

NUMERICAL METHODS TO ESTIMATE THERMAL
CONDUCTIVITY OF POROUS ALUMINOSILICATES

by

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A Thesis Submitted to the Faculty of the

DEPARTMENT OF MINING & GEOLOGICAL ENGINEERING

In Partial Fulfillment of the Requirements

For the Degree of

MASTER OF SCIENCE

WITH A MAJOR IN MINING, GEOLOGICAL AND GEOPHYSICAL

ENGINEERING

In the Graduate College

THE UNIVERSITY OF ARIZONA

2018

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Acknowledgments

I would like to begin with a big thank you to my research advisors and team for all their immense contributions, guidance and support throughout the research period. The simulations and experiments for this work required some training and setup of laboratory equipment and I appreciate the technical support I received from the faculty members and students for the same. National Institute for Occupational Safety and Health (NIOSH) sponsored me throughout this research program and I am forever grateful to them for their continued financial support during this. The thesis defense was a great experience and I would like to give my committee members a big thank you for their support and encouragement. Lastly, a special thanks to some of the mining faculty members who guided me through this program with their professional and administrative support.

Research Advisors – Dr. Moe Momayez (Mining & Geological Engineering), Dr. Krishna Muralidharan (Material Science), Dr. Keith Runge (Material Science)

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Research Team – Joshua Rohne (For experiment work; Student in Material Science), Pratish Rao (Student in Material Science)

Technical support – Lazaro Calderin (Faculty, Material Science), David Streeter (Faculty, Mining & Geological Engineering), Rafat Sadat (Former student, Civil Engineering)

Funding Agency - National Institute for Occupational Safety and Health (NIOSH)

Mining Faculty – Dr. Brad Ross, Sherri Raskin

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Abstract

The thermal transport properties of porous amorphous aluminosilicate structures are investigated using a combination of molecular dynamics simulations and finite element methods. The extent of porosity on the thermal conductivity of the aluminosilicate (AS) structures are characterized. It is seen that the thermal conductivity of the AS structures show a monotonic dependence on the amount of porosity introduced in the system for densities varying between 2.45 to 0.5 g/cc. Interestingly, for a given density (i.e. for a given volume of pores introduced), a larger distribution of smaller pores results in a lower thermal conductivity. This observation is correlated to more phonon-scattering centers in such systems. The results of this work will serve as the basis for designing thermal insulation coatings for mining and building applications.

Introduction

Insulation from heat is one of the great challenges that human civilization has been tackling from ages. Handling a cooking vessel, maintaining temperature in a shelter, keeping the food warm, preventing feet burns while walking in a hot weather, maintaining body temperature etc. are some of the daily life examples where innovative insulators are being used effectively. Quality of an insulator has direct implications in the form of energy consumption and thereby, efficiency in any thermodynamic process. In other words, more energy will be required to keep a system hot if it loses more heat. When the goal is to keep a system cool, more energy will be required to remove the heat from the system if its insulators cannot prevent the external heat from entering the system. However, the cost of developing some of the most effective insulators are quite high which prevents its usage in common scenarios. Take for example, the mining industry. As critical minerals are becoming scarce near the surface, mines around the world are getting deeper. One of the greatest issues with deep mines is strata heat. The high ambient temperatures make it impossible for humans to work without special ventilation methods, which are highly expensive. This is a great setback considering the higher cost of operation due to the increased depth and may have various market price implications eventually. Cost is a big factor for such industries and it is important to look for cheaper and effective solutions. Raw material and processing costs are the major drivers contributing to challenges involved with the development of highly insulating material. This research is oriented towards exploring options to use waste material from a mine to produce these insulating substances. Porous aluminosilicate material was identified with the potential to achieve this goal warranting further investigation.

Aluminosilicate material has shown highly insulating properties. Moreover, they are found in abundance in mine tailings. Thus, it had a great potential to reduce cost of development of highly insulating material for the industries. In addition, mine tailings management is a great ordeal for any operating mine and any use of the same in a mine essentially converts a liability to an asset. This is just one of many other industrial or domestic usages this material might have. However, there may be complications in the processing that may arise from high variation in the composition of mine tailings. At a nascent stage of development, a preferred path would be to use pure substances to develop the material with various structural features and then transition into the variable realm. Porosity has been identified as a key feature to achieve higher insulation from aluminosilicates.

The development of a novel material such as this requires tremendous amount of experimental trials due to the unknown number of factors that may affect the thermal conductivity of the final product. A different approach was used instead. Computational methods were incorporated to reduce the number of critical variables that could have the greatest impact on the thermal conductivity of the final product.

Now, various methods could have assisted in this effort. The selection of methods depended on the required level of details and its applicability. One can use atomistic methods to look at nanometer levels or bulk methods to study macro level features. Various numerical methods were compared in detail to select the most appropriate method for this case. Molecular Dynamics (MD) modeling was chosen to study the atomistic level of detail. This method uses an indirect and more fundamental approach to estimate the thermal conductivity of a material at a nanometer level. It provided the optimal composition of the material along with a trend for the variation of thermal conductivity with density of material at a nanometer level. These results provided a fundamental understanding of the material under investigation.

However, atomistic methods such as MD are computationally intensive and are thus, limited to small-scale calculations. Bulk materials usually exhibit different properties when compared to their

atomistic counterparts. For instance, a chemical product such as this will have variability in the reactions over space. These variations when combined represent a bulk material. An atomistic view cannot encompass such variations in its model. This is why, a bulk method is essential to scale up the atomistic results and make it more realistic. They use the outputs from the atomistic methods to compute the thermal conductivity of a bulk system. Finite Element Method was used to study the bulk properties of this material. This is discussed in detail in the following sections.

After the numerical methods were established to generate inputs for the experiments, testing methodology needed to be devised for the product. This provided valuable inputs to both improve the experiments and modify the simulations. Since the goal was to develop a high insulating material, measurement of thermal conductivity was a great challenge. Equipment to measure low thermal conductivity values are generally expensive and requires tedious details for the setup. Thus, a novel rapid and economical technique was developed as part of this project to overcome this drawback. The details are not provided due to the pending patent. However, the results of testing several control samples are presented in the following sections.

This completes the procedure loop of this project. The overall approach is outlined in Figure 1. It shows how the simulations output feeds into the experiments thereby, modifying the product features. The resultant will be taken through tests to support the simulation results and provide feedback for the next set of simulations.

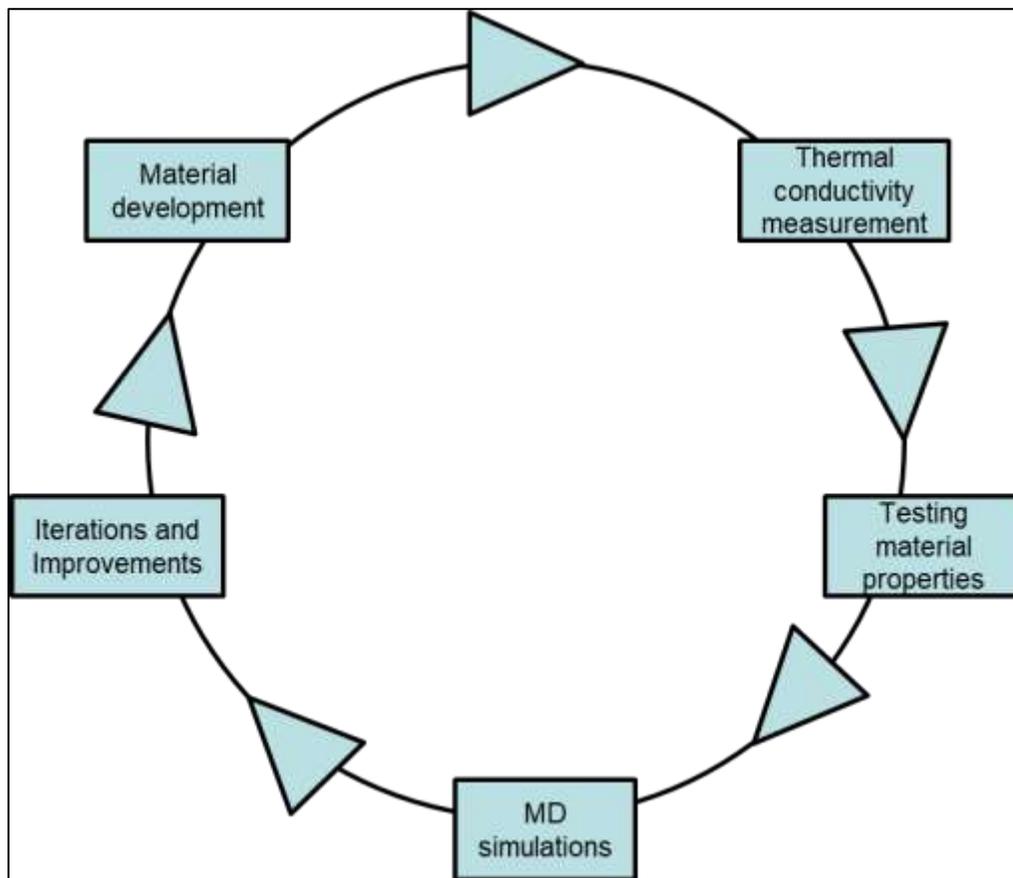


Figure 1: Flowchart portraying the approach for development of Porous Alumino Silicate material.

Chapter – 01: Aluminosilicates

Alumina and Silica are the most abundant minerals of the earth's crust. Aluminosilicates (AS) is a group of minerals, which contain these minerals in such a way that some Si^{4+} ions in silica are replaced by Al^{3+} ions as shown in Figure 2. The charge imbalance because of this replacement is covered by positively charged alkali ions such as Na^+ , K^+ etc. [1] as shown in Figure 2 [2]. Clay and feldspar are the major sources of AS [3], which exists naturally in both amorphous and crystalline forms.

