Thermophysical Property Measurements of Molten Salts: Perspectives on Fuel and Irradiated Salts

Ryan C. Gallagher*[†], Nick Russell*, Alex Martin*, N. Dianne Ezell*

**Oak Ridge National Laboratory, 1 Bethel Valley Rd., Oak Ridge, TN, 37830, gallagherrc@ornl.gov*
[†]*The Ohio State University, 2070 Neil Ave, Columbus, OH 43210*

INTRODUCTION

Molten salts are being considered for several innovative reactor designs to serve as coolant, fuel carrier, or both. Thermophysical properties of these salts must be understood to design, analyze, and optimize performance of new molten salt reactor (MSR) concepts using computational models and nuclear codes. Some of the most important material properties for thermal hydraulic analysts include density, viscosity, and thermal conductivity. Property data are also essential for analyzing safety basis scenarios and for building/qualifying new numerical multiphysics codes that help elucidate and predict salt behavior. Without accurate knowledge of these properties, design and optimization of advanced MSR concepts would be severely limited, and new modeling methods would lack the validation data required for qualification. Despite the importance of thermophysical property knowledge, major gaps and uncertainties in the thermophysical property data persist for many salt compositions. The US Department of Energy Office of Nuclear Energy Molten Salt Reactor Campaign is developing and refining methods and procedures to measure thermal properties to support the needs of the MSR industry.

Due to their high melting point, corrosivity, volatility, hygroscopicity, and surface wetting, measurement of these basic properties has been challenging. Therefore, many measurements are subject to relatively large uncertainties [1]. Myriad potential salt compositions are being considered for different MSR designs, including non-actinide–bearing salts, fuel-bearing salts, beryllium-containing salts, and irradiated salts, all of which present unique challenges. Table I summarizes major challenges anticipated taking property measurements on common reactor-relevant molten salts. Hygroscopicity is a major issue for nearly all salts; this restricts work to inert environments and limits it to salts that have been through proper purification steps, since impure salts have been shown to be more corrosive [2, 3]

For most non-actinide–bearing salts, several techniques are available or under development, depending on the composition. However, the least amount of data exists for fueled and irradiated salts; these are the most challenging to measure since they are likely to have all major measurement hurdles—wetting, hygroscopicity, corrosivity, and volatility—with added radiation and contamination hazards.

The ideal system for measuring these types of salts would utilize fully sealed vessels to reduce exposure and contamination of surrounding facilities, modularity or easily decontaminated components to allow for low-cost re-use when studying different salts with the same system, robust instrumentation that can be operated in high radiation environments (e.g., hot cells), the ability to measure multiple properties, and the capability for high-throughput rapid testing. Unfortunately, most of the more practiced techniques fall short of these criteria.

TABLE I. Difficulties when measuring molten salts

Property Problems	*Fluorides*			*Chlorides*		
	FLiNaK	*FLiBe*	*Fuel*	*KCl:MgCl$_2$*	*NaCl:MgCl$_2$*	*Fuel*
Volatile			✓			✓
Hygro-scopic	✓	✓	✓	✓	✓	✓✓
Corrosive	*Depends on moisture content*		✓	*Depends on moisture content*		✓
Wettable	*Depends on material/salt combination*					

This summary presents results from several techniques developed at Oak Ridge National Laboratory (ORNL) to measure molten salt density, thermal conductivity, and viscosity. The current limitations of these and other existing techniques when measuring fueled or irradiated salts are also discussed.

EXPERIMENT DESIGNS AND METHODS

Density Measurements

A custom system based on the Archimedes principle (Fig.1) was built to measure molten salt density [4]. The system uses a mass/volume calibrated high purity platinum plummet suspended from a precision balance by a thin wire. The sinker is lowered into a crucible inside a temperature-controlled furnace. While immersed, the balance is used to measure the weight of the immersed sinker. The plummet volume was calibrated using the measured weight in air and in a calibration fluid at room temperature, and the known density of platinum. Using the known diameter of the wire, a correction can be made for the buoyant force on the suspension wire. When operating at elevated temperatures, a correction for the plummet's thermal expansion must also be added.

