrease exponentially as it develops spatially through a medium. The absorption coefficient can then be defined as a function of the absorptive index through Equation (4.2),

$$\kappa_\lambda = 4\pi k_{\text{abs}}(\lambda) / \lambda$$

where $\lambda$ is the wavelength at the energy of interest.

The absorptive index is related to the complex dielectric of a material using Equation (4.3), the derivation of which is shown in [9] and reproduced as

$$k_{\text{abs}} = \frac{1}{2} \left( \sqrt{\varepsilon_{\text{re}}^2 + \varepsilon_{\text{im}}^2} - \varepsilon_{\text{re}} \right).$$

The dielectric tensor can be calculated using the methodology of Gajdoš et al. [24] based on the electronic density of states (DOS). The dielectric tensor, also known as the permittivity tensor, is a tensor quantity which defines the resistance imposed on the motion of an electric field through a material.
Therefore, the challenge is to determine accurate DOS for relevant materials. Once the DOS is known, the transitions can be calculated, and the dielectric tensor can be determined. The dielectric tensor can be transformed into the linear absorption coefficient useful for heat transfer calculations. Thus, computational efforts were undertaken using available simulation packages to determine the density of states in molten salts.

4.1.1. DFT and VASP

The Vienna ab-initio Simulation Package (VASP) [25] is a plane-wave Density Functional Theory (DFT) package capable of examining a wide range of material properties. Density functional theory is a computational strategy to solve for the electronic structure and the resulting forces and their effect on the positions of atoms within a periodic material. The utility of DFT is that it generates high levels of accuracy without the need for pre-determined potentials or without solving exceedingly complex mathematical problems.

It is not generally a challenge to solve for the force on a single electron using the Schrödinger equation

\[
-\frac{\hbar}{2m} \nabla^2 \Psi + V \Psi = E \Psi
\]

(4.4)

where \(\hbar\) is reduced Plank’s constant, \(m\) is the electron mass, \(\Psi\) is electron wave function, \(E\) is the electron energy and \(V\) is the external potential. The effect of Equation (4.4) is that the total energy of an electron is a function of its kinetic energy and the potential it is subject to. For electrons within a continuous media, the potential for the electron is a
function of repulsion by the negative charge of other electrons, as well as attraction to the positive charges of all nuclei. If there are numerous atoms with their attendant electrons in a computational domain, then the potential energy of the electron will be the summation of the interactions between the electron of interest and each of the other components. This process must be extended to all electrons in the system of interest. In this manner, Schrödinger’s equation for an individual electron is expanded to a system with $N$ electrons at positions $\mathbf{r}_i$ and $M$ positive nuclei at positions $\mathbf{R}_j$,

$$\left[ -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 + V_{\{\mathbf{r}_j\}}(\{\mathbf{r}_j\}) + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{M} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \right] \Psi_n = E_n \Psi_n \tag{4.5}$$

For all but the simplest and most elemental problems, solutions to the multibody Schrödinger equation exceed the capabilities of existing computational resources. [26] Density functional theory circumvents this numerical complexity through a set of simplifications that together produce a less intractable numerical problem while still leading to acceptable accuracy.

DFT is predicated on two theoretical developments. The first is the proof by Hohenberg and Kohn [27] that the total energy minimization of an electron density produces the electron configuration and energy of the ground state solution to the Schrödinger equation. Second is the development by Kohn and Sham [28] to treat the electronic interactions in the form of a charge density interacting with each electron separately. Thus, density-functional theory is a method where the many-body interactions
between electrons are replaced by looking at one electron at a time, lumping the effect of the other electrons into an effective potential, and fixing the error introduced by some approximation. If the error-fix is done by a functional (i.e. a function of a function, here of the electron density which is a function of position) that only depends on the local electron density, the fixing-approach is known as the local-density approximation (LDA). LDA potentials led to highly unrealistic lattice sizes for the pure crystals. As an improvement over LDA, other functionals have been developed that not only depend on the local density, but also on its gradient. A commonly employed parameterization of this approach is the generalized gradient approximation by Perdew–Burke–Ernzerhof (PBE) [29]. Although PBE underestimates band-gaps, it generally achieves accurate energies and bond lengths. Other approximations usually involve a tradeoff of computational speed, degree of parameterization and applicability to specific problems.

Once the electron structure is determined through solution of the Kohn-Sham equation, a wealth of information can be obtained without the extensive or, in some cases, any, use of empirical functions or parameters. For example, the electronic structure determines the potential field acting not only on the individual electrons, but also on the ions themselves. The simulation of the movement of ions in response to interatomic forces calculated using density functional theory is known as DFT-MD and is employed in the present work to generate the liquid disordered structures of interest.
4.1.2. VASP input files

VASP requires several input files in order to perform computations. A typical VASP calculation requires four input files: INCAR, POSCAR, POTCAR, and KPOINTS.

The INCAR file contains general computational settings and instructions for the VASP code. The values contained in the INCAR file determine what type of calculation is to be performed and how it is to be performed. Specific values used for various calculations are discussed in Section 4.2.2.

Initial atomistic positions are provided to VASP using the POSCAR file by defining a unit cell, with dimensions in Ångstroms and then defining the positions of each individual atom. For optical calculations, atomic positions are taken from the trajectory file, XDATCAR, which contains the positions of the atoms with time.

The POTCAR file contains information about the interaction energy between the core and the electrons in the various valence shells for each species. These files are generated by the VASP developer team and are available from online repositories. Projector-Augmented Wave potentials were used as part of this research, which include electronic properties of core and valence electrons, rather than just valence electrons, and thus are usually better for calculating optical properties. In this research, exclusively PBE-type potentials were used. Additionally, the filled orbitals for Lithium (Li_{sv}) were required to prevent the Lithium from behaving similarly to Hydrogen. The “hard” Fluorine potentials were required to be used as well, where “hard” means that the plane-wave energy
cutoff for the pseudopotential compared to the real potential is smaller, as the soft potentials led to errors calculating electronic properties.

The KPOINTS file tells VASP how to discretize the reciprocal space for numerical integration. More KPOINTS improve the accuracy of the computation, but increase the computational cost.

4.2. Computational Procedure

Predicting optical properties from DFT is an expensive calculation for crystalline materials. It is even more so challenging for amorphous structures, as amorphous structures lack symmetry, can vary significantly depending on atomic positions, and lack well defined structures to start from. [30] The following method was used to generate the absorption spectra for the materials of interest.

4.2.1. Procedure Outline

The details of the computational procedure are discussed in Section 4.2.2. As an introduction and an overview to aid the reader, the procedure is briefly outlined as follows:

1. An initial position vector is generated based on the crystalline structure for the material of interest.

2. The initial vector is relaxed briefly at 0 K to prevent errors caused by high potential gradients.
3. The relaxed structure is simulated using molecular dynamics at temperatures significantly above the melting point of the material in order to randomize the positions of the ions.

4. The randomized structure is simulated using DFT-MD at the temperature of interest for some period of time, and the structure at each time step is recorded.

5. A series of these structures are selected for higher fidelity electronic calculations and optical properties for each individual structure is calculated and averaged.

4.2.2. Procedure Detail

An arbitrary position vector for the desired number and types of atoms in a cubic region is used to begin, the size of which is guessed from the bulk material density. The LiF cell was seeded by generating a 2x2x2 supercell containing 64 atoms using the lattice constant of crystalline LiF. For all other cells, randomized initial positions were taken from the final position vector of the LiF cell, substituting the atoms of the desired mixture at the positions of Li or F as necessary. The chromium impurities were added arbitrarily at interstitial sites into the mixture.

Using the conjugate gradient method, the structure is relaxed at 0 K for 100-200 steps, allowing the ions to move and the box to distort using the IBRION=2 and ISIF=3 tags. This is done to prevent extremely close atoms from causing errors during MD at
temperature. Next, the IBRION tag is set to 0 in VASP to perform DFT-MD, and the atoms are allowed to move at a temperature significantly above the melting point of the material for 500-1000 steps. The temperature is reduced to the desired value and a set of MD runs are performed. The lattice parameter was adjusted by performing DFT-MD for 1000 time steps and examining the pressure trace after the simulation reached equilibrium. If the cell volume is too large, the calculated external pressure will be negative and the cell should be shrunk. If the cell volume is too small, the calculated external pressure will be positive, and must be expanded. The cell volume was adjusted until the mean pressure trace was within a few kJ of zero. This process is easy to parallelize by performing multiple simulations at slightly different densities and observing the resulting pressure.

Finally, a single MD run is performed at the final dimensions for 1500-2000 time steps, saving the position vector at each time step. Once the MD run has been completed, a series of points are selected from the MD run in order to perform optical calculations upon.

Optical calculations require higher fidelity electronic structures than are required for DFT-MD. There are numerous functionals available in VASP to calculate electronic structures and energies. As discussed previously, the default implementation to calculate electronic properties in VASP is the Perdew–Burke–Ernzerhof (PBE) functional to approximate the exchange correlation energy in the Kohn-Sham equation. While PBE accurately recreates bond lengths and physical structures, it can significantly under-
estimate the bandgap of materials. PBE was used for the MD calculations, but a higher accuracy method was desired for the optical calculations. In order to calculate accurate band structures, which are critical to accurately calculate optical properties, is it possible to calculate the exact Hartree-Fock exchange energy (which are known to over-predict the bandgap), and then blend these results with PBE functionals, using a tunable parameter, in order to match the bandgap to experiment as done in the Heyd, Scuseria and Ernzerhof (HSE) hybrid functional [31] However, this is computationally expensive and requires experimental bandgaps for the materials involved to be able to determine the tuning parameters. When averaged over all non-metals, the blending parameter AEXX is known to be 0.25 and this value can be used in the absence of experimental data. Experimental data is available for LiF, and a relatively large value of 0.42 was found to match the HSE results to the experimental results. However, experimental data is rarely available for poorly studied materials or materials with impurities and is not available for all materials of interest.

Another option to improve the accuracy of electronic calculations is known as meta-GGA functionals, in this case the specific functional considered is known as the Modified Becke-Johnson (MBJ) [32]. The MBJ implementation of meta-GGA is not self-consistent, meaning that the total energy calculated is not a physically relevant value. However, meta-GGA results in relatively accurate band structures at significantly reduced computation cost compared to HSE. Since accurate electronic band structures are required
for optical calculations, (though total energy and bonding is not) meta-GGA can be used to resolve these electronic structures.