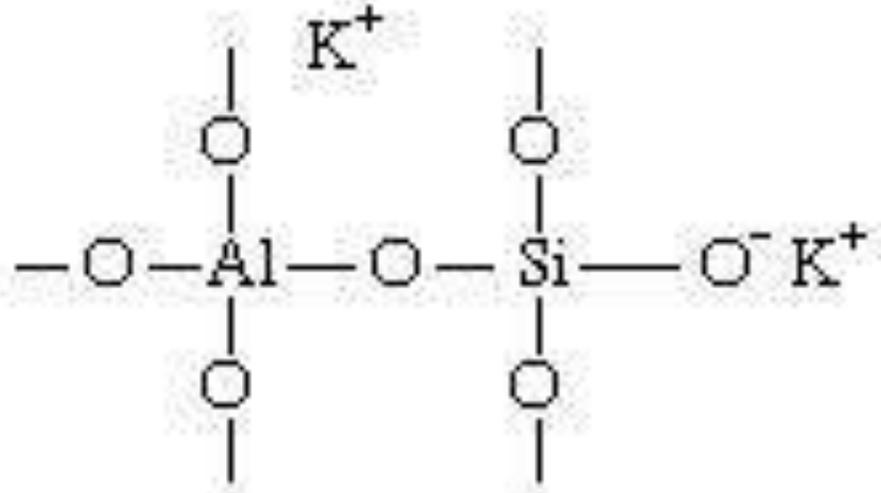


Figure 2: A schematic representation of aluminosilicate structure [2]

Zeolite is the naturally occurring as well as chemically synthesized porous crystalline form of AS. It has silicates and aluminates tetrahedral linked together in chains and has voids in the structure that can allow molecules to pass through (Figure 3). It is widely used for water softening using cation exchange. Aluminum ions impart an overall negative charge on the structure, which is balanced by alkali ions. This bonding is ionic in nature and is readily exchanged by dissolved alkali ions (Ca^{2+} and Mg^{2+}) in “heavy water”. It has also shown to have some shape-preferential adsorption and is thus, used in various molecular level sieving applications. Due to its molecular sieving and ion exchange properties, it is also used as catalysts in several industrial chemical reactions [4].

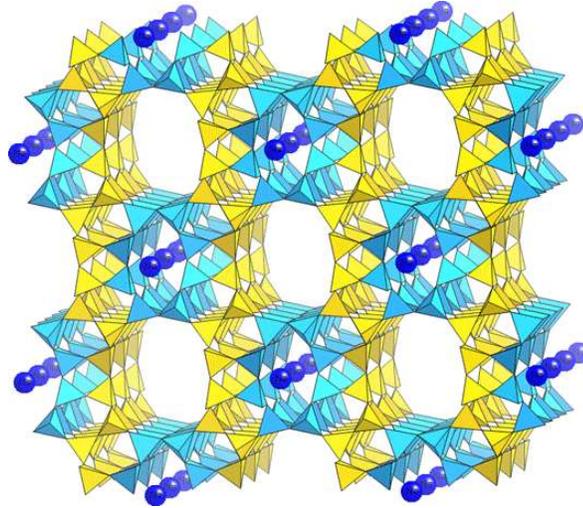


Figure 3: Mordenite - A zeolite mineral. Yellows are silicate tetrahedra and blues are aluminate tetrahedra [4]. Blue spheres represent charge balancing cations.

Aluminosilicates, like many other naturally occurring minerals, have low thermal conductivity. However, they have a better ability to include pores in their structures. Moreover, they are abundant in mine tailings, which makes it a very convenient choice for the development of a low cost thermal insulation material that can be applied in hot underground mines and buildings for heat insulation.

Thermal properties of porous aluminosilicate (PAS) material are analyzed in this work using numerical methods. Various numerical methods are compared at first based on which molecular dynamics along with finite element method are chosen for this case.

Chapter – 02: Numerical methods for thermal conductivity estimation

The measurement of thermal conductivity of a material is not trivial in a laboratory setup. Numerous complications may arise from various factors such as improper insulation, convection and radiation effects, and measurement errors etc. Not to mention, these experiments can take a tremendous amount of time, be expensive and that it may not be possible to record sufficient experimental data. In comparison, numerical methods are a convenient and powerful alternative to laboratory experiments for estimating the thermal conductivity [5]. They can generate an adequate amount of well-structured data in a comparatively shorter time and at lower cost. Data analysis can become much more detailed and relatively simpler. In addition, standards across multiple experiments can be maintained in a more rigorous fashion as opposed to their laboratory counterparts. One of the advantages of numerical methods in thermal properties studies is that it could accelerate the pace of investigation of material under study [6]. There are various forms of numerical methods available for thermal conductivity estimation. One shall select the appropriate method depending on the level of details required. Molecular Dynamics simulation (MD) provides atomistic level of details. Monte Carlo simulation (MC) can be ‘scale-agnostic’ depending on the way it is used. Boltzmann Transport Equation (BTE) is a meso-scale technique and can serve to bridge atomistic and macro scales. Finite Element Method (FEM) is typically applicable to macro scale systems. These methods are very effective when used appropriately. However, lack of understanding of their applicability for various cases can lead to flaws in estimation.

MD simulations are very effective for providing an atomistic window into materials phenomenology. It provides the time-evolution of the system under various conditions, which is a great benefit. Using statistical mechanics formulations, MD can provide important insights into phonon-driven thermophysical properties such as thermal conductivity of fluids and solids. However, classical molecular dynamics approach does not consider electronic degrees of freedom. Thus, it cannot be applied for examining metallic systems’ thermal conductivity. The accuracy of MD simulations is determined by the choice of an appropriate inter-atomic potential, which is necessary to account for atomic and molecular interactions. Further, the duration of the MD simulations as well as the size of the simulated system have to be chosen appropriately to prevent simulation artifacts.

Other atomistic alternatives to MD include MC simulations but MC lacks the ability to explicitly model, time-evolution of systems. At the meso-scale, BTE are well suited for thermal conductivity predictions but prior information on the dispersion relations of the material and lifetimes of thermal phonons are required. At the macroscale, FEM can be used for solving the heat transport equations, however, the thermophysical properties of the material constituents need to be provided. More details on each of the above methods are now discussed.

Molecular Dynamics

Molecular dynamics simulates motion of atoms based on Newton’s second law with the number of atoms varying between a few thousands to a few millions [5]. The motion of these particles are governed by a suitable interaction potential for a specific system. Thermal conductivity estimation through MD is carried out based on two methods – Equilibrium and Non-Equilibrium MD [7] [8]. Equilibrium Molecular Dynamics (EMD) uses the Green-Kubo relations [8] [9], which integrates the heat-current autocorrelation function (HCACF) over time to determine the thermal conductivity. The heat current vector is a time derivative of the sum of products of each particle’s position vector and total energy. It is calculated as:

$$\mathbf{h} = \frac{d}{dt} \sum_i \mathbf{r}_i E_i$$

Here, \mathbf{h} is the heat current vector, \mathbf{r}_i is the position vector and E_i is the total energy of the particle i in the system [10]. The Green-Kubo formula applies linear response theory to the fluctuations of this heat current to calculate the thermal conductivity. In multi-component as well as amorphous systems, high frequency modes arise in HCACF, thereby, care should be taken to achieve convergence. Since Green-Kubo method is highly dependent on the convergence of HCACF, it is difficult to produce reliable thermal conductivity estimations without any transformations performed on HCACF before integration [11].

$$\text{Thermal conductivity} = \frac{1}{k_B V T^2} \int \langle h(t) \cdot h(0) \rangle dt$$

Here, k_B stands for Boltzmann's constant, V is volume of the system, T stands for temperature and $h(t)$ is the heat current vector. The term $\langle h(t) \cdot h(0) \rangle$ denotes an ensemble average. This formula depends on the convergence of HCACF, which can be problematic sometimes. This is dependent on the phonon decay time for the system under investigation [12]. Theoretically, it should be an infinite integral, which means that HCACF will converge at $t = \infty$. However, in terms of computation time, it is unrealistic. Thus, a suitable end time needs to be determined, over which HCACF is integrated [8]. This however, comes at the cost of accuracy. Depending on what the end time is, the integration can yield different results for the thermal conductivity. Implementation of EMD for thermal conductivity estimation is considered comparatively straightforward with an existing code as pointed out by McGaughey et al. [13].

Non-Equilibrium Molecular Dynamics (NEMD), on the other hand, uses the source-sink principle to get the thermal conductivity of a system using Fourier's law [14]. The Fourier's law is expressed as $J = -k \nabla T$. Here, k is the thermal conductivity, J is the local heat flux and ∇T is the temperature gradient [15]. This approach is very similar to a typical hot plate technique for measuring the thermal conductivity where a temperature gradient is created for the heat to flow from the source on one end to the sink on the other. Due to this underlying principle, NEMD is most suitable for solving the heat equation in one-dimension [16]. It is not suitable to study lower thermal conductivity system since the time of simulation to reach steady state can be very high. This method, due to its transient nature, has been particularly proven most useful for simulating heat transport phenomenon in liquids [17]. EMD methods do not work very well with fluids due to large thermal fluctuations in energy. However, EMD handles fluids well. One major drawback of EMD, however, include a very high simulation time, which may lead to a smaller system size for analysis. It also is highly dependent on the types of heat baths used, further complicating the process [8].

Monte Carlo simulations

Monte-Carlo (MC) simulations is a class of computational algorithms used to solve problems that may lack an analytical solution. They rely on repetitive random sampling to obtain numerical solutions. MC selects inputs for the simulation from a probability distribution of the domain parameters, performs the calculation, and generates a probability distribution for the outputs. If the simulation is large enough, the distribution provides a good estimation of the result. It has wide variety of applications such as marketing analytics [18], risk analysis in businesses, finance, economics, operations management [19], understanding chemical reactions, healthcare practices, games and many more.

For examining thermal conductivity, MC uses the same principles – randomly sample the inputs and generate a large set of outputs, which when plotted, gives a probability distribution of the results. The inputs could be the position of atoms in a simulation cell, the temperature of interest and the active phonon

scattering modes (in case of solids), while the output is the thermal conductivity based on a large set of data collected for various positions and scattering events. MC evaluates space equilibrium averages for constant temperature ensembles [20]. The underlying equation used by MC is the Boltzmann Transport Equation (BTE) to analyze and calculate heat transfer [21]. MC does not solve this equation directly but it tracks a large number of phonons in the simulation cell based on which, it arrives at an approximate thermal conductivity. The process is described in detail by Chen et al. [22] to estimate the thermal conductivity of a silicon nanowire.