Since this method requires an open top, the entire system was placed into an inert glovebox. The open top also limits this technique to non-volatile salts that will not corrode and contaminate the sensitive instrumentation on the balance.

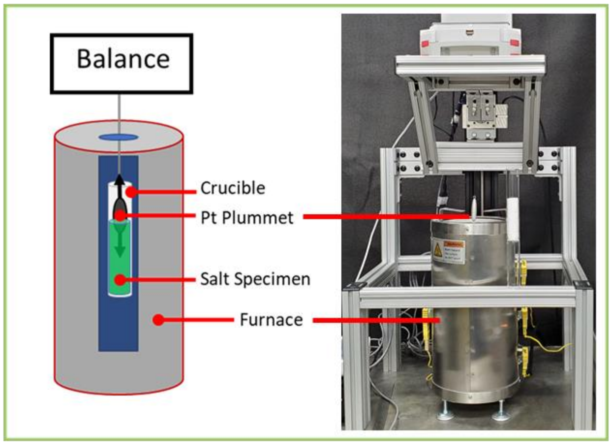

Fig. 1. Sketch and photo of the Archimedes-bob density system.

To allow for measurements of hazardous or volatile salts, sealed-vessel dilatometry is a more appropriate approach. This technique measures a known mass of salt in a volume-calibrated tube (i.e., graduated cylinder). The density change with respect to temperature is determined by measuring the changes in fluid height. This technique is generally performed optically with glass containers (possible with chloride salts), but an x-ray–based imaging system is currently under development to measure viscosity with non-transparent salts or crucibles for fluoride or fueled salts. A schematic of this technique using a detector plate with a portable x-ray generator is shown in Fig 2. This system can be modified to measure viscosity using a ball drop technique.

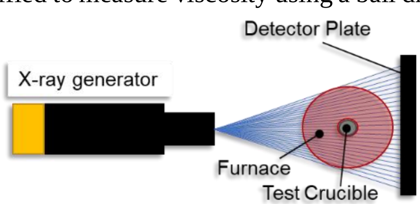

Fig. 2. Illustration of x-ray imaging used to measure viscosity or density with non-transparent fluids or crucibles.

Viscosity Measurements

Rotational viscometers are common in the field of high-temperature melt rheometric measurements, but they are bulky, requiring precision alignment and tight tolerance spindles to measure low viscosity fluids like molten salts, which can be below 1cP at the upper bounds of their operating temperature. These systems also require open top crucibles to allow access for the rotating spindle, which risks damage to the torque sensors by corrosion and contamination. Therefore, a different technique is being pursued.

A high temperature falling ball viscometer is under development to measure viscosity. The terminal velocity of a ball falling/rolling in a fluid-filled container is measured and used to calculate drag force, and subsequently, viscosity, using Stoke's law [5]. An optical camera or an x-ray generator and detector can be used to track the ball's descent, pending the transparency of the salt and container. This technique offers the advantage of using fully sealed containers, lowering the risk of instrument contamination. This technique can use the same setup as the dilatometric density measurements with minor modifications to the salt-containing crucible and furnace stand.

Thermal Conductivity Measurements

Thermal conductivity is generally considered the most difficult property measurement to obtain for high-temperature fluids. Laser flash thermal conductivity is the most prominent technique, but crucible design remains a major challenge since volatile species cannot be contained in current crucibles, and salts tend to wet the walls, biasing results (also an issue with differential scanning calorimetry measurements for specific heat) [6]. These systems also have a substantial amount of costly instrumentation and controls that could be damaged by radiation or contamination. Without a fully sealed crucible, these systems are not feasible for measuring volatile salts and will be extremely costly to install in radiation environments such as hot cells.

A modified version of the variable gap system developed under ORNL's Molten Salt Reactor Experiment was designed and built to measure thermal conductivity, as shown in Fig. 3 [7].

