A Molten Salt Aerosol Spectroscopy Approach to Online Process Monitoring in Molten Salt Reactors

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Abstract

Recent research and development in molten salt reactors (MSRs) has led to many advanced reactor designs, many of which have demonstrations planned in the next decade. However, a significant challenge that must be overcome before liquid fueled MSRs become viable globally is nuclear material accountancy (NMA) and safeguards. Liquid-fueled MSRs are problematic to safeguards because the nuclear material is in the bulk phase, inventories are constantly changing, and there are many potential outlet pathways that must be monitored, especially in designs coupled with online chemical processing. At the Idaho National Laboratory, we have developed an online process monitoring tool to circulate molten salt through a nebulizer and optical cell, where laser-induced breakdown spectroscopy (LIBS) and ultraviolet-visible (UV-VIS) are applied to track the elemental and oxidation states of the constituents in the salt aerosol. This approach has the potential to provide information on the actinides, fission products, and corrosion in the reactor or process. Preliminary testing in aqueous praseodymium chloride ($PrCl_3$) and neodymium chloride ($NdCl_3$) showed good sensitivity detection limits with developed calibration curves. Additional tests and analysis are ongoing in aqueous solutions while equipment is being scaled up for high temperature molten salt testing. Results for continued aqueous testing as well as a status of the molten salt design and anticipated commissioning are presented.

1 Introduction

While MSR technology offers incredible benefits to the nuclear industry (such as online reprocessing), safeguards and nuclear material control and accounting remains a complex issue that must be solved[1]. There are two basic approaches to safeguards for an MSR[2-3], the first is material balance of inputs and outputs as is currently performed on light water reactors (high fidelity measurements with containment and surveillance). This approach becomes increasingly challenging when applied to reactor designs with online reprocessing and liquid fuels. The second ideology is applying material accountancy throughout the process via salt sampling and analysis[2-3]. An early example of salt sampling from an MSR goes back to the molten salt reactor experiment where a sampler-enricher (S-E) was utilized to pull 10 g samples from the reactor[4]. This was a time intensive process under ideal conditions, and occasional mishaps occurred, such as lost capsules into the reactor pump which required shutdown and isolation to retrieve.

Consequently, the Department of Energy (DOE) and the nuclear industry are actively looking for modern sampling approaches with better accessibility and repeatability. One group is attempting to modernize discrete salt sampling using a freeze valve coupled with a pneumatic discharge approach[5]. While this promises to improve on the S-E, it is limited to discrete samples that require intensive off-line analysis to generate compositional data and fails to provide timely safeguards relevant information necessary to support material accountancy throughout the process. A recent patent discloses an online pneumatic micro-droplet generator for pyroprocessing molten salt systems and suggests its applicability to MSRs[6]. However, the proposed technology relies on a windowless port open to the environment in the process stream and relies on precise pressure control to prevent leakage, which may be challenging in an MSR.

Another salt sampling application being investigated is salt aerosol analysis via LIBS. Williams et al.[7-8] performed LIBS measurements in a molten salt aerosol generated using a batch Collison nebulizer in an optical cell and results indicated good limits-of-detection for cerium (Ce) and uranium (U). While this configuration addressed several limitations of LIBS in molten salts such as surface perturbations, salt opacity, and splashing; it resulted in development of salt films over the unprotected optics in the optical cell leading to signal degradation over time. More recently, researchers at Oak Ridge National Laboratory (ORNL) implemented a Collison nebulizer system utilizing an optical cell to monitor a surrogate (room temperature) MSR off-gas system[9]. In this application, the optical cell was equipped with aerosol focusing[10-12] enhancements to protect the optics from exposure to the aerosol phase. To date, only aqueous room temperature testing has been conducted at ORNL. Aerosol sampling approaches are in their infancy and so far, only batch nebulizers have been tested in molten salts and the connection between the molten salt reservoir and the nebulizer has yet to be resolved. Additionally, analyte matrixes have been simple and so far, only LIBS has been applied as an analytical technique which limits the type of information available.