MC simulations have many variations for solving thermal conductivity problems depending on the user's requirements. For instance, Neek-Amal et.al [23] used a modified MC simulation to study thermal gradient along a 2-D Ising system. They use a non-equilibrium method of thermal conductivity estimation. This is similar to the Non-Equilibrium Molecular Dynamics (NEMD) method. It has a high and a low temperature boundary, and the sample under investigation in between. For a thermal gradient, one needs a smooth gradient from the higher temperature end to the lower for homogeneous material. Now, that might not be the case in a simulation since it may develop local variations. Thus, a standard MC method for thermal conductivity estimation could not be applied for a non-equilibrium case. They had to choose a modified version of the same to account for these local variations and used that with the Fourier law of heat transfer.

Boltzmann's Transport Equation (BTE)

This method falls in between the atomistic and macro scales. This equation correlates the atomic properties of a material to its macroscopic properties such as thermal conductivity. This is why it is usually categorized under meso methods. BTE is a statistical approximation of this transport. It considers a gas at a molecular level and characterizes the effect of a force field on the position, momentum and collisions of the particles in a system. This characterization is performed statistically by BTE using a suitable distribution function for the system under investigation. The distribution function could be the Maxwell-Boltzmann, Bose-Einstein or any other distribution, depending on the system under investigation.

The Maxwell-Boltzmann distribution provides the velocity distribution of atoms/molecules in an ideal gas system. They argued that the velocities of molecules in a system are different and based on certain assumptions, follows a particular distribution for specific temperatures [24]. The distribution function is written as:

$$f(v) = \sqrt{\frac{2}{\pi}} \frac{v^2 e^{-\frac{v^2}{2a^2}}}{a^3}, v \geq 0, a = \sqrt{\frac{k_B T}{m}}$$
. Here, k_B is the Boltzmann's constant, v is the molecular speed, T is temperature and m is mass of a molecule of the gas [24]. This distribution is also termed as classical since particles described here are 'distinguishable'.

Bose-Einstein distribution on the other hand is for a quantum mechanical case where particles are 'indistinguishable' from each other. Thus, the state of the gas can be identified by plotting the states of collection of these particles. This distribution is written as:

$$\bar{N} = \frac{1}{e^{\beta(\epsilon_r - \mu)} - 1}$$
, where N is the no of particles in a gas, β is inverse $k_B T$, ϵ_r is the energy of a particle in a state say r and μ is the chemical potential [25].

The term 'transport' in BTE, refers to the response of electric or heat currents in a system to an applied field, electric or thermal. When there is a field applied across a material, it disturbs the state of equilibrium of the material. The material thus, 'responds' to the field by generating these currents. The

transport equation attempts to delineate the correlation between this applied field and the response. This response could be linear or non-linear depending on the system.

The BTE for phonon transport can be expressed as: $\mathbf{V}_g \cdot \nabla T \frac{dn}{dT} = \left(\frac{\partial n}{\partial t} \right)_c$ [22]. Here, \mathbf{V}_g is the group velocity, n is the distribution function, T is the local temperature and $\left(\frac{\partial n}{\partial t} \right)_c$ is the rate of change of the distribution function n due to the collisions denoted by letter c . This collision part is unknown for this equation and is not trivial to solve. It requires the knowledge of how the particles in a system interact with each other and which distribution governs this interaction.

Finite Element Methods (FEM)

This method is applicable for bulk systems and includes macroscopic characteristics of the material under investigation such as fissures, cracks, shape, pore size etc. for estimating its thermal conductivity. Finite element method (FEM) is used to estimate or test various material properties based on computer generated models and input parameters. Thermal conductivity estimation is one of the many uses of FEM including deformation analysis, fluid flow, electrostatics etc. It divides a system into smaller and regular shaped parts or elements, which are connected through nodes. These elements could be 2-D or 3-D depending on the system and type of analysis. Then, the underlying equations for the problem under investigation are applied on these nodes and solutions for the overall system is calculated. This means, more the number of nodes, better the accuracy. In other words, smaller the elements, better the accuracy. However, if the elements are too small, even rounding off the numbers can lead to significant errors in the results. FEM uses “Finite Differencing” between elements to get overall thermal properties. If the elements are too small, the differences can be so small that even rounding them off can skew the results significantly.

It is challenging to define an accurate equation that works for any bulk property of a system including thermal conductivity. FEM uses a ‘piecewise polynomial interpolation’ to circumvent this limitation [26]. It interpolates the desired parameter over the entire structure using this method. The quality of the thermal conductivity estimations depend on some key factors – 1) How good and appropriate the meshing for a particular system is 2) How well the time is discretized (for transient methods) 3) How the boundary conditions are applied and 4) the type of material selected [27].

Chapter – 03: Comparison of the numerical methods

Thermal conductivity estimation using MD is an expedient way to overcome many experimental challenges in getting a numerical approximation (or sometimes “trends”) when investigating the thermal characteristics of a system. One of the key features of MD is that it produces large volumes of organized data for every simulation with a timestamp, which can be extremely difficult to produce from laboratory experiments [5]. The timestamping helps the users to see a process flow for each simulation with a greater level of detail, and understand how the experiment progressed over time. This can be a critical factor in many studies. Experimental setups where temperature parameters are at the extreme end can be simpler to simulate with MD. For instance, Galamba & Castro [28] show how thermal studies for molten salts can be difficult using experimental methods due to its high melting point. However, these practical constraints are removed by using numerical estimations through MD. Further, for a nanoscale system, setting up a lab experiment for thermal conductivity estimation can be both very challenging and expensive. Because MD is naturally suited for examining materials at the nanoscales, it is a suitable alternative to experimental techniques [5]. The results can later be used to create a conduit between the atomistic and macroscopic scale through ‘consistent embedding techniques’ [29]. Here, K. Runge talks about effective use of fundamental information of a system (quantum-level) to evaluate its macroscopic properties. This is essentially multiscale modeling, which is discussed later in this section. When studying thermal properties of nanofluids, Sun et.al [9] study the effect of rotation of a nanoparticle in a fluid enhances its thermal conductivity by inducing microscopic convection. This study would have been extremely difficult to perform in laboratory environments however, atomistic methods such as MD made it possible to simulate it in a computational environment based on desired theoretical conditions.

While MD reduces the experimental burden, it often shows a great discrepancy with experimental measurements, sometimes several orders of magnitude [8]. Thermal conductivity estimates of certain solids from MD have been shown to have more than +/- 25% disagreement with experimental values. This discrepancy can reach 40-110% for amorphous solids (silica) [13]. A difference of +/- 20% has been considered acceptable [13], which shows how inconsistent MD could be with respect to experimental thermal conductivity values, especially in solids. There are several reasons for these variations. G. Volz & Chen [30] have shown that the thermal conductivity of silicon nanowires is one to two orders of magnitude less than the bulk Si thermal conductivity. They attribute this to a phenomenon called boundary scattering of phonons (a quasi-particle for thermal energy transport). The scattering increases in nanowires compared to bulk Si due to the small cross section area of nanowires. For the experiments carried out by G. Volz & Chen, this scattering is desirable. However, it identifies the importance of shape and size of solids in MD simulations. Moreover, MD simulations for perfect crystals will provide a substantially different thermal conductivity when compared to the bulk conductivity since the latter might have defects in the structure. Both MD and MC need an initial atomic structure to run thermal conductivity simulations. These modeled structures are compared with actual structures by means of radial distribution functions (RDFs). Actual bulk material can have significantly different RDFs, which can another reason why atomistic methods such as MD show discrepancies with experimental thermal conductivity values.

Thermal conductivity estimations can be challenging in the case of highly thermally conductive crystals. Heat is transported in non-metal solids primarily through phonons. To estimate thermal conductivity, MD uses phonon relaxation times in the simulation. If there is a high scattering of phonons in a structure, this relaxation time is lower compared to when there is less scattering. In other words, the higher the scattering of phonons, the lower the thermal conductivity and vice-versa. Lattice structures with high thermal conductivity are characterized by low-scattering cross-section for phonons. Since scattering

is low in these lattice structures, phonon takes a longer time to decay which increases the computational time considerably. Moreover, for a valid simulation, the cell size has to be larger than the mean free path of these phonons. For crystals, these paths are longer, thus, a bigger simulation cell is required, which may further increase the computation load exponentially. For lattice structures with lower thermal conductivity however, MD is much faster compared to other methods as shown by Wei et.al [31] for CuInTe₂. Thus, for solids, MD is more suitable for lattice structures with lower thermal conductivity values. Similar logic can be applied for amorphous solids. MD estimates the thermal conductivity faster since amorphous solids tend to scatter the phonons more, thereby, comparatively reducing the computational time. The results may still show some discrepancies with experimental values, sometimes large, as we discussed earlier [13].

For fluids however, MD has been a very reliable option, with the smallest amount of discrepancies compared to experimental values. Fluids have no long-range order and thermalize quickly. For example, while studying the thermal effects of Pt-nanoparticles suspended in Xenon gas, which acts as a base fluid, Eapen et al. show that thermal conductivity estimations through MD have great conformance with experimental results [32]. Thermal properties of liquids are widely studied using numerical methods such as MD because they do not have a general thermal transport theory available for them [33].

One of the most important parameters for any MD simulation including thermal conductivity is the selection of an appropriate interatomic potential for the system under investigation. While working on understanding the effect of various computational parameters on the predicted thermal conductivity of carbon nanotubes (CNT), Salaway & Zhigilei show that the thermal conductivity of the same system, when estimated using different interatomic potentials (along with other factors), results in high variation [34]. These interatomic potentials govern the motion of atoms in a system. Thus, an incorrect potential will lead to improper interactions thereby, skewing the estimated thermal conductivity.