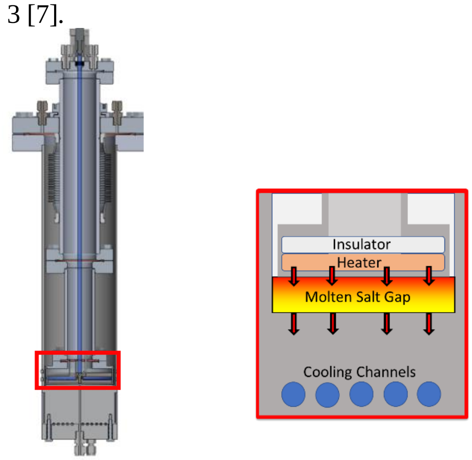

Fig. 3. Assembly and illustration of the variable gap thermal conductivity system

Improvements were made using modern finite element analysis (FEA) and computational fluid dynamics (CFD) codes to reduce uncertainty caused by convection, which is a major concern with steady-state conductivity techniques [1]. The variable gap technique uses 1D approximations of Fourier's law by measuring the temperature difference across a variable, thin layer of salt which is heated from the top with a resistive heater and cooled from the bottom with cooling channels. The heat flux through the salt is calculated using the power and area of the heater. Thermal resistance between thermocouples above and below the salt layer is a function of the salt thickness, assuming the heat flux vectors are nearly unidirectional. The thermal conductivity is deduced by the reciprocal of the slope of the thermal resistance vs. the change in gap thickness. This method requires corrections for radiative heat, which is described in the literature [7, 8, 9]. To reduce the uncertainty of radiative heat transfer, the emissivity of the internal components was minimized by mechanical polishing to a mirror finish, but optical properties are still necessary for more accurate results.

The variable gap technique offers the advantage of a fully sealed system and robust instrumentation, so it is ideal for measuring fueled and irradiated salts. Most components are replaceable and easily machined with conventional methods, so it is a cost-effective solution that can be integrated into rad facilities.

SELECTED RESULTS

Density, thermal conductivity, and viscosity of a commercial nitrate salt (MS-1) from Dynalene, Inc., were used to validate the measurement systems. Dynalene MS-1 features a low melting point and is less hygroscopic and corrosive than most molten salts, so it does not require inert environments and is ideal for rapid qualification of measurement techniques if they can withstand the corrosion and temperature of reactor-relevant salts. Proof-of-concept studies with room temperature fluids were also completed for the x-ray density viscosity systems

Density Measurement

Measured results for the density system with Dynalene MS-1 are shown in Fig 4. The maximum relative error was found to be less than 6%, with the largest deviation at low temperatures. The source of this error is expected to be due to a non-uniformly melted specimen during measurement. Additionally, correction was not made for the surface tension of this salt since it is not available, and it would tend to bias measurements towards a slightly higher calculated density. Surface tension will also need to be measured for the most accurate results

As stated earlier, if the Archimedes method were applied to fueled salts, then the major drawbacks would be the requirement for known surface tension values, an open-top crucible, and the potential for salt wetting and migrating up the wire. This could result in system contamination when using highly wetting or volatile salts.

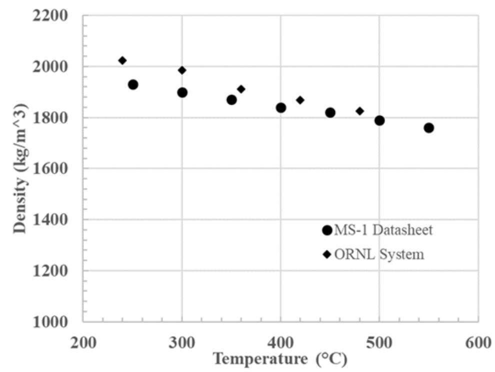

Fig. 4. Density measurement of MS-1 Salt with Archimedes method

However, under stringent procedures and handling, this method has some potential for use in measuring more hazardous salts. Density measurement by dilatometry offers several advantages since it can be performed in a sealed system, and none of the instrumentation must contact the salt. This technique is currently under development at ORNL.