In order to ascertain the viability of each method, the bandgap of a 2-atom cell of Lithium Fluoride was calculated by various methods: PBE, HSE and meta-GGA (mGGA) using the MBJ method. Due to a small number of atoms and perfect symmetry, even accurate energy calculations were relatively quick to run. The electronic densities of states (DOS) were calculated by VASP for the various functionals described above and are shown in Figure 46.

![Figure 46. Density of States for Lithium Fluoride calculated with PBE, HSE, and MBJ meta-GGA](image)

Figure 46. Density of States for Lithium Fluoride calculated with PBE, HSE, and MBJ meta-GGA
The bandgap can be read from a plot of the DOS as the difference in energy between the highest occupied state, near zero in the above plots, and the onset of the conduction band. A dashed line is shown at the energy corresponding to the experimental bandgap for LiF. For the functionals investigated, PBE significantly under-predicts the bandgap (8.7 eV), while meta-GGA (13.1 eV) and HSE (13.34 eV) approximate the experimental bandgap (13.6 eV). The values of the bandgaps in Figure 46 appear slightly smaller than the values given in the text due to smoothing.

Meta-GGA and HSE both provide reasonable approximations of the experimental bandgap, with HSE performing marginally better, especially considering that HSE could be made to match exactly by more rigorous determination of the blending parameter. Thus, in terms of accuracy, both meta-GGA and HSE are promising, with an edge to HSE. In terms of computational time, the choice is less ambiguous.

For the sample case, the PBE calculation required approximately 0.26 CPU-hours, meta-GGA required 2.9 CPU-hours, and the HSE calculation required approximately 30 CPU hours. Thus, in this case, meta-GGA achieved comparable accuracy to HSE with an order of magnitude lower computational time. While PBE is faster by another order of magnitude, the fact that it grossly underestimates the bandgaps indicates that it would be a poor choice for the present work. Meta-GGA does not produce self-consistent energies, which are required to determine some properties. Fortunately, the properties which meta-GGA fails for are not required for the present research, though these properties could be
gained by performing PBE calculations if they were desired. Thus, meta-GGA is chosen for all electronic structure and optical property calculations.

A series of structures are randomly selected from the output of the DFT-MD simulations. Identical optical calculations are performed on the individual structures in order to generate comparable data.

VASP calculates the potential fields of the electrons, and from this, the frequency dependent dielectric matrix. Once VASP has computed the dielectric coefficient, a post-processing script is used to convert the complex dielectric tensor into a value of $\kappa_\lambda$. Finally, the absorption coefficients for the individual snapshots were averaged using equal weights for each snapshot. Equal weights were applied to all snapshots as there is no unambiguous parameter which would clearly emphasize the most representative snapshot.

4.3. Computational Results

Several compounds were investigated as part of the present research: Lithium Fluoride, Lithium Fluoride plus Chromium, FLiNaK, FLiNaK plus Chromium, FLiBe, and KF-ZrF$_4$. LiF was selected as it is a pure compound with few components where results can be validated to some degree vs. experiment. LiF with Chromium was selected to investigate how transition metal impurities would affect the electronic structure of the molten fluid using the simplest case possible. Specifically, Chromium is readily extracted from high performance alloys by many candidate salts. [33] The FLiNaK compounds and FLiBe were included due to the prominence of these compounds in discussions of advanced
reactor coolants. Finally, KF–ZrF$_4$ was simulated to investigate how a transition metal fluoride salt might behave, as opposed to a non-transition metal salt with impurities. Additionally KF–ZrF$_4$ potentially serves as an analog to how heavier metals such as Actinides or Lanthanides might affect absorption in molten-salt fueled reactors.

4.3.1. Lithium Fluoride (LiF)

LiF is a common constituent salt proposed as a base member of molten salt eutectics. Additionally, its properties have been more thoroughly explored due to its wide use as an optical glass. Thus, it is examined first.

For molten LiF at 2200 K, the box volume of 64 atoms was found to be 567.01 Å$^3$, corresponding to a density of 2.43 g/cm$^3$ as compared to experimental values between 1.81 and 2.64 g/cm$^3$ (solid) and the pressure averaged over 2000 steps was found to be 4.433 ± 13.4 kB.

Once atomic positions were generated, the structures at various time steps were used for electronic calculations, and the output of those electronic calculations were used to determine absorption spectra. A script was written to extract atomic positions at a random selection of time steps, and to convert those positions into input files for optical calculations.

For the optical calculations, the electronic energy was converged to a tolerance of $10^{-6}$ eV. A 4x4x4 Monkhorst Pack grid of k-points and the tetrahedron method were used for Brillouin-zone integration. For the LiF calculations, 13 snapshots were taken from the
available data. The energies of the selected points are highlighted on the energy trace shown in Figure 47.

Figure 47. Energy trace of DFT-MD at 2200 K for molten LiF.

For each of the snapshots below, a plot of the density of states (DOS) over the optically relevant energy range is shown in Figure 48.
Figure 48. Density of States for molten LiF at 2200 K computed with Meta GGA. The dots represent DOS from individual snapshots, while the black line is the equal weight average.

As can be seen, the bandgap for molten LiF is approximately 10 eV, 3.1 eV less than the bandgap calculated for the 0 K crystal. However, the bandgap is still substantial, resulting in low absorption coefficients. The spectra from the individual snapshots are shown in Figure 49.
Figure 49. Individual absorption spectra for molten LiF

The variation between the individual spectra is relatively minimal, and this was observed in general for the homogenous salts. The average absorption spectrum for molten LiF is shown in Figure 50.
Because LiF is a pure material with a wide bandgap, it exhibits absorption only at relatively low wavelengths, or high energies. Absorption at higher wavelengths tails off rapidly. This fits with the assumption that molten salts are broadly transparent through the visible and infra-red regions.

4.3.2. LiF-NaF-KF (FLiNaK)

The eutectic mixture LiF-NaF-KF (FLiNaK, 46.5-11.5-42 mol %) has been the focus of much early research on molten salt cooled reactors, since it has a much lower melting temperature of 454°C as compared to the 845°C of LiF. As a pure mixture of ionic halides, its absorption properties should be broadly similar to LiF. Due to the small number of atoms in the present simulation, the eutectic ratio was approximated as best as possible. The initial positions for FLiNaK are shown in Figure 51.
Figure 51. Initial Atomic Positions of FLiNaK Simulation cell for MD.

The simulation box contains 15 Lithium (green), 13 Potassium (purple), 4 Sodium (yellow) and 32 Fluorine atoms (gray) within in a box of volume 673.34 Å$^3$. Careful observers will note a discrepancy between the numbers given and the number visible in Figure 51. Some of the F atoms are not visible due to shielding by larger ions, and atoms placed exactly on the boundary are repeated by the periodic boundary conditions for display purposes. After 2000 time steps of 1.2 fs, the atoms had become well mixed within the box (Figure 52). The pressure during the simulation was 0.699 ± 5.278 kB.
The average DOS for pure FLiNaK is shown in Figure 53. FLiNaK, similar to LiF, displays a relatively wide bandgap of 7.5 eV. As such, it is expected to be broadly transparent.
Snapshot locations from the DFT-MD generated amorphous structures were chosen arbitrarily, as the homogenous materials exhibit similar structures regardless of energy. The spectral absorption in LiF-NaF-KF, relative to pure LiF, can be seen in Figure 54.
While there are differences at high energies, both materials have similar absorption behavior at wavelengths into the infrared, with FLiNaK exhibiting slightly higher electronic absorption compared to pure LiF, potentially from the more weakly bound outer shell electrons of Sodium and Potassium compared to Lithium. As LiF is observed to be broadly transparent, and the electronic absorption spectrum of FLiNaK is very similar to that for LiF in the infrared, it is likely that photon-electron interactions will not be significant for heat transfer in pure FLiNaK.

4.3.3. FLiBe

The molten salt FLiBe is used in some reactor designs, since the Beryllium in the salt can be used to thermalize neutrons. As it is a pure halide salt, it is expected to have similar photo-electric absorption properties to LiF and FLiNaK in the visible and IR
spectrum. Examination of the DOS for molten FLiBe, as seen in Figure 55, shows it to be a relatively wide bandgap material, exhibiting a bandgap of 7.0 eV.

As expected, FLiBe has strong absorption in the high energy region, but little at the longer wavelengths. The spectra from individual snapshots are nearly identical to each other, indicating that the few snapshots used were sufficient to capture the expected properties of the salt. The absorption of FLiBe compared to LiF is shown in Figure 56.
Similar to FLiNaK, photon-electron interactions should not be expected to contribute strongly to absorption as it pertains to radiative heat transfer in pure FLiBe. Photon-phonon effects may prove significant, as the phonon absorption edge in FLiBe is at higher energy, 4 μm, than for LiF or FLiNaK, 6 μm. [3]

4.3.4. LiF with Chromium

In order to examine the effect of corrosion products within coolant salts, LiF was re-examined after insertion of a single chromium atom into the pure LiF structure from section 4.3.1. One atom of chromium in 32 ion pairs of LiF results in roughly 6% chromium by weight or 1.5% by atom. The ions were relaxed at 0 K to prevent numerical errors caused by high stress tensors. A similar procedure was then performed to that which had been done for the LiF and FLiNaK. The structure for the LiF with Chromium after 1600 time
steps is shown below in Figure 57. It can be seen that the addition of Cr does not break up any of the LiF molecules, which stay together in the liquid like in the previously modeled salts. Thus, the Cr is an isolated ion in the melt with only weak interactions with the surrounding molecules.

![Figure 57. Relaxed structure after DFT-MD for LiF + Chromium (blue)](image)

The final pressure-reduced volume ended up slightly larger than that for the LiF due to the addition of the Chromium atom, with a volume of 637.26 Å³. Due to large variability in the results, a larger number of snapshots were used, 33 for LiF with chromium compared to 13 for pure LiF. The snapshots and the energy trace are shown Figure 58.
The average density of states for the salt with the chromium impurity was calculated. It is shown in comparison to that for LiF in Figure 59.

Figure 58. Energy Trace and individual snapshots for LiF + Chromium
The insertion of Chromium is shown to create additional energy states within the bandgap compared to pure LiF. The position of these states shift from snapshot to snapshot, leading to high variation in absorption spectra. The mid-gap states will later be shown to be partially filled single spin $d$ shell states of chromium impurities. The effect these additional energy states have on absorption is shown in Figure 60, where the absorption coefficient was calculated for each of the selected snapshots.
The absorption spectra for the LiF with the Chromium impurity exhibits significantly more variation in the individual spectra compared to the individual spectra in the pure salt. The average absorption spectrum is shown relative to that for pure LiF in Figure 61.
Figure 61. Comparison of absorption spectrum for LiF + Cr to pure LiF

The insertion of a small concentration of Chromium is shown to dramatically increase the absorption coefficient, and more so to increase it at wavelengths relevant for heat transfer.