The main motivation for this work is to develop and test a continuous aerosol sampling approach utilizing a novel venturi nebulizer that is coupled with multiple optical spectroscopy methods that can be applied in a complex salt stream. The approach is to utilize a patented system[13] of venturi pumps and nebulizers to circulate the sample fluid through an optical cell where spectroscopy measurements can occur. This concept, called the *MSR high-Temperature Aerosol Phase Spectroscopy (TAPS) system*, is shown in Figure 1. Similar to other nebulizer designs[14], in the novel venturi nebulizer, the compressed gas mixes with the molten salt to form an aerosol. However, unlike many designs, the nebulizer/venturi pump creates a vacuum and draws the fluid from the main salt vessel. The aerosol phase, containing gas and salt droplets, is piped into an optical cell (with aerosol lensing features). The main components of the sampling approach are a venturi pump that draws the salt into the system and nebulizes the salt, an optical cell allowing for spectroscopy measurements, and a coalesce filter which removes the aerosol from the gas stream.

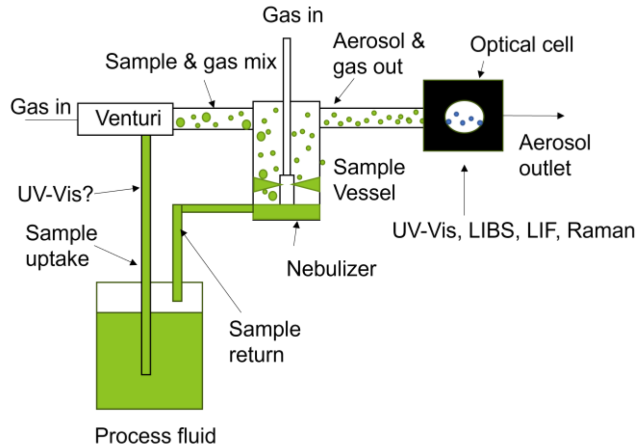

Figure 1. Concept of MSR-TAPS

With continuous salt sampling as described above, spectroscopy techniques can be applied through an optical cell to analyze the chemical composition of the aerosol online. Spectroscopy techniques are particularly valuable in this application because they provide a nondestructive, real-time, and in situ analysis used to identify and quantify atomic elements, oxidation states, and speciation of corrosion and fission products[15-16]. Several spectroscopy approaches, including LAMIS[17-18], LIBS[19], and LIF[20] have demonstrated the ability to resolve isotopic compositions of special nuclear materials. The literature is rich with examples of optical spectroscopy in molten salt applications, including Raman[21-23], infrared (IR) spectroscopy[24-26], UV-VIS[27-29], fluorescence[30-31], and LIBS[7-8, 32]. While few spectroscopy approaches have been performed in environmental aerosols[33] and room temperature liquid aerosols[34], to our knowledge, only LIBS has been applied to a molten salt aerosol . In this work, we present preliminary aqueous experiments from combined in situ LIBS and UV-VIS analysis.

2 Materials and Methods

A low temperature prototype of MSR-TAPS was built using off the shelf components and 3D printed parts as shown in Figure 2. This design utilized two venturi pumps (Norgren, R73) to circulate the sample through a Collison nebulizer (CH Technologies USA, 3-jet). Argon gas was supplied to the circulating venturi's and nebulizer at 70 psi and 40 psi, respectively. A needle valve between the sample tank and the nebulizer was used to control the fluid flow in the circulating loop to 1 gallon per hour (GPH). Built into the sample uptake pipe was a flow cell (Avantes, 5 mm path) with SMA fiber connections. This flow cell was utilized for UV-VIS measurements of the sample. The aerosol output from the nebulizer was focused through a 6 mm nozzle into a custom 3D printed optical cell with 25 mm diameter sapphire windows. In this optical cell LIBS measurements were conducted in the aerosol stream.

For UV-VIS, a Cary 60 spectrometer operating between 400 and 900 nm was connected to the flow cell via SMA fiber connections. Measurements were taken at a scan rate of 600 nm/min. For LIBS, a Nd:YAG laser (Quantel USA, Q-Smart 450) was focused into the aerosol stream via a 75 mm plano-convex lens. The laser was operating in the fundamental 1064 nm mode at 40 mJ of energy. Light collection occurred via fiber optics. The spectrometer was an EMU 120/64 (Catalina Scientific). Preliminary measurements occurred using a gate delay of 3 µs with a gate width of 1 ms.