Thermal Conductivity Measurement

Thermal conductivity of MS-1 salt was measured with the variable gap system after a validation measurement with helium (Fig. 5). The result showed reasonable agreement with Dynalene's technical data and with literature values of helium thermal conductivity with high repeatability. Both measurements were biased towards a higher measured thermal conductivity near higher temperatures due to heat losses away from the resistive heater into the structural material, a common issue with steady-state thermal conductivity techniques. The addition of guard heaters and improvements to the heat flux calculation using a comparative technique will be investigated to reduce errors due to heat losses. However, this technique offers high potential for use with more hazardous salts.

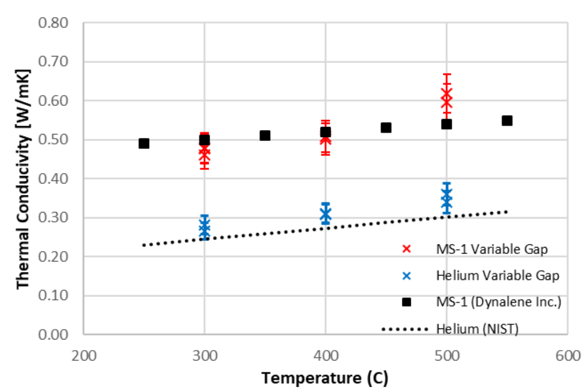

Fig. 5. Thermal conductivity of MS-1 and helium measured with the variable gap system.

Viscosity Measurement

Preliminary viscosity results show general agreement with expected behavior and reveal various obstacles known to molten salt researchers. Optical measurements of Dynalene MS-1 confirm the decrease in viscosity as temperature increases, as shown in Fig. 6. However, bubble convection and beading greatly hindered initial Dynalene MS-1 tests. Experiment design and operating procedures were modified to remedy issues associated with calibration, crystal melting, surface tension, and bubble production. When possible, optical measurement of viscosity by the falling ball is a promising technique that requires minimal instrumentation aside from low-cost cameras and lighting that can be easily replaced.

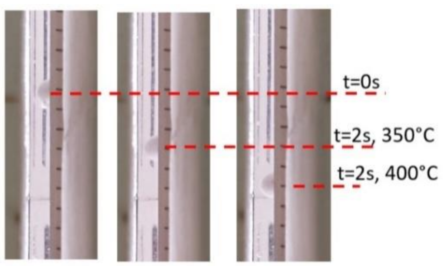

Fig. 6. Ball descent at different temperatures in MS-1 salt.

Optical measurements are inherently limited to transparent tubes which may be unsuitable for especially corrosive or hazardous salts. Methods and procedures are being developed for the use of x-rays to record ball descent in opaque metal tubes. Proof-of-concept for x-ray imaging is given in Fig. 7, with a stainless-steel ball in a ¼ in. alloy C-276 tube. This technique is still under preliminary testing to calibrate the system with known fluids before moving to molten salts. This system would be difficult to adapt in a high radiation environment due to the sensitivity of the detector plate, so background radiation would need to be kept to a minimum.

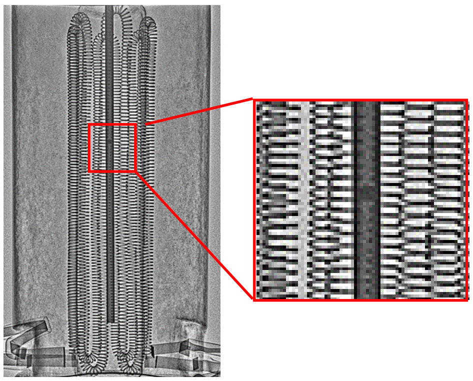

Fig.7. Radiograph of ball within the viscosity system's furnace

Techniques used to measure density, viscosity, and thermal conductivity of molten salts are being developed at ORNL. While the work herein is promising, substantial development remains to adapt existing techniques or develop novel ones for more hazardous salts or more challenging environments associated with irradiated or fueled molten salts.

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