In the same study, Salaway & Zhigilei also show the dependency of thermal conductivity on the system's dimensions, in this case, the length of the CNT [34]. For NEMD method of thermal conductivity estimation, there is a heat source and a heat sink on either side of a system. They showed that the thermal conductivity of the system using NEMD was dependent on the length between source and sink until a cut-off length. Beyond this cut-off, they found the thermal conductivity to be constant. The reason for that, as they point out, can be explained based on the phonon mean free path with respect to the length of the system. If the mean free path is longer than the length of the system, then the phonons behave in a ballistic fashion, and Fourier's laws are not applicable [35]. Ballistic transport is when phonons travel from one end to the other without any resistances. In other words, the length of the system is smaller than the mean free path of the phonons. Diffusive transport on the other hand occurs when the phonons have collisions before they reach the opposite side of the system. For diffusive transport, length of the system is more than the mean free path. Fourier's laws describe diffusive, not ballistic transport. For ballistic transport, the thermal conductivity in theory is infinite. However, thermal conductivity will converge if diffusive type transport dominates in the system. In this case, Salaway & Zhigilei observed that by increasing the intermediate length of CNT beyond a cutoff of 200nm, thermal conductivity flat lines to a constant value. In other words, as the CNT system length increases – compared to the phonons' mean free path, the thermal conductivity results become more reliable. They suggest that a careful selection of system dimensions is critical to arrive at a realistic thermal conductivity value with MD. This however, can be difficult and time consuming to identify for a new system under investigation. This drawback however, can be overcome by using EMD with periodic boundary conditions. Periodic boundaries ensure that there are no surface effects and is implemented by repeating the MD system under study in all three directions. Thus, any atom 'exiting' the system is put back into the system by enabling it to 'enter' the system via the opposite end.

Boundary scattering as discussed earlier, can significantly affect the thermal transport in atomistic systems [35]. Thus, MD results can be highly affected by this. While studying the thermal conductivity of Graphene Nanoribbons (GNRs), Hu et al. found that the scattering of phonons at the boundary of the simulation cell could significantly affect the thermal conductivity of the GNR [36]. When the simulation cell is oriented in different directions with respect to a GNR structure, the edges have different forms Zigzag and Armchair. They found that the thermal conductivity of the zigzag edged simulation cell was 20-50% higher than the armchair edged simulation cell. Although the purpose of this experiment was to study this effect, it may cause some issues in other cases where this study was not intended. Thus, for a simulation, the edges of the simulation cell need to be carefully monitored to avoid any unintended variation in thermal conductivity estimation. A good approach would be to try various edges and select the optimal solution. However, that will increase the complexity and time required for any study using MD.

Another key parameter is the number of particles in a system. While studying the enhancement of thermal conductivity in nanofluids, Sarkar & Selvam noted that the thermal conductivity of argon based fluid with Cu nanoparticles varies with the number of atoms in a fashion similar to size-dependent variations [7]. This can be explained with the mean free path of the phonons as well. With higher number of atoms, the effect of ballistic transportation is reduced and diffusive transportation becomes the dominant mode. As discussed earlier, thermal conductivity will keep on increasing infinitely in a ballistic transport mechanism. Thus, inclusion of more atoms in the system would make the system more prone to lose momentum due to collision and thereby, making the thermal conductivity approximation more realistic. This consideration, however, adds to the complexity of the MD simulation. Thermal conductivity simulation is a time intensive process, where computation time increases rapidly with the increasing number of atoms in the simulation cell [37] [33]. For a few hundred to thousand atoms in a system, the calculation of potential energy and force among other parameters, considering the complex interaction potential between all atoms for several thousands of time-steps is understandably computation intensive. This is one of the major drawbacks of a statistical method like MD for atomistic methods.

For metals, thermal conductivity estimation using MD is usually not a viable option. In metals, thermal conductivity is governed by electron transport, which is not allowed in classical MD approach. There are ways to circumvent this issue. However, they are not trivial to implement [5]. MC simulations on the other hand, can work with BTE for estimating thermal conductivity, which in turn consider both electron and phonon heat transport. This makes BTE and by extension MC, suitable for thermal conductivity simulation in metals along with other materials. BTE can supplement MD for metals, while the latter performs adequately for modeling non-metals.

For low thermal conductivity material, the user needs to be vary of the tolerance of a simulation result. Thermal conductivity estimations from MD has a tolerance associated with it that varies with simulations. It is important to consider this as part of the estimated value. In other words, if the estimated thermal conductivity becomes comparable to the simulation tolerance, the associated variance would be significantly high thus, making the estimated value unreliable.

One of the key advantages of MD over MC is ‘timestamping’ of various states achieved at all the time intervals. Calculations of various properties/parameters associated with the particles in a system are done at every time step for MD. It thus, provides the data on evolution of the system. It is possible to get the information on the state of the system at every time step with MD. MC on the other hand, uses a random input taken from a user defined distribution function (e.g., Maxwell and Bose-Einstein distributions) and calculates the thermal conductivity. It just relies on the resultant thermal conductivity distribution and does not factor time in it.

As discussed earlier, phonon relaxation time is one of the key factors in thermal conductivity estimation using MD. MD needs to allow enough simulation time for phonons to dissipate. This can also be observed on the HCACF function, which should converge to almost zero when phonon dissipates. If the simulation time is not enough, thermal conductivity can be substantially underestimated. Monte Carlo simulations does not have such issues. However, convergence for MC can take more time for a better accuracy.

MC usually has a lower computation time and cost compared to MD [21]. However, it can get time intensive if the number of data set required is very high but same goes for MD. In particular, energy convergence in MC is faster. MC simulations work with only the particular inputs required for a specific simulation whereas MD simulations use the same number of parameters to estimate both energy and thermal conductivity. Since energy requires only the position of atoms to be known, MC converges faster whereas MD takes more time since it does calculations for all the parameters. Thermal conductivity however, requires more inputs for MC (it uses BTE as underlying equation) but MD still uses the same number of parameters, which is why the calculations become slower for MC. MC has also been proved to have better accuracy for larger nanoscale objects [37]. However, it does not provide information on time dependence and magnitude of fluctuations of position and momentum variables away from their equilibrium values [20].

MC simulations generally use BTE as an underlying equation [38] to get the thermal conductivity of a system. Now, BTE requires solving a very complex equation when a distribution function is included in the equation. For example, Chen et al. [22] show that when Plank's distribution is used in BTE, it becomes highly challenging to solve it by brute force. This is where MC appears. Instead of solving the BTE, it uses a probabilistic approach to find the 'most-likely' solution. It gets a distribution function as an output, which is then interpreted appropriately by the user. In other words, it uses a well-established equation to get thermal transport in an atomistic system without solving a highly complex equation.

Another aspect of solving BTE is use of Bessel functions. Heat conduction is shape dependent and thus, the equations vary based on that. These functions are used to solve those complex equations and thus, making BTE even trickier for complex shapes. This is where MD, MC and finite element methods are better. MD considers atomic interaction potentials for its estimations and thus, shape is not a consideration even if it affects the solution. MC uses probabilistic methods to solve BTE thereby taking away this complexity. FEM breaks the system into smaller pieces. Thus, thermal conductivity of very complex geometries can be estimated with great precision without the need of solving any complex equation unlike BTE.

BTE is typically used for examining pristine materials (perfect crystals) [39], and introducing defects complicates the BTE based solution. Further, a key aspect of using BTE for thermal conductivity modeling is use of Bessel functions, which introduces complexity. Thus, combining with MC provides a useful framework towards this end. However, as noted earlier, thermal conductivity estimation from BTE require prior knowledge of the dispersion relations of the material [40], and can be more computationally intensive as compared to MD. Thus, MD provides a more straightforward framework for modeling thermal conductivity of 'real' materials with defects.

For heterogeneous complex macroscale systems, FEM is suitable for estimating thermal conductivity. An example is the work of Yibin Xu & Koichi Yagi, who used FEM to estimate thermal conductivity of randomly, dispersed composites instead of using any analytical methods because of this reason [41].

In various equations for thermal conductivity estimations, shape is an important factor. Most of the equations rely on simple shapes and boundary conditions, which is not the case usually in real-life scenarios [27]. FEM can provide solutions to this problem since it relies on dividing these complex systems into regular shaped smaller elements, solving the underlying equations and extrapolating it over the bigger object.

FEM however, approximates the shape properties. When an object is divided into smaller regular-shaped elements and then reconstructed, it may not be the same exact shape. It is similar to a digital image of any object. The image is divided into regular-shaped pixels. Thus, the digital image approximates the real object and is not the exact replica. What it means in terms of thermal conductivity is that it is an approximate value and does not correspond to the exact shape of the object under investigation. Having said that, it can still provide very high accuracy thermal conductivity estimations [27]. Huang & Usmani however, warn about the unforeseeable sources of errors in the solutions, which the users should be wary [27]. One needs to be cautious when using these results and shall analyze and compare solutions with expectations and available literature in order to be sure about the results.

One of the most critical aspects of FEM is that it requires some sort of knowledge of thermal conductivity or related macroscopic material property before it can estimate the same for a bulk object. Micro and meso methods, usually estimate thermal conductivity using assumptions that are more basic and indirect relationships. Thus, the estimations have a better fundamental basis however, only for a very small system. Results from these methods are used as inputs with FEM in many cases. For instance, Dongfan Yan et al. studied the variations of thermal conductivity of composite materials with the orientation of fibers within it. They used the Fourier's law of heat conduction to get the thermal conductivity of the composite, which needs information on heat flux across the system [42]. The knowledge of this thermal conductivity can also be obtained in conjunction with other methods such as MD. MD works at atomistic scales while FEM is a macro scale method, which is why this type of conjunctions are called multiscale modeling. MD and FEM thus, complement each other to arrive at a more precise thermal conductivity by using this method. Goddard et al. discuss this multiscale modeling to estimate thermal conductivity among other things for organic materials [6]. While modeling the thermal conduction in graphene epoxy nanocomposites, Bohayra Mortazavi et al. used multiscale modeling [43]. They used MD simulations to get the thermal conductivity of this material at an atomic scale, used the results to develop representative volume elements (RVE) for FE (micro scale) and modeled the material at a macro scale using FEM.

Atomistic methods like MD can show significant differences in thermal conductivity when compared to those of experimentally determined values of macroscopic systems, especially if bulk defects are not accounted for in MD. Thus, a proper understanding of the 'pros' and 'cons' of obtaining thermal conductivity values from MD has to be obtained before these data are fed into FEM simulations. Further, interfacial resistance to thermal transport as well as the roles of surfaces in nanoscale objects (which have high surface area to volume ratios) have to be properly evaluated in MD before they are scaled up to FEM [44]. Thus, one needs to be careful how the thermal conductivity information from atomistic methods is used with macro-methods like FEM.