4.3.5. FLiNaK with Chromium

As FLiNaK is more likely to be used as a reactor coolant than LiF, it was desired to verify if the effects of Chromium in LiF are mirrored when Chromium is inserted in FLiNaK. Since FLiNaK is not inherently that different from pure LiF, it is no surprise that the insertion of Chromium in FLiNaK results in broadly the same absorption spectra as for LiF with Chromium. The DOS for FLiNaK with 1.5% at Chromium is shown in Figure 62.
The absorption spectrum for FLiNaK + 1.5% at Chromium is shown in Figure 63 relative to absorption by pure FLiNaK.

Figure 63. Absorption Spectrum for FLiNaK + 1.5% at Cr compared to pure LiF
Chromium is thus shown to increase absorption at relevant wavelengths in both LiF and FLiNaK. Although simulations with Chromium in FLiBe were not performed, it would be surprising if the effect of inserting Chromium into FLiBe did not produce similar effects as in LiF and FLiNaK.

4.3.6. KF-ZrF₄

Another molten salt under consideration as a coolant is KF-ZrF₄. Unlike the previously considered salts, KF-ZrF₄ is not a pure halide mixture with trace levels of transition metals, rather it contains a transition metal fluoride as a primary component of the mixture. This is potentially interesting because the zirconium, in its metal state, exhibits no bandgap and strongly absorbs photons throughout the electromagnetic spectrum. Thus, it is possible that KF-ZrF₄ will be substantially opaque, even without added transition metal impurities. The behavior of KF-ZrF₄ is also of interest because it might provide insight into the absorption spectra of other salts which contain high concentrations of transition or heavy metal ions, specifically the heavy metals (both fuel and fission fragments) which would be present in a molten-salt fueled reactor.

In order to gain insight into the absorption properties of KF-ZrF₄, a simulation containing 11 atoms of potassium, 8 zirconium, and 45 fluorine was performed at 800 K. 15 snapshots from the DFT-MD simulations were taken and optical calculations were performed to determine the allowable energy states and resultant optical properties. The
density of the states for each of 13 snapshots is shown in Figure 64, along with the resulting average.

![Graph](image)

**Figure 64. Averaged DOS near Fermi level for molten KF-ZrF₄**

The bandgap for KF-ZrF₄ is substantially smaller than for the other salts analyzed, measuring approximately 0.6 eV, compared to 10 eV in LiF for example. This results in substantially higher absorption. For the 13 selected snapshots, the absorption spectra were calculated. As KF-ZrF₄ is a homogenous material, there is relatively low variation in the various absorption spectra. The average absorption spectrum for KF-ZrF₄ is shown in comparison to that for LiF in Figure 65.
Figure 65. Absorption spectra for KF-ZrF$_4$ and pure LiF.

KF-ZrF$_4$ exhibits dramatically higher absorption than pure LiF at wavelengths throughout the electromagnetic spectrum. Although no experimental data has been found which can confirm the computational results, KF-ZrF$_4$ has been anecdotally observed to be black, or opaque to all visible wavelengths, giving some confirmation to the above. As bond lengths increase, bandgaps are expected to shrink. Rather than being caused by absorption at discrete midgap states, increased absorption in KF-ZrF$_4$

4.4. Discussion

Investigation with VASP indicates that whether present due to impurities (such as Chromium) or present as a component of the salt (Zirconium), the addition of transition metal ions to pure halide salts will substantially change their optical properties.
To understand the reason for this, the nearest neighbors to the Chromium atom in the impure LiF simulation were calculated at each time step. Atoms further than 2.8 Å were not included in the results. The distances of three instructive Fluorine atoms are plotted at each time step and shown in Figure 66.

![Figure 66. Trace of two Fluorine atoms relative to Chromium](image)

Fluorine #42 stays within the search radius for the entire simulation, though its bond length oscillates between 1.7 and 2.7 Å. Fluorine #58, on the other hand, moves into a nearest neighbor position for roughly half of the simulation before being displaced by Fluorine #51. Due to the counting methodology, the average distance for all three atoms is similar, where essentially what is being measured is the average position while interacting. The average and minimum distance of all the atoms in search is calculated and shown in
Figure 67, where the atoms to the left of the dashed line are all Lithium and to the right of the dashed line all Fluorine.

![Graph showing mean and minimum neighbor distances for Chromium in LiF.]

**Figure 67. Mean and Minimum neighbor distances for Chromium in LiF**

Examination of Figure 67 shows that the Chromium does not form close bonds with a fixed group of Fluorine atoms and so does not behave like a molecule. Rather, the Chromium atom forms a loose and shifting connection to a wider group of Fluorine atoms. Most of the Lithium atoms spend some time in a loose second shell, and as such more Lithium than Fluorine are shown in Figure 67.

Since there are no clearly defined bonds, the increase in absorption coefficient is likely not due to electrons participating in a bond, rather it is due to absorption by electrons...
in the $d$ orbitals of the Chromium atom itself, which do not have anything to bond to. This can be more closely examined by investigating the DOS for the individual atoms in a simulation. The impure FLiNaK simulation was analyzed in this manner, and the resulting DOS for an atom in each species is shown in Figure 68, weighted by the number of each atom type.

![Figure 68. Species DOS for elements in impure FLiNaK](image)

Since this calculation was performed solely for analysis of the cause of the defect state, Figure 68 was generated using PBE, which results in a compressed band gap, but should still result in accurate orbital DOS. Examination of the orbital DOS for the state shows that the midgap state seen in Figure 68 is composed entirely of a $d$ orbital state in
the Chromium atom. Since there are no other electrons for the d orbital electrons to bond to, the absorption spike is a property inherent to the Cr atom itself, not its interactions with surrounding atoms.

The increased absorption observed for salts with transition metals can thus be understood as a product of interactions between photons and the d orbital electrons of the transition metals, which are significantly less strongly bonded to the nucleus than the outer shell electrons for the lighter elements. As the neighbor environment changes for the atom, these changing forces on the d orbital electrons result in different absorption spectra, but broadly these interactions produce states close to a defined mean. For the salts with mostly light ions and only trace impurities, there are a relatively small number of these weakly bound electrons.

Conversely, a salt such as KF-ZrF₄ does not contain free ions. Observing the DOS for molten KF-ZrF₄, there are no discrete states caused by absorption in specific orbitals from non-bonding electrons. Rather, the electrons participating in the ZrF₄ bonds exhibit valence bands and conduction bands that are not aligned with the valence and conduction bands of the KF bond. Thus, the bandgap is small, leading to high absorption throughout the spectrum.

4.4.1. Scaling of Absorption Coefficients

Although the manipulations of the extinction coefficient lead to a dimensional value of the absorption coefficient, VASP has not been validated to return accurate dimensional
values of the absorption coefficient. Regardless, it was decided still to show the absorption coefficient dimensionally in the above sections. VASP is expected to show accurate relative values. [34] Prior research efforts have endorsed the idea of scaling the absorption coefficients produced by VASP. This can be done in the present case by examination of the absorption coefficient of pure Lithium Fluoride. H. H. Li [7] provides absorption data at a wavelength of 4300 nm, in crystalline Lithium Fluoride, measuring a value of $5.9 \times 10^{-3} \text{cm}^{-1}$. From this, a scaling factor can be estimated between the results returned by VASP for Lithium Fluoride at the same wavelength and the measurement reported by Li. The resulting value of this scaling factor for the present simulation in VASP, $f_V$, is shown in Equation (4.6).

$$f_V = \frac{5.9 \times 10^{-3} \text{cm}^{-1}}{0.67 \text{cm}^{-1}} = 8.81 \times 10^{-3}$$ (4.6)

By this method, the value of the scaling factor is extrapolated from a single data point at a single wavelength. As such, it is potentially questionable to simply apply the scaling factor to the entire wavelength. If the values produced by application of the scaling factor agree with experimental data in another part of the spectrum, confidence would be greatly increased.

Sarantopoulu et al. [35] measured the absorption coefficient for LiF in the wavelength region 120-220 nm. Their measured data, as well as the data for the same wavelength region as computed by VASP, scaled by $f_V$, is shown in Figure 69.
Figure 69. Scaled Absorption Coefficient for Molten LiF from VASP and measured absorption coefficient for crystalline LiF from Sarantopoulou

The data does not perfectly align; it is larger than the measured data by a factor of 2-3 over the region of interest. That said, considering the magnitude of the scaling factor, and uncertainty inherent in experimental data for real materials compared to theoretical calculations, agreement within a factor 3 is encouraging. This level of agreement at such disparate wavelengths provides more confidence in the validity of the scaling factor and the experimental results from UV through IR wavelengths, at least for LiF. This doesn’t mean necessarily that the same scaling factor would apply for FLiNaK, FLiBe or KF-ZrF₄, nor for these mixtures with impurities. The data to guarantee validity for these extrapolated calculations does not exist. Some confidence is gained by the fact that the pure materials
all exhibit similar absorption coefficients in the impurity dominated regions, as they are expected to be broadly similar in these regions. As VASP can be expected to produce reasonably accurate relative values, this improves confidence for the impurity doped mixtures.

The absorption spectra can be examined now with the scaling factor applied. The scaled absorption curves for the pure halide salts, LiF, FLiNaK and FLiBe are shown in Figure 70.

![Image](image_url)

**Figure 70. Scaled absorption coefficients for pure halide salts, UV to mid IR.**

The absorption spectrum is shown from 150-6000 nm in order to be able to distinguish the curves, ignoring the high energy absorption (<150nm) irrelevant for heat
transfer, and stopping at the IR cutoff for LiF (>6000 nm) where phonon absorption begins to dominate. For all these salts, the absorption coefficient is very low in the region of interest, and it would be reasonable to treat the salts as completely transparent in heat transfer calculations.

Once the chromium impurities are added, absorption in the impurity region increases substantially. Due to the weights of the atoms changing, but keeping the number approximately constant, a singly chromium atom represents 4% chromium in FLiNaK by weight as opposed to 6% in LiF. Applying the same scaling factor to the data for LiF and FLiNaK with chromium added produces the curves shown in Figure 71.

![Figure 71. Scaled absorption spectra for LiF and FLiNaK with a single added chromium. 150-6000nm](image)
The concentrations simulated in VASP were necessarily large, due to the computational expense of running optical calculations on large numbers of disordered atoms with magnetic impurities. Concretions of chromium as high as 4% by weight will not ever be seen as a result of corrosion.