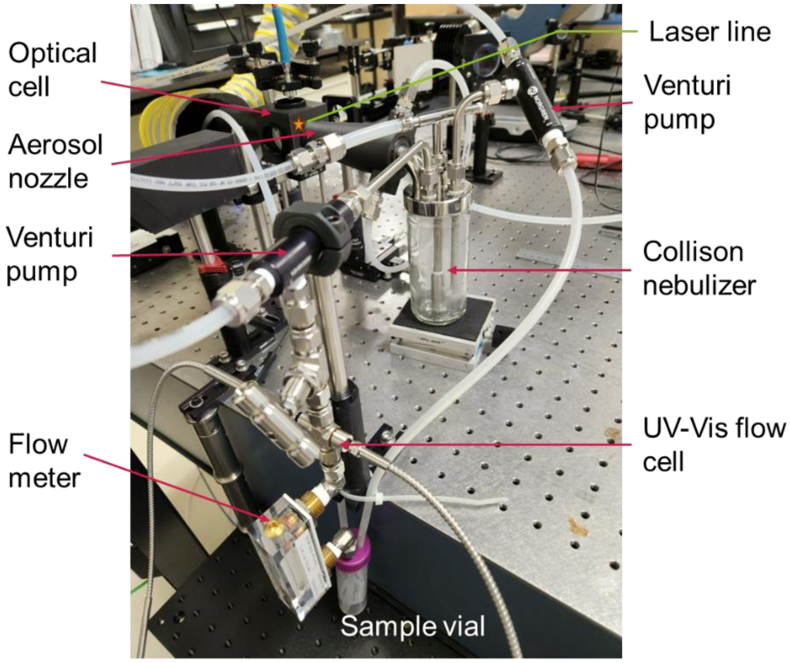

Figure 2. Photo of the MSR-TAPS prototype.

Samples were prepared from $NdCl_3$ and $PrCl_3$ to test the spectroscopy measurements. For $NdCl_3$, standards were made ranging from 0.05 M to 0.2 M. For $PrCl_3$, standards were also made but ranged from 0.2M to 0.5 M. These standards were made by weighing out small amounts of salts and then mixing with 2% nitric acid.

3 Results

Preliminary experiments were conducted using the $NdCl_3$ and $PrCl_3$ standards and mixtures using LIBS and UV-VIS with low temperature setup shown in Figure 2. Figure 4 shows absorption spectra from MSR-TAPS as a function of the analyte concentration, where the absorption increased linearly with concentration, as expected.

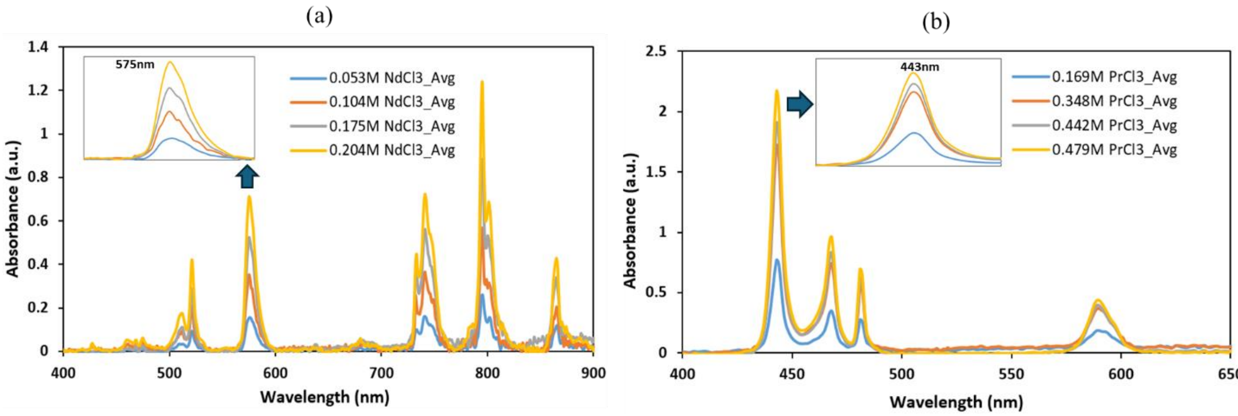

Figure 3. UV-VIS absorption spectra for (a) NdCl3 and (b) PrCl3.

For LIBS, multiple Nd and Pr lines were identified with signal to noise ratios greater than 5. An example of several of these lines are shown in Figure 5 in a region of interest (ROI) between 524 nm and 526 nm. Again, as the concentration of the analyte increases, the intensity of the light also increased linearly as shown in Figure 6.