Based on the above comparisons, MD simulations seem to be the best numerical method for thermal conductivity estimations for amorphous porous aluminosilicates since – 1) It does not require prior knowledge of thermal properties of the system; 2) Converges faster for thermal conductivity simulations compared to MC; 3) It is less complicated compared to BTE. Thus, MD is chosen for characterizing thermal properties for PAS in this study. Since MD simulations work for nano-scale systems, the results are supported by finite element method.

Chapter – 04: MD simulations for PAS

These simulations are aligned to – 1) Get an optimal Si to Al ratio for better insulation of PAS, 2) Understand variation of thermal conductivity with the density of PAS, and 3) Study the effect of pore size distribution on the thermal conductivity of PAS.

The interatomic interactions of atoms in PAS system were based on the work of Sadat et al. [45]. Here, Morse potentials in conjunction with electrostatic Coulombic interactions were shown to work best for this system. Morse potential consists of two contributions –short-range attractive and repulsive interactions. Here, the short-range potential is a measure of the bond dissociation energy, while the repulsive term prevents unphysical interactions between atoms when they are too close to each other. A suitable cutoff distance is used for both these types of interactions. The following equation denotes the interaction potential used in this work.

$$U(r) = \frac{z_i z_j e^2}{r} + D_{ij} [\{1 - e^{a_{ij}(r-r_o)}\} - 1] + \frac{C_{ij}}{r^{12}}$$

Here, $U(r)$ represents the potential energy corresponding to two atoms i, j that are separated by a distance r . z_i is the charge on a particle i , e is the elementary charge, D_{ij} is a measure of the bond dissociation energy, a_{ij} is the function of slope of the potential energy well and r_o is the equilibrium bond distance. These values are mentioned in Table 1.

Table 1 – Constants in the Morse potential equation for the constituent atoms [45]

Interacting atoms	Dissociation constant, D_{ij}	Function of slope of potential energy well, a_{ij}	Equilibrium bond distance	C_{ij}
Na - O	0.023363	1.763867	3.006315	5.0
Al - O	0.361581	1.900442	2.164818	1.0
Si - O	0.340554	2.006700	2.100000	1.0
O - O	0.042395	1.379316	3.618701	22.0

For equilibration of samples prepared by either method, the following protocol was adopted: NVE ensemble was run for 0.2 ns followed by heating and quenching the system from 300K to 4000K back to 300K in NVT ensembles, which took 2.4 ns overall. This was followed by an NPT ensemble for a nanosecond. Since this equilibrated structure was used for other simulations, in those simulation runs, heating and quenching was replaced by just a 0.2 ns NVT ensemble to stabilize the structure. To get the thermal conductivity, the Green-Kubo method was used and HCACF was obtained for eight nanoseconds of simulation time.

Simulation Setup and procedure

The PAS system consists of Sodium (Na), Aluminium (Al), Silicon (Si) and Oxygen (O) as constituent atoms. The quantities used for this simulation are mentioned in Table 2. Note that this particular system has a Si-Al ratio of 3:1. This ratio was found to be the most optimal based on its tensile strength [45] and mechanical stability (discussed later). In total, 5616 of these atoms were initially defined in a cubical unit cell. The numbers of each kind of atoms were based on the stoichiometric ratios and a desired cap of around 5000-6000 atoms. The simulation cell was assumed to have periodic boundary conditions. Initially it was heated to 3000 K and gradually quenched to 300 K to form amorphous structures.

Table 2- Constituent atoms in the system with their mass, charge and number

Atoms	Mass	Charge	Number of atoms
Al	26.980	1.8	432
Na	22.980	0.6	432
O	16.000	-1.2	3456
Si	28.065	2.4	1296

Next, the system was equilibrated at 300 K to ensure that the system was at a local energy minimum. The ensuing structure was compared with previous work performed by Sadat et al. [44], to ensure structural consistency. To simulate materials with different densities the following was performed: 1) Changing the density of the simulation cell by expanding it, and 2) Creating a spherical pore within the simulation cell.

The 300 K equilibrated structure for a PAS structure with Si to Al ratio of 3 is shown in Figure 4. The corresponding density equaled 2.62 g/cc. The simulation cell size was approximately $42 \times 42 \times 42 \text{ \AA}^3$.

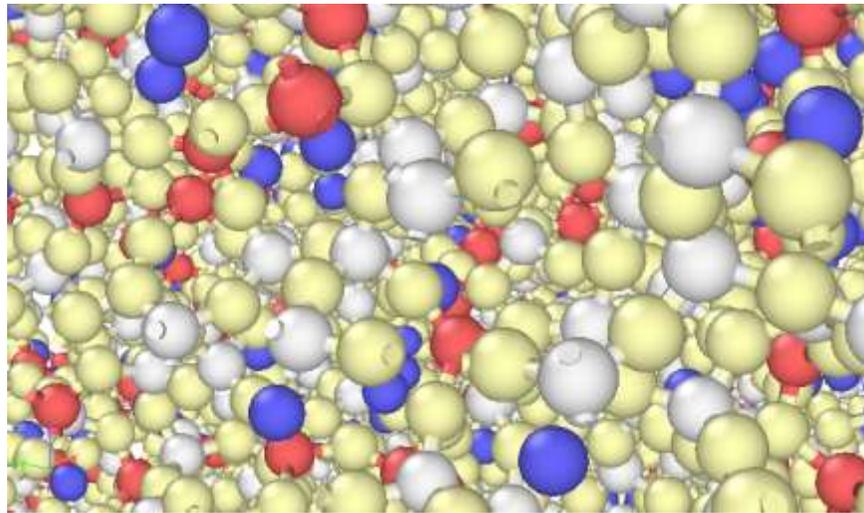


Figure 4: Equilibrated PAS structure for Si-Al 3:1 (using OVITO). Yellows are oxygen atoms, whites are Silicon, blues are sodium and reds are Aluminium ions.

For the density runs (i.e. method 1), the positions of atoms were uniformly scaled to a preset volume, and then the system was subjected to a constant pressure of 0 bar at 300 K (Figure 4). This leads to small sub-nano metric pores formed within the cell. Expanding the equilibrated simulation cell to different preset volumes resulted in different densities. Thermal conductivity values for these densities were then obtained and analyzed to characterize trends.

In method 2, (i.e. spherical pores method), atoms were removed from the center of the simulation cell, while ensuring stoichiometry. This was achieved by re-introducing atoms (if necessary to maintain stoichiometry) in random locations within the cell (Figure 5).

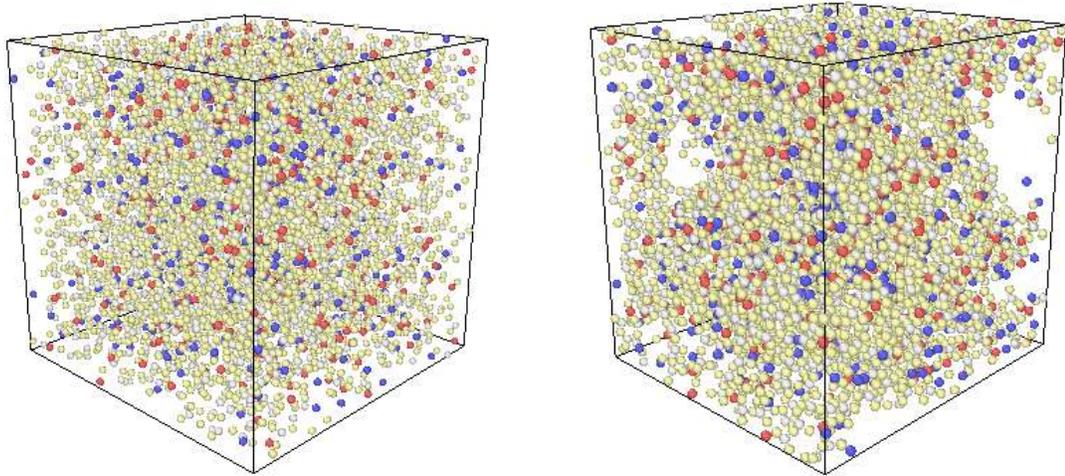


Figure 5: Section of a 3-D simulation cell. Left: Simulation cell after blowing up the side length, Right: Atoms in a stable structure after the simulation.

MD simulation results

As a first step, the effect of Si to Al ratio was studied. Figure 6 shows that Si-Al ratio of 1:1 and 3:1 had lower thermal conductivity compared to 2:1. Si-Al ratio of 3:1 was selected for further analysis since it has better tensile strength compared to 1:1 [45]. In addition, for the porous systems, the thermal conductivity values were found to be lower for Si-Al ratio of 3:1 as compared to 1:1. This is illustrated in Figure 6.

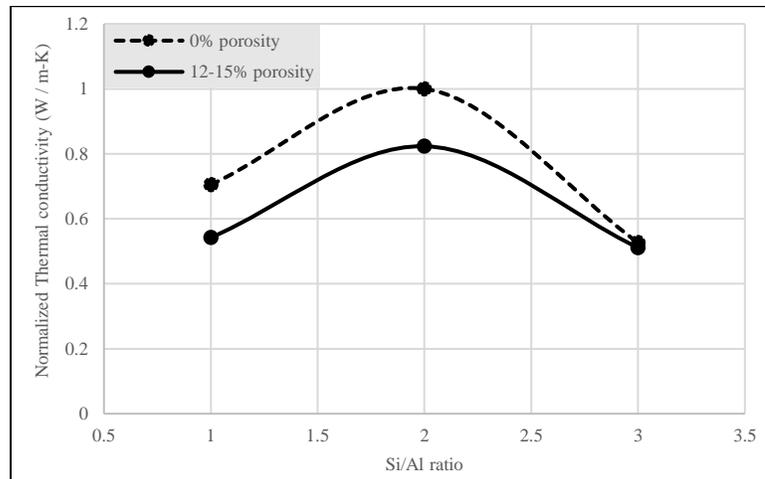


Figure 6: Normalized thermal conductivity vs Si to Al ratio for the Aluminosilicate geopolymer system

After the optimal Si-Al was established, the effect of density (from Method 1) on thermal conductivity was studied. It was observed that with decreasing density, the thermal conductivity decreased as well in a proportional fashion as shown in Figure 7.