4.4.2. Absorption Characteristics

An interesting validation of the present work can be found by comparing the absorption spectrum of FLiNaK with Chromium to the Data by Young and White [16] as well as a better understanding of the mechanics by which Chromium influences photon absorption. Young and White measured absorbance from chromium dissolved in FLiNaK within the visible spectrum. This was done as part of an effort to use spectroscopy to identify salt constituents and better understand the chemistry of the salts. The absorbance, defined as the relative absorption of impure FLiNaK compared to pure FLiNaK, is shown in Figure 72. At the top of the figure is data computed from VASP and below is the original experimental data from Young and White.
Two absorption peaks are seen in the UV-visible portion of the EM spectrum. To understand how this influences absorption, the absorbance in the visible spectrum for impure FLiNaK (as calculated by VASP) from Figure 72 is plotted as a function of photon energy in Figure 73.
Figure 73. Absorbance as a function of energy for FLiNaK with impurities in the visible region.

Plotted in this manner, it is apparent that the absorption in the visible spectrum occurs primarily in two spectral peaks, one corresponding to a photon energy of approximately 2.3 eV and another at 4 eV. Examining the band structure for impure FLiNaK indicates a potential source of these absorption peaks. The DOS shown in Figure 62 is reproduced in Figure 74, magnified in the region of the midgap states. The DOS for several individual snapshots are shown in order to see the peaks more clearly. The valence band upper edge is located at 0 eV. If the conduction band energy is the same as pure
FLiNaK, as seen in Figure 53, then the conduction band begins at approximately 7.5 eV. Plotting the data in this manner shows that at least two defect states are created in what used to be the bandgap. The average for all snapshots, as well as the DOS of representative snapshots are shown in Figure 74.

![Figure 74. Average DOS for FLiNaK with impurities, as well as multiple individual snapshots.](image)

The energies of these states move relative to the conduction band, which varies from snapshot to snapshot. When the band structure is shifted to align the valence band, the peaks move and this smears the average position of the peaks. However, observing the
individual snapshot shows that these smeared peaks are the result of two distinct midgap states approximately 4 and 6.3 eV.

Thus, it is apparent that the absorption in the visible spectrum occurs primarily at two spectral peaks, one with energy of approximately 2.3 eV and one with energy of 4 eV. These peaks could be explained as transitions from the valence to the 4 eV defect state, and transitions between the 4 eV and 6.3 eV states, depending on the occupation of the various states and the corresponding transition matrix elements, which however were not examined in detail within the scope of this work.

4.4.3. **Total Absorption**

The data thus far presented, including the data presented in Figure 70 and Figure 71, contains information only on electronic absorption resulting from photo-electric effects. To get the whole picture, we can also include intrinsic absorption resulting from photo-phonon effects, as discussed in Section 1.4. Doing so will allow us to get the full picture of the electromagnetic absorption spectrum for FLiNaK. The two curves for pure FLiNaK are shown, as well as a total absorption coefficient, in Figure 75.
Figure 75. Intrinsic absorption spectrum for FLiNaK.

As can be seen from Figure 75, FLiNaK reaches a minimum absorption at a similar wavelength to the reported value of approximately 4300nm for LiF, [7] an additional validation on the techniques employed so far. The overall trend is essentially the same as silica in Figure 3, giving us some level of confidence in our results.

For the pure salt data, and the simulations with chromium impurity, Beer’s Law which states that absorbance is proportional to the concentrations of the attenuating species [36] allows us to linearly extrapolate the increased absorption from Chromium to lower concentrations more representative of what might be seen in actual reactor chemistry. Curves for varying concentrations are generated using Equation (4.7),

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where \( w_{\text{Cr}} \) is the weight percentage of Chromium in the salt, 3.81\% is concentration of Cr in the simulations, \( \kappa^e_{\lambda} \) is the spectral absorption coefficient from electric effects calculated by VASP, \( \kappa^p_{\lambda} \) from estimated phonon effects, and \( \kappa^T_{\lambda} \) is the total spectral absorption. The impurity dependent absorption spectra for FLiNaK are presented in Figure 76.

\[
\kappa^T_{\lambda}(w_{\text{Cr}}) = f \left[ \frac{w_{\text{Cr}}}{3.81\%} \left( \kappa^e_{\lambda,\text{FLiNaK}} - \kappa^e_{\lambda,\text{Cr}} \right) + \kappa^e_{\lambda,\text{FLiNaK}} \right] + \kappa^p_{\lambda,\text{FLiNaK}},
\]  

(4.7)

Figure 76. Wide range absorption spectrum for FLiNaK, impurity and intrinsic.

Intrinsic electronic absorption decreases rapidly with increasing wavelength, while phonon absorption increases in the mid to far IR. At intermediate wavelengths, the region

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of optical clarity disappears once impurities are added to the mixture. Validation of the values presented will require experimentation and direct measurement.

With a spectral absorption curve in hand for FLiNaK and Cr, the efforts in Section 2.3, where an impurity averaged absorption coefficient was generated, can be repeated with a more accurate understanding of the spectral absorption coefficient as a function of the impurity content. Rather than generating an “impurity band,” the data generated by Equation (4.17) can be binned into spectral bands averaged over micron-width spectral regions. The discretized energy bands for 0.01% weight Chromium concentration is shown as a representative example in Figure 77.

![Spectral binning of absorption coefficient for FLiNaK with 0.1% wt Cr](image)

**Figure 77. Spectral binning of absorption coefficient for FLiNaK with 0.1% wt Cr**
By varying the impurity concentration, the heat transfer equivalent absorption coefficient as a function of Chromium concentration can be calculated. The results of doing so are shown in Figure 78.

Figure 78. Heat transfer equivalent $\kappa$ as a function of Chromium concentration in FLiNaK

The effect of Chromium in FLiBe was not investigated. The chemistry and absorption curves for LiF and FLiNaK are very similar to FLiBe, and the effects of chromium in LiF and FLiNaK are similar as well. It is likely that the absorption spectrum for FLiBe with Chromium would be broadly similar to FLiNaK and LiF.
It is not clear exactly why VASP requires a scaling factor to match experimental data, specifically a scaling factor of such magnitude. As such, it is with some trepidation that it is applied to the results for KF-ZrF₄. All other salts investigated contain significant fractions of LiF, and so it was more defensible to use the same scaling factor as one based on data for LiF. However, it is not unreasonable that the same or similar scaling factor would apply to the results for KF-ZrF₄ considering its relative magnitude seems plausible. Additionally, despite thorough checking, it is still theoretically possible that the magnitude of error resides somewhere in the post processing scripts or some implementation in VASP that does not affect the underlying data. With those caveats, the scaled absorption coefficient for KF-ZrF₄ is shown in Figure 79.

![Figure 79. Scaled Absorption Coefficient for KF-ZrF₄](chart.png)
If the results shown in Figure 79 are accurate, this would indicate that KF-ZrF$_4$ is essentially opaque throughout the electromagnetic spectrum. Although there is limited experience with metal fluoride salts, anecdotal evidence has described them as “completely black” or “muddy brown.” Absorption coefficients significantly above 10cm$^{-1}$ would in turn result in an optical thickness orders of magnitude greater than 1 for typical reactor geometries. Due to the nature of radiation transport, for extremely high optical thicknesses, the fraction of energy transferred by radiation is small, because the length scale shrinks below that for conduction. Based on these results, it is plausible that radiation heat transfer may well be irrelevant for reactors which employ transition metal fluorides as constituents of their working fluids. On the other hand, if these reactors employ geometries with small length scales, such as the 0.7mm rectangular sub-channel in the ATR design, radiation heat transfer may again prove relevant. Spectral results which would be useful to validate the above data should not be overly difficult to obtain, as if the salts truly are highly opaque absorption coefficients could be obtained anywhere within the electromagnetic spectrum. Due to the many designers currently planning to employ fuel-in-salt reactors at elevated temperatures, it would be useful to know if these salts truly are as opaque as indicated by VASP.

4.5. Conclusion

Molten salts have often been assumed completely transparent, especially from a heat transfer perspective. Using the VASP computational package, this assumption was
investigated for a set of halide salts under consideration for use as coolants or fuel carriers. The pure halide salts LiF, FLiNaK, and FLiBe were found to be broadly transparent in the wavelength range of 150-6000 nm. The addition of Chromium impurities to the salts resulted in significantly increased absorption through a broad portion of the spectrum. This absorption is caused by the creation of additional occupied states that exist within the bandgap for the pure salts. Using Beer’s Law, spectral absorption coefficients for FLiNaK as a function of chromium percentage have been presented. The spectral absorption coefficient for KF-ZrF$_4$ has also been presented, both as a salt of interest and as a potential analog for salts which contain heavier cations and cations with more than one fluoride ions per cation. KF-ZrF$_4$ was found to be broadly opaque to photons at relevant energies. In summary, we found that DFT is a powerful tool for exploring the properties of materials which are difficult or impossible to test through more traditional means. Also, with appropriate processing of the calculation results, the limited set of available experimental data corroborates our findings well. Further investigation of molten salt properties with DFT are fertile grounds for future work.
Chapter 5. Construction and Testing of the Integral Radiation Absorption Chamber (IRAC)

The measurement of absorption coefficients in molten salts present one of the most challenging design spaces for absorption coefficient measurements. Measurements on solids and room temperature liquids are comparatively more thoroughly explored design spaces. The high temperature and somewhat corrosive nature of molten salts causes extreme difficulty for absorption coefficient measurement techniques. Additionally, in order to determine absorption coefficients for heat transfer, a large swath of the spectral region must be measured, which further constrains experimental efforts. The design and computational analysis of the Integral Radiation Absorption Chamber has been described in Chapter 3. This design effort was undertaken in order to provide experimental values for the absorption coefficient in molten salts and address the lack of viable heat transfer oriented absorption techniques for high temperature molten materials. The chamber was constructed using available funds in an attempt to validate the proposed technique. Ultimately, the experimental technique was not able to make measurements of the absorption coefficient of molten FLiNaK for a number of reasons that will be discussed.
within. For posterity, a description of the experimental setup and challenges are included as reference for future efforts that might seek to leverage this experimental technique.