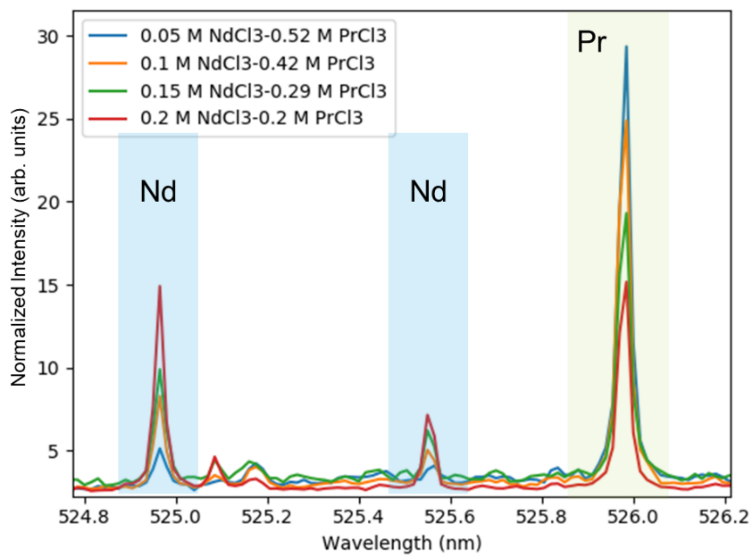

Figure 4. Region of interest for LIBS

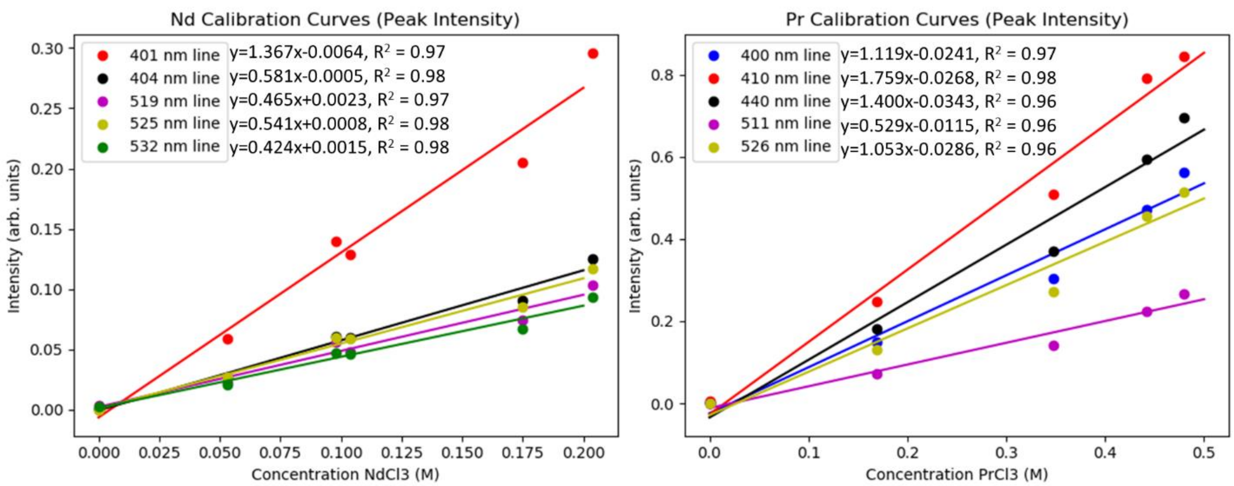

Figure 5. Calibration curves for LIBS. (left) $NdCl_3$ and (right) $PrCl_3$.

In addition to the spectroscopy measurements, a key concern was that material would accumulate on the windows over time. However, after >10 hours of operation, no material accumulation on the windows was observed. Indicating that the aerosol focusing nozzle and sheath gas provide ample protection for the optical windows.

For scaled-up molten salt testing, a high temperature nebulizer was designed and manufactured as shown in Figure 3. This nebulizer is constructed of 316 stainless steel that is sealed using a custom flange and graphoil seal. A Collision nebulizer tip is positioned centrally to the nebulizer jar via a Swagelok fitting. One challenge we needed to address was how to prevent the nebulizer tip from freezing into the salt during cooling after an experiment. Our solution was to extend the nebulizer feed gas line up out of the heated zone and seal it with PTFE fittings that can be loosened to adjust (slide) the nebulizer tip out of the salt. To prevent salt vapor/aerosol from passing up the tube and freezing, the nebulizer gas line is shrouded with a concentric tube in which a small amount of gas flows to prevent material buildup. In this manner, post experiment, the tip can be pulled from the salt before it freezes. Once the test is completely cool, the flange lid can be removed to extract the salt inside the nebulizer jar. Efforts to fabricate a high temperature optical cell and aerosol nozzle are ongoing and descriptions will not be presented in this paper.

Figure 6. (left) High-temperature nebulizer staged in the furnace planned for initial testing. (right) The high-temperature nebulizer for initial tests.

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