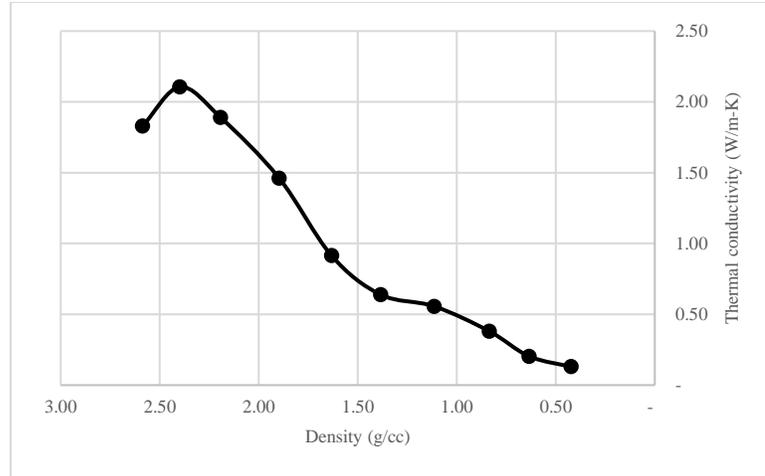


Figure 7: Thermal conductivity vs density for the Alumino Silicate geopolymer system

Next, attention is paid to a PAS structure corresponding to Method 2. Specifically, a system with density = 2.5 g/cc with a central pore of radius varying from five to nine angstroms, was examined to compare and contrast the role of a central pore versus many smaller pores for an equivalent system-density. Thermal conductivity for this central pore system was estimated to be 1.85 W/m-K. This falls within the variation bar for the thermal conductivity of approximately 2.0 W/m-K for many pores at a density = 2.5g/cc (Figure 8). This shows that the morphology of pores does not affect the thermal conductivity of PAS.

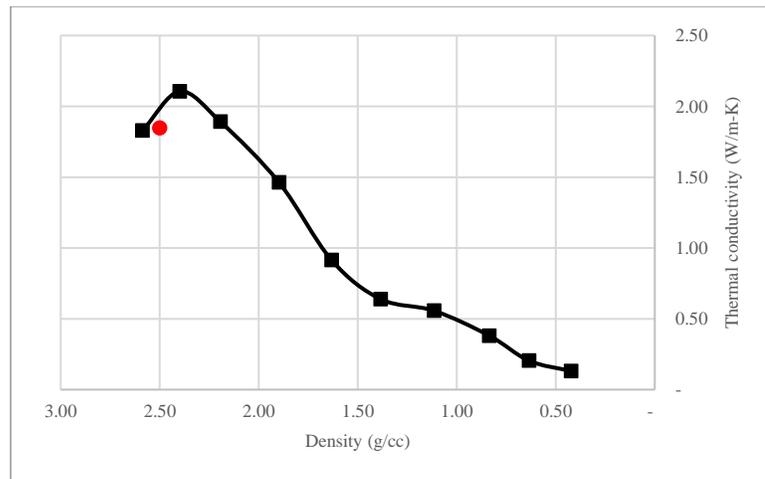


Figure 8: Thermal conductivity of a central pore (red dot) @ 2.5 g/cc compared to that of many pores for the same density

Finally, to understand the role of charge balancing alkali atoms, the sodium atoms were replaced by heavier potassium as well as calcium atoms. Only fully dense structures were considered. Note that calcium atoms are divalent and thus the number of calcium atoms would be half of that of sodium atoms. However, the role of the charge compensating cations had negligible effect and all three systems for a Si-Al ratio equaling 3 showed similar thermal conductivity approximately 2 W/m-K.

Having used MD for examining the role of nano pores on thermal conductivity of PAS, a macroscale FEM model is used for examining the role of macro pores on PAS thermal conductivity. This will allow a direct comparison of ‘scale’ effects of pore-size on thermal conductivity.

Finite Element Modeling

FEM for heat transfer in solids is applicable only to macroscopic objects/features. Heat transfer modeling in COMSOL Multiphysics 5.3 software was used to achieve this task. The goal here is to understand how thermal conductivity would change if the matrix of PAS has pores of various sizes. Three kinds of simulation cell setup were used for this – 1) Pores of same sizes placed regularly in the matrix, 2) Pores of different sizes placed regularly in the matrix and, 3) Pores of various sizes spread across randomly in the matrix.

Simulation setup and procedure

A cubic cell of 2-micron side was examined, with the pristine material's thermal conductivity equaling 1.9W/m-K for a density of 2.62g/cc as obtained from the MD results. Heat capacity is estimated using Dulong-Petit law, which states that the molar heat capacity of a material is three times the gas constant [46]. This comes out to be 95.14 J per kg-K for the pristine material. To solve Fourier's law, a heat source was set up at one face and the temperature was obtained at the opposite face while all the other boundaries were insulated. Thermal conductivity was then estimated using a steady-state equation. Heat rate is set at 50 MW per square meter. Meshing is applied based on physics that automatically tracks the sizes of various features and varies the element sizes accordingly. The simulation runs until the heat source at one end raises the temperature of the opposite face from an ambient temperature of 293.15K to 298K. The temperature at the heating source at the end of the simulation is recorded and used to calculate the thermal conductivity of the overall matrix. Thermal conductivity is calculated using the Fourier's equation for steady state conditions, given below:

$$\dot{Q} = -k A \frac{\Delta T}{\Delta x}$$

Here, \dot{Q} is the heat rate in Watts, 'k' is the thermal conductivity in W/m-K, 'A' is the cross section area through which the heat flux flows (square meters) and $\frac{\Delta T}{\Delta x}$ is the temperature gradient across the thickness of the material. A negative sign is placed to make the overall equation positive since the temperature decreases from the heat source to the sink thereby generating a negative gradient.

Pores of various sizes and at locations are then created in the matrix and air is used as the material for them. Effective density of the system will thus, be less than the dense matrix itself (less than 2.62 g/cc) since air density is much lower. The resultant converged temperature value is then calculated and plotted against this effective density. It is important to keep in mind that the aim here is to generate the trend of thermal conductivity based on porosity and not to get the actual thermal conductivity values. FEM uses the k as input and generates the thermal conductivity of the overall system according to the defined physics in the model. It unlike MD, does not calculate the thermal conductivity from indirect parameters.

Results

Based on the porosity, the converged temperature at the heat source side varied as observed in the max temperature chart in Figure 9, Figure 10 and Figure 11. This value is observed to be changing based on the sizes and number of pores but is independent of their locations within the matrix.

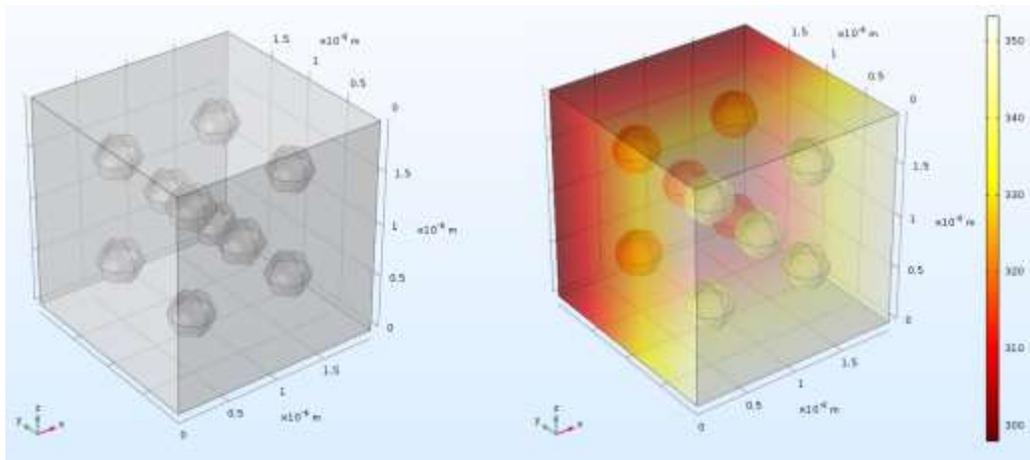


Figure 9: FEM model for ten same size pores placed regularly in the PAS matrix. The yellow side is where the heat source is placed and the red is the face opposite to that.

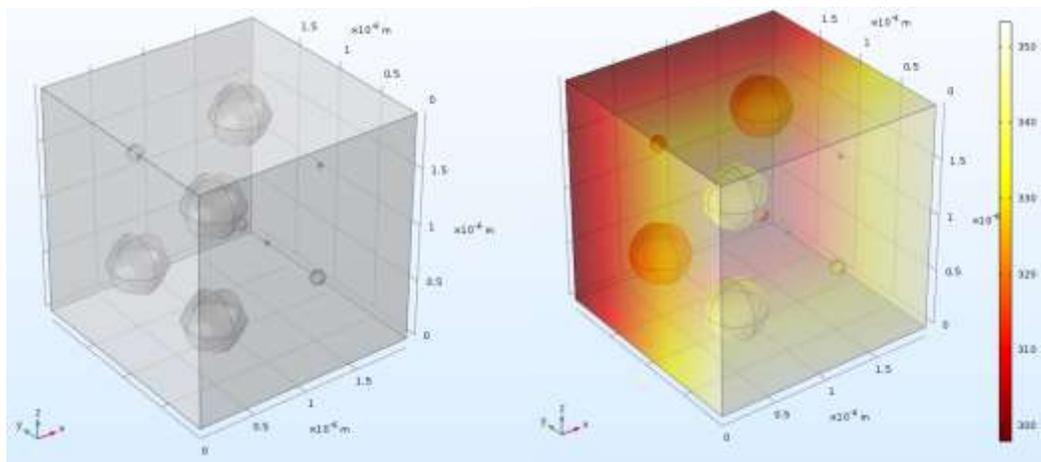


Figure 10: FEM model for ten different sized pores placed regularly in the PAS matrix. The yellow side is where the heat source is placed and the red is the face opposite to that.