5.1. Overview

The general description of the measurement principle is to measure the heat flux through a sample chamber that is capable of containing a molten salt, where the chamber is also the primary heat flow path between a heat source and heat sink. The 4th power temperature dependence of the heat flux through the chamber is calculated, and this dependence is related to the radiative properties of the volume inside the chamber. In order to account for experimental unknowns, one measurement is taken with the chamber empty, and one with the chamber filled with insulation. An empty chamber corresponds to an optical thickness of effectively zero, while a chamber filled with opaque material represents an optical thickness approaching infinity. If a molten salt is placed within the chamber, it’s optical thickness will behave somewhere between zero and infinite optical thickness. By creating a model that is matched to the zero and infinite case, the optical thickness of the chamber with salt – and from this the absorption coefficient of the material within the chamber – can be estimated. In Chapter 3, the radiation parameter, \( X \), was defined

\[
X = \frac{\sigma(T_1^4 - T_2^4)\Delta z}{\Delta T}
\]  

(5.1)

This is the driving function for radiative heat transfer divided through by the linear temperature gradient. Additionally, the effective conductivity was defined
This is the heat flux divided again by the temperature gradient. Observing the data as a function of these two parameters allows information on the radiative dependence to be clearly demonstrated, as the linear temperature gradient is canceled out.

In order to facilitate understanding of the following chapter, it is worthwhile to describe what the experimental data is expected to look like. This will allow the reader to understand the methodology and better follow future discussions.

If the experiment were performed between two infinite plates at different temperatures, and if the surface temperatures of each plate along with the total heat flux were known exactly, then calibration would not be necessary and the model would be greatly simplified. As a thought experiment, it is still instructive. In this hypothetical experiment, the temperature of the two plates is raised, one higher than the other, and the heat flux between the plates is measured. The experiment is performed 3 times. First, with a perfectly transparent vacuum, resulting in zero conductivity as well, between the black surfaces. Second, with a participating medium which absorbs some fraction of the energy, with an optical thickness of \( \tau = 0.5 \) for demonstration. Finally, data would be taken with a non-conducting, completely opaque material. For these conditions, lines are plotted of the form

\[
k_{e} = k_{s} + k_{w} + B_{e}e^{-\tau}X - A_{rad}X
\]  

(5.3)
where the exponential approximation is used for the transfer term for purely absorbing materials and $A_{\text{rad}}$ is used to approximate various radiative effects. $B_2$ encapsulates the potential for the emissive surfaces to not emit and absorb the maximum amount of radiative energy for streaming through the chamber. The data for the experiment would then be represented by the equations

$$
\begin{align*}
\tau = 0 : & \quad k_e = 0 + 0 + e^{-0}X - 0 \\
\tau = 0.5 : & \quad k_e = 0 + 0 + e^{-0.5}X - 0 \\
\tau = \infty : & \quad k_e = 0 + 0 + e^{-\infty}X - 0
\end{align*}
$$

These equations are plotted in Figure 80.

![Figure 80. Representation of Hypothetical Experimental data for infinite plates](image)

Plotting the data in this manner is done because any phenomenon which affects heat flux, but scales proportionally to the linear temperature gradient, is will not contribute
to the derivative. The y-intercept of all lines in Figure 80 is 0, as that is the non-radiative conductivity of perfect vacuum. As seen in Equations (5.4), for the opaque chamber, the line has a slope of zero, because no increase in heat flux is correlated with increased radiation parameter. For the transparent chamber, the increase in effective conductivity correlates perfectly, and the line has slope $e^{-0} = 1$. For the non-transparent chamber, the line has slope $e^{-0.5} \approx 0.61$.

Next some complications are included. Being finite, the chamber must have bounds, and these bounding walls necessarily add some amount of thermal power that can pass between the plates by conduction. Additionally, these walls will be capable of emitting some amount of radiation energy from the container, and this power emission will scale closely with $X$. Outwardly directed radiant energy emitted by the wall is not measured by the heat flux transducer and is essentially “lost.” This means that these losses must be calibrated and accounted for in order to determine by how much to compensate the model. Lastly, the inclusion of a salt will increase the effective conductivity of the chamber relative to the case with some hypothetical non-conducting, radiatively-participating medium.

Equations which incorporate these effects are shown below

$$
\begin{align*}
\tau = 0: & \quad k_e = 4 + 0 + e^{-0}X - 0.1X \\
\tau = 0.5: & \quad k_e = 4 + 0.92 + e^{-0.5}X - 0.1X \\
\tau = \infty: & \quad k_e = 4 + 0 + e^{-\infty}X - 0.1X
\end{align*}
$$

(5.5)

where the container walls have a conductivity of $4 \text{ W/m-K}$ and the salt has a conductivity of $0.92 \text{ W/m-K}$ and 0.1 is an approximation for all radiative loss effects.
A representation of what this data might look like is shown in Figure 81.

![Diagram showing effective conductivity vs radiation parameter for different values of \( \tau \).](image)

**Figure 81. Representation of Hypothetical Experimental data for non-infinite plates and conducting salt**

The y-intercept for the two calibration curves (\( \tau = 0 \) and \( \tau = \infty \)) are identical, but the intercept for the participating line is higher because \( k_e \) is increased by the conductivity of the salt. The slope of the opaque chamber is now negative, as radiation increases (reducing heat flux) with increasing \( X \), but no process is present that increases heat flux with increasing \( X \). The slope of the transparent chamber is now less than one, but it is still positive. Radiation streaming through the chamber causes heat flux to increase faster than it is lost by emission. The salt line has a more negative slope, but it is still positive,
indicating that radiation transfer dominates radiation losses. If the additive model given by Equation (3.15) were appropriately fit to the two calibration curves, the optical thickness of the data curve (in this case $\tau = 0.5$) could be measured to high accuracy.

There is no reason why streaming through the chamber would necessarily dominate radiation losses from the walls, and whether this is the case or not doesn’t necessarily compromise the validity of the experiment. As geometric complexity and surface roughness increases, the external emissivity of the chamber will increase, increasing radiation losses. Additionally, the emissive surface may not radiate the maximum amount of energy due to non-black surfaces, radial temperature profiles of the emissive surfaces, and other variation. This is represented by setting $B = 0.4$. However, so long as the sensitivity of the measurement is such that the two curves ($\tau = 0$ and $\tau = \infty$) can be separated, then viable data can be generated. Equations describing this set are shown below.

\[
\begin{align*}
\tau &= 0: & k_e &= 4 + 0 + 0.4 \times e^{-0}X - 0.6X \\
\tau &= 0.5: & k_e &= 4 + 0.92 + 0.4 \times e^{-0.5}X - 0.6X \\
\tau &= \infty: & k_e &= 4 + 0 + 0.4 \times e^{-\infty}X - 0.6X
\end{align*}
\] (5.6)

These equations are plotted Figure 82.
Figure 82. Representation of Hypothetical Experimental data for non-infinite plates and conducting salt with high radiation losses

Here, the slope of the $\tau = 0$ and $\tau = \infty$ lines are both negative, as is the slope of the participating line. The magnitude of the difference in slope between the $\tau = 0$ and $\tau = \infty$ lines corresponds to the maximum sensitivity of the experimental technique. The greater the difference, the greater the sensitivity of the experiment. Comparing the situation shown in Figure 80 to that shown in Figure 82 highlights this. Assume $\frac{dk_e}{dX}$ is measured for a participating salt in both situations and this measurement unknowingly contains a constant error that is equal in magnitude for both situations. The difference in $\frac{dk_e}{dX}$ between $\tau = 0$ and $\tau = \infty$ is five times greater in Figure 80 than in Figure 82. Propagating through,
this same measured error will result in roughly 5 times greater error in measured $\kappa$ between the two situations.

If radiative losses are strong, the information content of the experiment is “compressed” into a smaller numerical range, but the information is still recoverable. This “compression” does not invalidate the model, only increases the sensitivity to errors. Performed accurately, an experiment which resulted in all three lines having negative derivatives would not fully compromise the results.

Thus, the goal is to perform the experimental calibrations and determine the modeling parameters that accurately describe the physically created geometry. For a successful experiment, there must be enough “spread” to distinguish the change in properties from transparent to opaque data. If this can be reliably measured, then the experimental technique provides useful data by observing where the measured slope of a participating salt falls in relation to the two known bounding values.

5.2. Experimental Description

The components of the IRAC shown in Figure 35 and described in Table 1. IRAC Thermal Components and their FunctionTable 1 are discussed below. The heater is a repurposed BlueWave scientific 1.6” Inconel heater originally designed for substrate deposition heating. A spare heater was available from an unrelated project, and due to the expense of comparable heaters, it was the first component selected. The rest of the design
was conducted in order to accommodate it. The heater was thermally bonded to an Inconel upper plate using a silver ceramic thermal paste.

The materials which can reliably withstand molten salt environments at temperatures exceeding 1000K do not comprise an exceedingly-long list. All metal salt contacting surfaces were constructed from Nickel 201 Alloy, which is essentially pure nickel. Without chromium or iron, the chamber walls would be minimally susceptible to oxidation or corrosion by the salt. To seal the chamber, Garlock pure graphite gaskets were used at the upper and lower seals to bond the upper Inconel plate to the Nickel 201 flanges.

The baseplate is the ultimate heat sink for the experiment; as such, it will be required to remove heat to maintain the baseplate and bell jar at a safe temperature despite extremely high temperatures inside the system. In order to cool the baseplate, a milled block of aluminum was constructed with channels for water from the building’s chilled water utility flowing through it. This heat sink was machined flat and bolted to the bottom of the vacuum baseplate.

After initial set up and testing, it was determined that the thermocouple in the HFT was somewhat unreliable and a larger than expected temperature gap was noted between the heater body and upper flange. In an attempt to address this, additional thermocouples were added by bolting them between the Monel fasteners and the flange material. The thermocouples and their positions on the crucible are shown in Figure 83.
Although a more centrally located location would have been desirable, due to operating and time constraints, it was decided not to weld the thermocouples to the body closer to the centerline. Another option would be to embed the thermocouple in the gaps between the heater/crucible interface and the HFT/crucible interface. This would have required machining the gap into the components before assembly and testing, as the non-negligible thickness of the thermocouples would have prevented adequate thermal contact between the various positions. The outward radial position of the bolts means that the measured temperature is substantially different from the centerline temperature. However, using the bolts was the best available of limited options, and investigation of the numerical

Figure 83. Location of additional thermocouples
model and analysis technique indicated that the results were not as sensitive to the exact temperature as expected and that the success of the technique is dictated by the temperature scaling and measurement of the heat flux through the chamber, not the exact temperature at the interface.

5.2.1. Salt Preparation

In order to limit the exposure to atmospheric water and oxygen, the salt was mixed and prepared in an argon-filled glove box at room temperature at less than 1% oxygen. Ideally, the salts would have been individually baked at 500K for several hours to reduce the water content and ensure accurate weights during mixing. Unfortunately, the furnace was not installed in the glove box during the time in which the mixing needed to be done, so the salt could not be heated to drive off what water there might be. However, separate testing at OSU had shown the water content of the constituent salts to be minimal and have insignificant effect on melting temperature. Additionally, due to other experimental challenges, the salt was never melted into the crucible.

The plan to melt the salt into the chamber had originally been to use a filling chamber attached to a filling port. This chamber would hold the powdered salt, which is far less dense than the salt in a molten state. The crucible would be rotated 90 degrees and brought to temperature, and the salt would flow into the crucible in this configuration. The filling port had two 90-degree bends would allow the salt level to fill the chamber while
keeping the stainless steel filling port out of contact with the salt. This filling port is visible in Figure 35.

Tests with water showed that the viscosity of the salt might prevent it from flowing down the narrow fill tube, especially coupled with the presence of entrapped air which might prevent full filling of the chamber. A new filling procedure was developed whereby the fill tube was sealed and would be used as a small expansion volume. The bottom of the crucible would be removed and the heater/crucible assembly would be inverted on the support rods. The mass of salt which would fill the volume of the chamber would be weighed out and the powder would be placed within a nickel tube of equal diameter to the crucible which would serve to hold the salt above the crucible during melting. The salt that entered the filling tube would serve as an expansion reserve to fill the gaps that might be left below the full fill line after the crucible was re-assembled. After cooling to temperature, the lower crucible plate would be re-attached and the plug removed from the fill port. The crucible would be oriented vertically and when melted under a vacuum, the salt would fill the chamber completely, as any entrapped air would be able to escape through the fill port. Finally, the fill port would be re-sealed to prevent excess salt vapor from escaping the test chamber.

A perhaps more ideal solution would be to have designed enough room and additional heaters into the vacuum chamber such that the salt could be melted into the chamber with the crucible sealed and using the filling chamber as designed. Since
performing the filling in this manner would mean the salt is melted under a vacuum, there would be no concerns over gas pockets being left in the chamber to prevent issues with filling.

5.2.2. Chamber Assembly

The heat sink was connected to the building chilled water supply. The fired Aluminum Silicate insulation was placed on the baseplate. Sheet metal was arranged over the insulation to prevent direct heating by radiation in an attempt to protect the ceramic, though this may not have been necessary. The cold finger, heat flux transducer and crucible were placed on the vacuum baseplate and aligned by hand. The lower assembly is shown below in Figure 84.
Thermal contact paste was applied to the heater face and the depression machined in the upper Inconel plate to interface with the heater. Due to the difficulty of machining Inconel with carbide, a machining error was made that was not realized until assembly: a small raised portion was left on the Inconel plate where the cutting bit did not fully remove material under the center of rotation. This meant that the upper contact surface between the heater and flange was not planar, and this degraded the thermal contact between the heater and the upper plate. In set-up testing, this was identified by a large temperature gap between the measured temperature in the heater and the upper flange thermocouples. The spot was
visible after disassembly as the only point of contact between the heater and crucible. The hot spot on the upper mating surface is shown in Figure 85.

![Figure 85. Hot spot caused by non-planar upper mating surface of flange](image)

This fault was not discovered in time to re-machine the upper plate. Extra contact paste was applied in an attempt to fill the gap and this did substantially improve the thermal contact between the heater and crucible body, though perhaps not sufficiently.

The heat flux transducer is sandwiched between the bottom of the crucible and the top of the cold finger by compression of the upper bracket through the top of the heater. The upper heater bracket compress the assembly when the three alignment nuts are tightened on the main threaded rod supports. These nuts are visible in Figure 86.
Due to the use of ceramic spacers with uncertain strength within the heater body, the nuts were only tightened with a wrench until snug. Thermal expansion and the flex in the upper bracket maintained the stack compression as the temperature varied.

5.2.3. Test Procedure

After assembly of the crucible stack with the desired internal conditions, a set of sheet metal guards were arrayed around the stack to prevent direct radiant heating of the bell jar surface and vacuum feedthroughs. An inner set of two partial cylinders were placed outside the stack but inside the vacuum feedthroughs, allowing the wires to pass through without creating a path for radiation. A larger diameter cylinder was then placed around
the feedthroughs as a radiant break to limit re-radiation from the inner shields to the bell jar. A final thermocouple was placed in this gap to monitor ambient conditions. Plain carbon steel sheet metal was used as opposed to more traditional insulation, to prevent decomposition of insulation by radiant heating. Additionally, metal has the benefit of reflecting energy back to the stack, due to the high shift in index of refraction at the air/metal boundary. The woven silica insulation originally intended to insulate the outside of the chamber emitted significant outgassing, possibly from trapped atmospheric humidity, which compromised the vacuum and so it was not used at all. The entire assembly with circumferential shielding is shown in Figure 87.
Figure 87. IRAC shown with radiant shielding in place

The aluminum foil ball above the heater is in place to shield the plastic thermocouple from direct heating. The braided insulation wiring is the electrical connection for the heater leads. The HFT wiring and additional thermocouple leads wrap around the inner shield and are connected to the vacuum feedthroughs.
After covering the entire assembly in two layers of aluminum foil, the bell jar with Viton gasket was placed on the baseplate. Vacuum grease was not used at the interface because under experimentation, its presence did not positively affect the vacuum conditions and there was some concern over volatilization at high temperature for the grease not under the gasket.

The vacuum pump was engaged and allowed to draw pressure down and for the pump oil to increase in temperature until it reached its recommended conditions. The vacuum pump used was a Diebold D16/A, which is designed for use in corrosive and molten salt environments. The minimum recorded pressure reached by the pump was 18 mTorr. The design operating pressure for the pump is less than 1 mTorr.

A chamber opaque to radiation across the spectrum is required for experimental calibration. To accomplish this, layers of woven silica insulation were interspersed with circular pieces of sheet metal in an attempt to block all transmission through the chamber. The sheet metal should reflect incoming radiation, while the woven silica should scatter and absorb that which is re-radiated, while simultaneously blocking conduction. The insulation is shown below in Figure 88, resting on top of the lower crucible flange.
Once the vacuum pump reached the observed minimum steady pressure, the heater power was turned on and ramped over one hour to the identified set-point power. 23% heater power (approximately 70 watts). This power setting was identified under testing as one which would bring the average crucible temperature to the melting point of molten FLiNaK. Once at the designed set point, the temperatures were monitored until they had reached approximately steady state. The model is only valid if the temperature gradients are linear, and so the experiment was allowed to run at each set point until the heater thermocouple returned identical values over three consecutive readings spaced 30 seconds apart. Due to heating of the baseplate and the thermal inertia of the large amount of metal in the system, it was not feasible to reach true steady state, as the heat sink temperature increased steadily but slowly during the experiment as more heat was added than removed.
However, under sufficiently small temporal derivatives, data was well composed on a line, indicating that temporal effects are not significant to the overall result. That is, the movement in data as temporal effects resolved did not shift the final fitting of a line through the data.

5.3. Results

In order to calibrate the radiation loss term, the chamber was filled with material to render the optical thickness of the chamber infinity. Measurements were taken at multiple power settings to create variation in the radiation parameter, $X$. Multiple data points were taken at each power point to observe the development of $k_e$ and $X$ over time while better averaging over small variations. With the insulation in the crucible, the data points acquired are shown in Figure 89. Included on the plot are the values of the fitting parameters and line fit. The $k_e$ with respect to $X$ was -0.057.
After performing the opaque chamber calibration, the stack was disassembled and the insulation was removed. The crucible was re-sealed and the stack re-assembled. With the empty chamber, another experimental run was performed. The raw data, along with the model results, are shown in Figure 90.
Initially, it was thought that the results for the transparent calibration had yielded acceptable results. The line slope of the transparent chamber was -0.032, while the line slope of the opaque chamber was -0.057. There had previously been some variation observed in the data, specifically the total flux, during each of the initial testing runs that was not specifically attributable to any intentional variation. It was decided to repeat the transparent calibration with the hope that perhaps better alignment, cleaning of contact surfaces, and greater stack compression would improve the results. The results from the 2\textsuperscript{nd} attempt at performing the vacuum calibration are shown in Figure 91.

**Figure 90. Experimental and Model data for transparent chamber (1\textsuperscript{st} attempt)**
The slope of the improved transparent chamber calibration was -0.093. This is a more negative slope than for the opaque chamber. No further experimentation was attempted as the calibration indicated that unintentional variation between individual setups was greater than the intentional variation intended to be captured by the calibration parameters.

5.4. Discussion

The experimental results indicated that further testing would be unproductive, as it would be impossible to generate usable data with the equipment available. The data for the three calibrations performed (one for $\tau = \infty$, and two for $\tau = 0$) are shown in Figure 92.
Figure 92. Line fits for data calibrations

The black arrow in Figure 92 demonstrates how significant a shift could be introduced unintentionally. Although the y-coordinate of points on each line does not directly bear consequence on the overall efficacy of the experiment, overall the values are substantially lower than what was seen in the Fluent model. The average value of $k_e$ for the three fluent calibrations in the complex case, seen in Figure 30 for example, were an order of magnitude higher than the experimental results, a consequence of higher loss terms and poor (and variable) thermal contact. If the experiment could be assembled and disassembled repeatably then the y-coordinate of the points on each line would be expected
to be closely related. What is more significant is the shift in the slope of the lines. Due to the high degree of radiation emitted, and poor repeatability, each calibration is essentially measuring only the radiation loss, and that degree of loss is varying with each unique during setup. This resulted in data with higher uncertainty content than information.