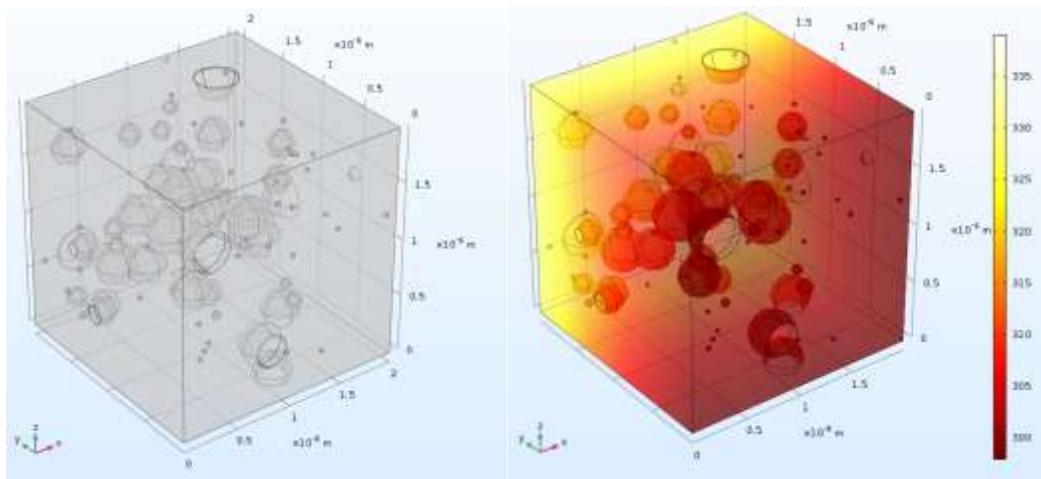


Figure 11: FEM model various pores of random sizes distributed randomly in the PAS matrix. The yellow side is where the heat source is placed and the red is the face opposite to that.

Thermal conductivity vs Effective density for all these approaches is plotted in Figure 12. It shows linear relationship between the two for all the approaches. This essentially means that the thermal conductivity calculated from FEM (COMSOL) gets an effective value of the system based on the volume fractions of these materials in a linear proportion. In other words, regardless of the pore size distribution and location, the thermal conductivity of a certain effective density will be the same.

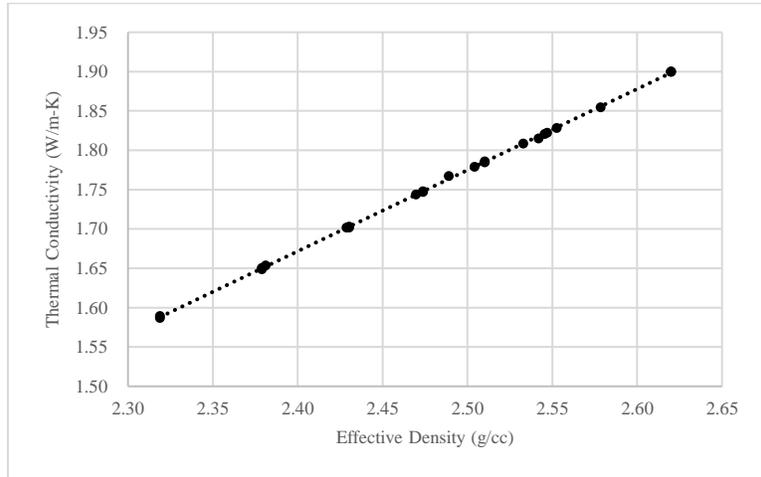


Figure 12: Thermal conductivity versus the effective density of the PAS.

Thus, FEM provides a simple macroscopic relation (based on mixing laws) between the pore size distribution and thermal conductivity in this case. However, it confirms the trend shown by MD simulations.

Chapter – 05: Thermal Conductivity Measurement

The results from numerical approach have endorsed the hypothesis of low thermal conductivity of PAS material. Measuring such low values experimentally however, is a tremendous challenge. Experimental setup required for highly insulating material are usually expensive and requires meticulous sample setup. Thus, a novel approach was necessary to overcome the issues. A cost effective special thermal conductivity measurement setup was devised details of which, are not disclosed due to a pending patent.

There are two ways to characterize thermal conductivity of a material – Steady-State and Transient methods. Steady-State methods are named such since it requires a steady heat flow (Q) across the sample under investigation. The sample is placed between a heat source and a heat sink and the difference in temperature across its ends are measured (ΔT). This, along with the heat flow and sample dimensions I used to calculate the thermal conductivity of a material using Fourier’s Law of heat conduction.

$$\dot{Q} = -k A \frac{\Delta T}{\Delta x}$$

Here, Q is the heat flow rate in Watts across the material, A is the cross section area of the investigated sample, ΔT is the temperature difference between the heat source and heat sink ends and Δx is the distance between them. The biggest advantage of this method is its simplicity. However, it takes very long to reach a steady state heat flow in any material under investigation. A much faster alternative to this technique is Transient method. The data acquisition time is significantly shorter, however, the calculations associated with it could be more complex depending on the type of transient method used and the geometry of the sample under investigation among other attributes. Zhao et al. have described these methods in detail [47].

Both Steady State and Transient methods were used for these measurements. Transient method was preferred due to shorter experiment time and higher accuracy for our particular setup. To validate the results obtained using our method, samples with known thermal conductivity values were used. These samples were selected to represent a wide range of k values. All of the measured thermal conductivity values of the test samples were fairly close to the values obtained from the manufacturer or reported in the literature (Table 3).

Table 3 - Thermal conductivity values of test samples (Actual vs Measured)

Sample	Actual k (W/m-K)	Measured k (W/m-K)	%Error
Pyrex Glass	1.09	1.08	0.74%
Granite	2.47	2.27	8.03%
Basalt	2.30	2.35	2.06%
Sandstone	2.327	2.30	1.07%
Aluminum-6061 T6 alloy	167	162.21	2.87%
Copper-C110	401	399.87	0.28%
Steel-1010	49.80	48.56	2.48%
Stainless steel-304	16.20	16.13	0.43%

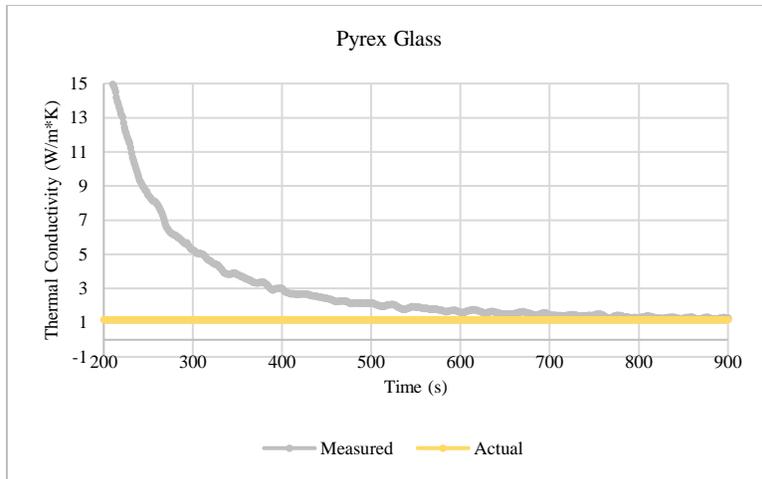


Figure 13: Thermal conductivity of Pyrex glass

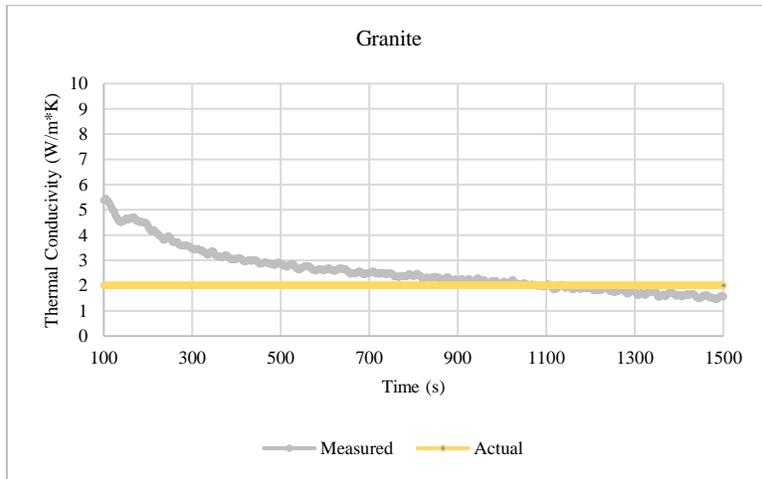


Figure 14: Thermal conductivity of granite

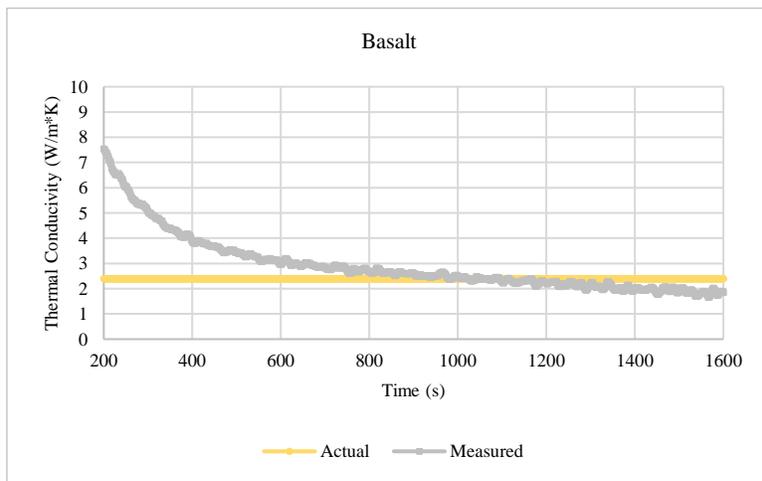


Figure 15: Thermal conductivity of Basalt

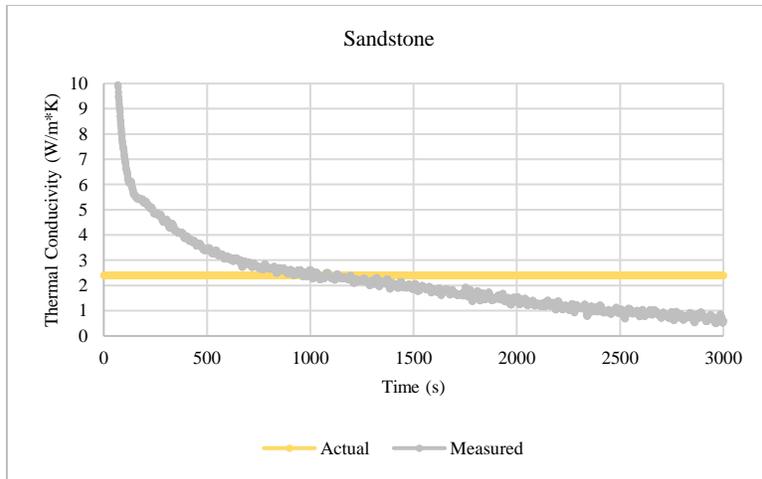


Figure 16: Thermal conductivity of Sandstone

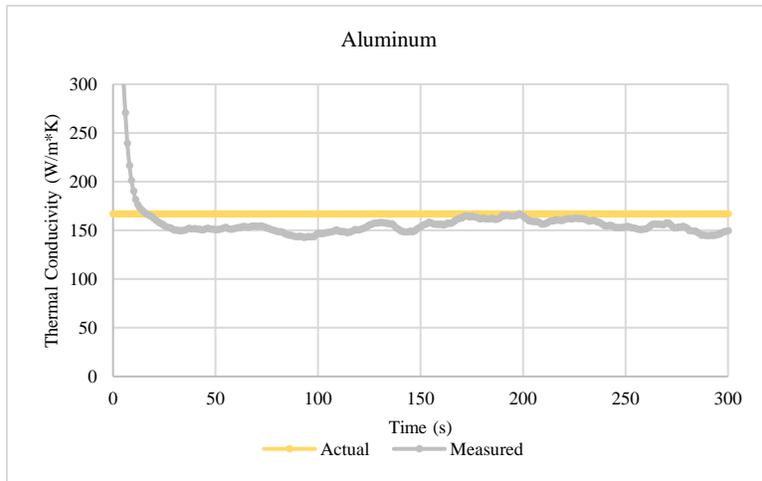


Figure 17: Thermal conductivity of Aluminum

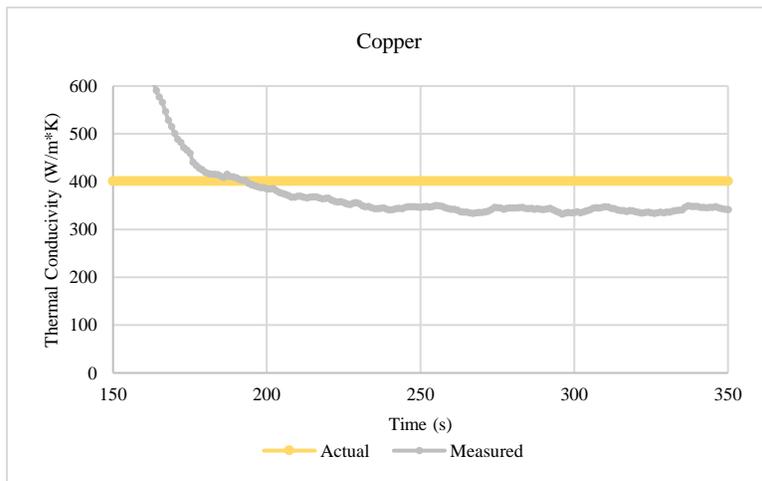


Figure 18: Thermal conductivity of copper

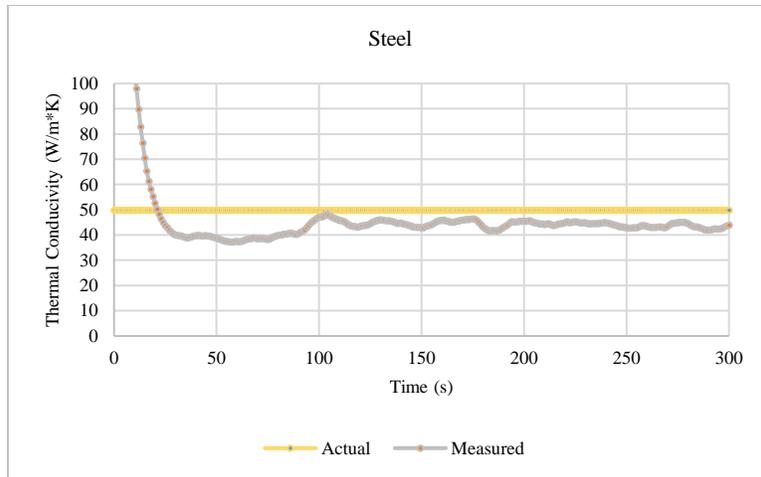


Figure 19: Thermal conductivity of steel

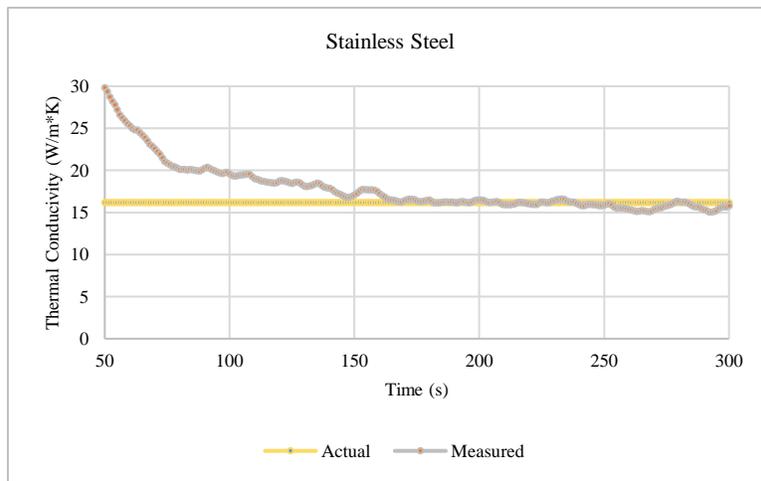


Figure 20: Thermal conductivity of Stainless Steel

Figure 13 to 19 shows the results from transient method for various test samples from insulating material like Pyrex glass and rocks to highly thermally conductive metals. All the samples have shown promising results where expected values reached soon after beginning the experiment. The time of convergence varies with the sample but none within the sample space considered went beyond 20-25 minutes to reach convergence.

Experimental constraints at the time of writing this document prevented us from making a sample of suitable size to test using this method. Moreover, work on measuring the thermal conductivity of highly insulating materials such as porous aluminosilicate materials through this method will continue beyond this thesis.

Chapter – 06: Conclusion & Recommendations

Conclusion

MD is an effective tool to study thermal behavior with an atomistic level of detail. It thus, serves as a great alternative to often-difficult laboratory experiments pertaining to nano-scales. It provides a time-evolution of the system under investigation for thermal simulations. Fluids system are better simulated in MD compared to solids. Within solids, it works better for non-metals and is ineffective for metals as a standalone. For highly conductive crystals, MD can be impractically time intensive. When using MD, it is most essential to select a system-appropriate interatomic interaction potential. Along with that, determination of sufficient simulation time, appropriate size and orientation of the system and the constituent number of atoms is crucial for reliable thermal conductivity estimations.

MC simulations transcends the boundaries of atomistic or macro level of details depending on way it is used. It uses, BTE as its underlying equation to study thermal properties of a material. Although BTE is a very widely used equation for studying thermal properties of a material, it is a very complex equation and can be very difficult to solve using brute force. MC simulations resolve this issue since it uses probabilistic methods to get the solution. BTE is considered better for crystalline material with no defects. MC is usually faster than MD in case of energy convergence but is usually slower for HCACF convergence. However, unlike MD, MC does not provide a time-evolution of the system undergoing thermal changes.

For bulk systems, FEM is considered one of the best methods for thermal conductivity estimations. However, it requires some prior knowledge of thermal conductivity. Thus, it is sometimes used with MD, MC or BTE to come up with the bulk material's thermal conductivity. This way of thermal conductivity estimation is called multiscale modeling since it involves using methods in various scales.

For Porous Aluminosilicates (PAS), MD provided an atomistic insight on the effect of porosity/density on the reduction of thermal conductivity. Thermal conductivity for PAS decreased with increase in porosity and did not depend on the morphology of pores. Higher Si to Al ratios in PAS showed better strength and insulation. However, heavier charge balancing alkali ions did not result in significant reduction in thermal conductivity. FEM provided an insight on the bulk thermal properties of PAS. Thermal conductivity was shown to reduce with increase in porosity. However, a linear trend indicated that the thermal conductivity was calculated using volume fractions in linear proportions. In other words, thermal conductivity estimations depended on effective density of the system and not on pre distribution.

A novel experimental setup was devised to measure thermal conductivity of various material. This setup has great potential to reduce costs related to these measurements. It has shown promising results for a wide range of material from insulating material like Pyrex glass and rocks to highly thermally conductive metals. However, some experimental constraints prevented the use of this method for PAS. Moreover, there are some setup related modifications necessary to use PAS. Further work is required to achieve this goal. The details of the setup has not been disclosed due to pending patent.

Aluminosilicates is highly abundant in mine tailings. This coupled with the MD and FEM results make it a highly suitable insulating material for mining and construction industry.

Recommendations

It was established that the introduction of porosity enhances the insulation properties of PAS material. However, the numerical analyses did not cover the effect of the shape of nanopores on the thermal conductivity, which could be another avenue to explore. In addition, the positioning of these pores in the matrix could be another area that needs more information. Eventually, the chemical process should account for ways to create these in reality based on the numerical simulation results.

As discussed in previous sections, one of the essential atomistic feature that governs the thermal conductivity of an insulator is the mean free path of the phonons. It may be another project avenue to develop a model to track the path of phonons and correlate it to the overall thermal conductivity. This could include investigating the effect of various structural features on the path of a phonon.

Overall effectiveness of this product should not just be measured by its insulation properties but also by the complexity of manufacturing process, cost and ease of application. Complex manufacturing process will inevitably lead to higher costs. Thus, a careful consideration may be required. There could be numerous challenges associated with applying the material in real scenarios. If it is applied on walls or ceilings, it needs to have enough strength to hold itself. Thus, strength should be big criteria along with insulation for practical applications.

Effects of various climatic conditions such as humidity on the product should be studied to mitigate any adverse effects on the thermal and structural properties. In mines, groundwater percolation is a common phenomenon that may deteriorate the product and compromise its structural integrity. This should be part of the development program.

From safety perspective, flash point of the material should be in consideration to understand how prone the product may be to catch a fire. At present, it is understood to have fire-retarding properties but this may change in the final product.

Environmental consideration should be another factor in devising a manufacturing process. Any material that can potentially cause environmental damage will eventually be of no use to the industries.

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