5.4.1. Experimental Post-Mortem

The reasons why the experiment failed to produce useful data are unfortunately both intertwined and varied. The experiment exhibited poor repeatability. Perhaps more than any other cause, unintentional variation introduced between experimental runs degraded the ability to accurately calibrate the chamber and produce useful data. There were too many components which required re-assembly and dis-assembly, where this could not reliably be performed. The heat flux transducer and cold finger had no alignment strategy designed into them, and the HFT wiring was extremely stiff. This made it quite difficult to centrally and flatly align the HFT, cold finger, and crucible. During initial development of the radiant shrouds, it was found that the data could be distorted by changing only the shielding, however, this change was small compared to setup variation and was attempted to be eliminated through more consistent arrangement of the sheets. The use of low-carbon steel as reflective sheeting was likely not optimal, as it appeared to oxidize during exposure to the prolonged thermal radiation fluxes at poor vacuum. A re-design should focus on improving repeatability of the setup.
Compounding the poor repeatability was the higher than anticipated radiation losses. Radiative losses in and of themselves are not unacceptable, but the stronger they are relative to transmission through the chamber increases the measurement uncertainty. The higher radiation losses than anticipated, and than acceptable, was due to a number of design choices that should be revisited. The number of bolts and the size of the flanges was more a product of attempting to minimize manufacturing complexity (and then cost) and an abundance of caution than engineering necessity. The experiment was originally designed with SS316 bolts. The use of high-strength Monel fasteners, which maintain their strength to far higher temperature than was experienced or than SS316, limited the chance that bolt fatigue would allow a salt leak. The use of 10 bolts, and the flange size required to fit ten bolts, increased the radiative area substantially. The bolted flange with black bolts was a far more complex surface than was modeled, which would have a higher effective area. Due to the lack of polishing and the use of black bolts, the emissivity may also have been substantially higher than was modeled. Emission by the chamber was so large that any increase in radiation by streaming was dominated by losses, and the variation in these losses caused by poor repeatability was larger than the measured increase in transfer. It is uncertain, but plausible, that the graphite gaskets did not create an effective thermal bond to the upper plate, and as such did not emit energy effectively from the upper surface, nor transmit absorbed energy through the lower surface. This would have limited the ability to observe streaming radiation by shrinking the B₂ calibration term.
These factors were the primary cause of the experiment failing to produce useful data. There were numerous secondary factors which would have been survivable, but exacerbated the existing challenges. There were unanticipated challenges reaching an acceptable vacuum. The vacuum pump and components should have been able to achieve pressures below 0.1 mTorr, at which pressure conductive losses from vacuum would have been significantly reduced, however, even under the most favorable testing, the lowest pressure observed was only 18 mTorr. This increased conductive losses away from the crucible, increased bell jar heating, increased baseplate heating, and lowered the measured heat flux. The vacuum issues are discussed in more depth in the next section.

There were numerous issues with thermal contact. The thermal contact paste hardened to a ceramic and could not be reapplied repeatedly. This led to reduced use of the paste, as it was not strong enough to hold the components together, but cracked under disassembly, which then necessitated being removed and reapplied. It also appeared to vent some gas when heated in vacuum conditions. This resulted in poor thermal contact between the various components. These large temperature gaps increased the radiation emitted, distorted the linearity of the temperature profile, and decreased the measurement accuracy of the thermocouples by placing them across a poor thermal gap. This was a more significant factor on the HFT, which as a result also measured a lower portion of the heat flux.
Another issue which was more significant than anticipated was the lack of thermocouples close to the graphite surface. Experimentation with the Fluent model showed that the measurement location of the thermocouples would only slightly affect the results of the technique, but it would affect the sensitivity. The further the thermocouples are from the surface, the more radiation loss occurs between the measured temperature and the actual surface temperature. Designing thermocouples into the experiment, ideally embedded directly into the graphite, would improve the sensitivity substantially.

Finally, it is important to be able to adequately cool the baseplate to remove any heat which builds up. Due to the high temperature gaps between components, the heater was required to run to higher than anticipated temperatures to reach desired temperatures. With poor vacuum and high radiative losses, this lead to substantially more heat entering into the environment of the experiment than had been designed into the baseplate cooling.

5.4.2. Vacuum

One of the assumptions in the design of the experiment was that losses from the heat flow path, that is, energy exiting the experiment without being measured by the heat flux sensor, would be a function of radiative power only. Being performed in a vacuum, it was assumed that the thermal conductivity of air would be negligible. After attempting the experiment, it is likely that this assumption was inaccurate. The experiment was not able to reliably reach low enough pressures for thermal conduction to be negligible.
The poor vacuum resulting in heating of the glass bell jar to unsafe temperatures, which required the experiment to be terminated at lower than desired temperatures. The thermal conductivity of absolute vacuum is zero. As such, the experiment theoretically required only radiative insulation and an ultimate heat sink capable of removing the heat input in order to avoid increasing the temperature of the bell. During the initial experimental testing, average pressure was in the range of 400-700 mTorr (50-90 Pa). After numerous efforts to improve the vacuum, pressures in the 50-80 mTorr (6-10 Pa) range were observed. This pressure is simply not low enough to achieve the level of thermal resistivity required to prevent heating of the bell.

As pressure decreases, thermal conductivity of air does not decrease linearly. To fairly low pressures, as density decreases, the mean free path of the atoms increases, which compensates closely for the decrease in density. Potkay et al describe the thermal conductivity of air at vacuum pressures. [37] The conductivity relative to the STP value is a function of the length scale, pressure, and temperature, and is shown in Equation (5.7).

\[
k_{air} / k_{air,0} = \left( 1 + \frac{7.6 \times 10^{-5}}{P \frac{d}{T}} \right)^{-1}
\]  

(5.7)

where \(k_{air,0}\) is the thermal conductivity of air at STP, \(P\) is the pressure in Pascal, \(d\) is the length scale, and \(T\) is the temperature in K. For a length scale of 5cm and 500C, the thermal conductivity of air as a function of pressure is shown in Figure 93.
As can be seen from Figure 93, the thermal conductivity of air at a few hundred mTorr is essentially unchanged from STP values. At pressures less than a hundred mTorr, the thermal conductivity is reduced, but only by a factor of two to three, not enough for the vacuum to function as effective insulation such as would be required to maintain the hundreds of degrees of temperature gap between the crucible and room temperature. This excessive heat loss had another effect of significantly decreasing the total value of the flux through the sensor, such that the uncertainty in the data logger for the heat flux sensor was a significant percentage of the total measured flux.
Based on the Fluent modeling, the heat flux through the heat-flux sensor was expected to be approximately 70-100 watts. This corresponds to a measured DC voltage of 1-2 mV, while the data logger used was accurate to within 1 µV. With the higher than expected heat loss, the measured voltage was only in the range 180-230 µV, increasing the uncertainty on heat flux by almost an order of magnitude. This doesn’t directly correspond to an increase in uncertainty on optical thickness, but it does contribute.

Another effect of imperfect vacuum was caused by pressure increasing as a function of temperature. As the heater power increased, the pressure was observed to increase correspondingly, and then very slowly decrease as the pump removed gasses. This behavior would fit the pattern of either the thermal contact paste or some other material or deposition present in the chamber increasing in volatilization with increasing temperature. For the insulated calibration, the trace of pressure versus temperature is shown in Figure 94.
Figure 94. Heater Temperature and vacuum pressure during representative run

This behavior of increasing pressure with temperature would represent a nonlinear and inconsistent variation in the heat flux that is not well captured by the models. However, estimation of the effect of this slight and slow increase in pressure on the data fitting shows that this increase was not likely to have a measurable effect on the data.

5.5. Conclusions and Future Work

Although the computational results indicate that the experimental concept holds promise, numerous experimental challenges still exist to be resolved. Based on experience with the current iteration of the IRAC, there are numerous improvements which could have greatly improved the measurement sensitivity and accuracy.
5.5.1. *Future Work*

The most significant improvement to the design would have been changes which allowed the chamber to be reliable and repeatedly disassembled and re-assembled. The second would be to reduce the emissive surface area. To that end, a second revision of the IRAC was designed, based on the lessons learned from the failings of the first iteration. A CAD mockup of what an improved experimental setup might look like is shown in Figure 95.
Instead of a flange and graphite gasket, the upper salt surface, which would be under at most atmospheric pressure to drive leaks, is replaced by a single piece of isomolded graphite, which exhibits more uniform conductivity than the gasket graphite.
used in the present design. A tightly fitting piece of graphite is pressed into the upper portion of the crucible, which is machined with a sharp lip for the graphite to seat into. The graphite is held in place by the heater face, and due to the direct contact between graphite and the heater, the use of thermal contact past is obviated. A space for a thermocouple is machined into the graphite to more accurately monitor graphite temperatures. With this methodology, the heater does not need to ever be removed once in place, good thermal contact is ensured, mass and emissive surface is removed from the upper, hotter, portion of the crucible, and the graphite temperature is more accurately known. Three long bolts are used to bolt the heater in place by compression through the lower welded flange.

Instead of the 1” diameter heat flux transducer, a custom 1.6” HFT would replace the HFT in the original iteration. Through this manner, a higher portion of the heat flux would be sampled, and less would be lost to radiation through the bottom surface. The lower graphite seal is similar to the upper seal, with a sharp lip at the bottom of a tightly machined depression in the crucible serving as a sealing surface for the molten salt. The graphite has a machined slot for the placement of a thermocouple in the space between the HFT and graphite. The larger crucible can be aligned much more precisely as it would be the exact same diameter as the graphite. Welded to the cold finger is a bracket which contains bolt holes which align with the lower welded bracket of the crucible. The cold finger bracket also contains the bolt holes to attach the stack to the threaded rod supports. Performing the alignment and compression in this manner aligns the cold finger,
compresses the HFT and graphite, and places more material at a colder portion of the system. Additionally, the walls of the chamber are reduced in thickness from 0.100” to 0.050” in the re-designed version, limiting the conductive portion of heat transfer.

5.5.2. Conclusion

Despite the challenges in this specific iteration, integral measurements of heat flux may be one of the only ways to effectively determine broad spectrum absorption coefficients in molten salts. As these coefficients will be of interest as advanced reactor designs mature, another attempt to acquire data in this manner would be warranted. The presented re-design addresses many of the shortcomings of the existing design and should improve the accuracy and sensitivity of these techniques.
Chapter 6. Conclusions

For the next generation of nuclear reactors, there has been widespread interest in the use of molten salts, such as the eutectic LiF-NaF-KF, as coolants. Molten salt coolants have numerous advantages over water or liquid metal, including the ability to operate at extremely elevated temperatures. Higher operating temperatures lead to higher thermal efficiency and other advantages. However, high temperatures also potentially lead to regimes in which radiation heat transfer (RHT) becomes significant. In order to accurately model RHT in reactor components, estimates are needed for the absorption coefficients of in these salts. Without experimental results, enough data exists in the literature to make a reasonable estimate of the phonon-edge absorption coefficient, whose effects dominate heat transfer, in many candidate salts. Performing this effort for FLiNaK indicates that the effective absorption coefficient ranges from approximately 5 m$^{-1}$ for clean salt to 25 m$^{-1}$ for salt with a high concentration of metal impurities. With estimates for the absorption coefficient, higher fidelity analysis can be undertaken, which is required to observe the effects of RHT. In general, incorporating RHT in analysis increases the quantity of energy transferred to a salt. The amount with which total heat transfer will increase depends primarily on the pipe diameter and wall temperature, as well as properties of the salt. The
emissivity of the walls and the Reynolds number of the flow are also factors worth considering. In general, it is valid to treat radiation by considering it as an additional energy transfer mechanism without considering how it affects conduction and convection at a given axial location.

At the present time, there is essentially no reliable data for spectral absorption coefficients in molten salts relevant for heat transfer. This is due to numerous and potentially intractable experimental challenges faced with measuring salts in this manner. However, integral measurements of heat flux may be one of the only ways to effectively determine broad spectrum absorption coefficients in molten salts. The IRAC, while not able to provide useful data in its current incarnation, describes an experimental technique that may prove useful to future researches wishing to catalog salts in terms of their absorption properties. The presented re-design contained in this dissertation, based on lessons learned, addresses many of the shortcomings of the presented iteration and should improve the accuracy and sensitivity of the technique.

Without experimental results, information can still be gleaned on the absorption coefficients in salts of interest. Using VASP, a set of halide salts under consideration for use as coolants or fuel carriers was investigated. The pure halide salts LiF, FLiNaK, and FLiBe were found to be broadly transparent in the wavelength range of 150-6000nm. The addition of chromium impurities to the salts resulted in significantly increased absorption through a broad portion of the spectrum. This absorption is caused by the creation of
additional partially occupied states that exist within the bandgap for the pure salts. Spectral absorption coefficients for FLiNaK as a function of chromium percentage have been presented. The spectral absorption coefficient for KF-ZrF₄ has also been presented, both as a salt of interest and as a potential analog for salts which contain a high fraction of transition or heavy metal fluorides. KF-ZrF₄ was found to be broadly opaque to photons at all relevant energies. The presented work indicates that VASP is a powerful tool for exploring the properties of materials which are difficult or impossible to test through more traditional means. Its potential to explore properties such as thermal conductivity or the absorption coefficients of a wider class of materials is left as fertile ground for future work.

Incorporating radiation heat transfer in the design of reactor components will allow the heat transfer engineer to leverage the increases in heat transfer associated with RHT. Though RHT will not represent a tremendous effect, even small increases in the efficiencies of multi-billion dollar reactors translate to substantial economic benefits.
References


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Appendix A – Derivation of Optical Thickness Relation for IRAC

In order to determine a more accurate functional form to use to replace the P1 approximation in the additive model, the exact equations were solved for the conditions of interest. The generalized result from the P1 approximation for a participating media with absorption coefficient $\kappa$ between two boundaries at $T_1$ and $T_2$ separated by a distance $L$ has been found to be:

$$q_{rad} = A \frac{1}{1 + \frac{3}{4} \sigma (T_1^4 - T_2^4)}$$  \hspace{1cm} (A.1)

However, this ignores the fact that changes in the radiative heat flux distort the temperature profile, which distorts the energy transfer by conduction, which in turn affects the energy transfer by radiation.

For a planar medium, the energy equation including conduction and radiation, but not convection or source terms, is given below.

$$\nabla \cdot \left[ k \frac{dT}{dz} \right] = -\nabla \cdot \bar{q}_{rad}$$  \hspace{1cm} (A.2)
For one dimensional planar geometry between two plates located at 0 and \( L \), the radiative heat flux can also be solved exactly as a function of position, and the solution is given in Equation (A.3). [9]

\[
q_{\text{rad}}(\tau) = 2\sigma T^4(\tau = 0)E_1(\tau) - 2\sigma T^4(\tau = \tau_L)E_1(\tau_L - \tau) \\
+ 2\int_0^\tau \sigma T^4(\tau')E_2(\tau' - \tau')d\tau' - 2\int_\tau^{\tau_L} \sigma T^4(\tau')E_2(\tau' - \tau) d\tau
\]

(A.3)

where in this instance, the optical coordinate is defined, \( \tau = \kappa z \), and the optical thickness is defined \( \tau_L = \kappa L \). The functions \( E_n(x) \) are exponential integrals defined as

\[
E_n(x) \equiv \int_0^1 \mu^{n-2} e^{-\mu x} d\mu
\]

(A.4)

where the dummy variable \( \mu \) corresponds to the cosine of the angle between the direction of motion of a photon and the path normal.

An analytical solution for \( T(z) \) to Equation (A.2) using equation (A.3) is not possible, and must be solved by numerical approximation and iteration, as the temperature distribution must be known to calculate the integral terms. Thus, even the “exact” solution requires some level of numerical approximation. This can be done to arbitrary accuracy, but even with modern computing, solving these equations in an iterative manner requires extensive computational time.

The solution to Equation (A.2) using equation (A.3) was accomplished by numerically discretizing the domain into a number of nodes \( i \). In one dimension, with
fixed boundary temperatures, the divergence of conductive heat flux for an internal computational node is discretized

\[ k_m(T_i) \left( \frac{T_{i+1} - T_{i-1}}{\Delta z^2} + \frac{d k_m}{dz} \right) \frac{T_{i+1} - T_{i-1}}{\Delta z} = \phi_i \]  \hspace{1cm} (A.5)

where the source term is calculated by numerically computing the gradient of \( q_{rad} \)

\[ \phi_i = -\left. \frac{dq_{rad}(z)}{dz} \right|_{i} \]  \hspace{1cm} (A.6)

Equation (A.5) can be solved initially if the source terms, \( \phi_i \), are assumed to be zero. Once the temperature distribution has been solved using Equation (A.5), Equation (A.3) can be solved for the radiative heat flux, and from this the source terms can be calculated in Equation (A.6) and used to solve Equation (A.5). This procedure is iterated until the residual of equation (A.5) converges to some acceptably small value.

The temperature profile at steady state can be characterized by the non-dimensional radiation-to-conduction number

\[ N_r \equiv \frac{k_m \kappa}{4\sigma T^3} \]  \hspace{1cm} (A.7)

where \( T \) is a reference temperature, \( \kappa \) is the gray absorption coefficient, and \( k_m \) is the thermal conductivity of the medium. For molten salt at typical reactor temperatures, \( N_r \) is likely to be between 0.01 and 0.1. The temperature distribution for various values of \( N_r \) is shown in Figure 96.
Figure 96. Temperature Distributions in planar geometry for various values of $N_r$.

For large values of $N_r$, the gradient of temperature is constant as a function of position and is equal at all points to the overall gradient. This is exactly true if thermal conductivity is constant and approximately true if thermal conductivity is temperature dependant. Mathematically,

$$k_m(T) \frac{dT}{dz} \mid_z \approx k_m \frac{T_1 - T_2}{z_1 - z_2}$$

This means that for a case with $N_r > 1$ an additive approximation of conductive heat flux is largely accurate.

$$q_{con} = A \times k_m \frac{T_1 - T_2}{z_1 - z_2}$$

(A.9)
As seen in Figure 96, for small values of $N_r$, the gradient of the temperature profile is not constant, it is distorted by changes in the absorption coefficient and temperature. Thus Equation (A.8) is not valid, and Equation (A.9) will miss some change in the overall heat flux caused by distortion of the gradient at the boundaries. Assuming the conductive and radiative heat fluxes are independent is a shortcoming of an additive solution incorporating the $P_1$ approximation, such as that reproduced below.

\[
q_{ir} = Ak_m \frac{T_1 - T_2}{z_1 - z_2} + A \frac{1}{1 + \frac{3}{4} [\kappa(z_2 - z_1)]} \sigma \left( T_1^4 - T_2^4 \right) \tag{A.10}
\]

In order to address this discrepancy, the total heat flux separated by a participating, conducting medium with the temperature dependent thermal conductivity of molten FLiNaK, was calculated using Equations (A.3) and (A.2). The coefficient of the radiative heat flux can be determined by fitting a function of the same form as Equation A.10 to heat fluxes calculated in this manner.

Doing so produces an additive relationship given by Equation (A.11).

\[
q_{ir} = Ak_m \frac{T_1 - T_2}{z_1 - z_2} + A \frac{1.028}{1 + 0.649 [\kappa(z_2 - z_1)]} \sigma \left( T_1^4 - T_2^4 \right) \tag{A.11}
\]

This relation produces values of the heat flux over a range of absorption coefficients and temperatures that is well fit to the heat transfer properties of molten FLiNaK.
Appendix B – Nomenclature

It has been attempted to maintain a consistent nomenclature throughout the text.

For reference, symbols used throughout the text can be found here.

\[ \omega_0 = \text{fundamental vibrational frequency} \]
\[ m_i = \text{mass of individual component} \]
\[ f = \text{Szigetti force constant} \]
\[ f_v = \text{VASP scaling parameter} \]
\[ \mu = \text{absorption coefficient} \]
\[ \kappa = \text{absorption coefficient} \]
\[ \kappa_g = \text{gray absorption coefficient} \]
\[ \langle \kappa \rangle = \text{impurity averaged absorption coefficient} \]
\[ \varepsilon = \text{wall emissivity} \]
\[ \varepsilon_{\text{em,rc}} = \text{dielectric tensor} \]
\[ k = \text{thermal conductivity} \]
\[ k_{\text{abs}} = \text{absorptive index} \]
\[ k_e = \text{effective conductivity} \]
\[ r = \text{radial coordinate} \]
\[ \tau = \text{optical coordinate, } \kappa \times r \]
\[ \tau_0 = \text{optical Thickness, } \kappa \times R \]
\[ D = \text{pipe diameter} \]
\[ R = \text{pipe radius} \]
\[ N^m = \text{Molar number density} \]
\[ \rho = \text{mass density} \]
\[ M = \text{molar mass} \]
\[ T_{\text{cl}} = \text{centerline temperature} \]
\[ T_m = \text{mean temperature, } \int ru_x T \, dr / \int ru_x \, dr \]
\[ T_w = \text{wall temperature} \]
\[ T^* = \text{Corrected temperature} \]
\[ I_b = \text{total blackbody intensity, } \frac{\sigma T^4}{\pi} \]
\[ I_{b,\lambda} = \text{spectral blackbody intensity} \]
\[ q_c = \text{conductive heat flux} \]
\[ q_r = \text{spectral integrated radiation heat flux} \]
\[ q_{rt} = \text{heat flux between plates} \]
\[ Q_r = \text{total power transferred to the salt by radiation} \]

Subscripts

\[ m = \text{FLiNaK mixture, property of medium} \]
\[ x = \text{specific sub-component of mixture} \]
\[ s = \text{value associated with salt} \]
\[ g = \text{value associated with graphite} \]
\[ \lambda = \text{differential w.r.t. wavelength} \]
\[ w = \text{value associated with wall} \]
\[ j = \text{denotes energy band} \]
\[ i = \text{impurity band index} \]