

Final Report for Project 18-15093
Determination of Molecular Structure and Dynamics of Molten Salts by
Advanced Neutron and X-ray Scattering Measurements and Computer
Modeling

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Abstract

The design and development of fully functional Molten-Salt Reactors (MSR) require detailed knowledge of the molten salt properties in order to understand and predict the salt's behavior. Fundamental properties of interest include molecular structure, speciation, and dynamics (such as diffusion coefficients) of salt components and dissolved corrosion and fission products. Computer modeling is necessary to predict changes in physical and chemical properties due to irradiation, burning of dissolved fuel, and corrosion. The modeling requires experimental data, and advanced neutron and x-ray scattering and spectroscopy provide the most reliable and direct determination of the structure (Pair-Distribution Functions, PDF), and dynamics of ions in the melt.

This project dealt with both fluoride and chloride salts. The PDFs have been measured by a combination of neutron and x-ray diffraction. We utilized the techniques of isotope substitutions, a very powerful tool available for neutron-scattering, to extract the details of the liquid structure. Although similar measurements have been done before, modern advanced neutron and x-ray-scattering techniques allow collecting the data at much higher resolution and in a wider range of temperatures. Importantly, we were among the first to study fluoride salts by neutron scattering. The importance of impurities and their effects on salt properties have become apparent recently and so new methods of salt purification were developed. We took advantage of these developments to produce reliable data, which have been used for computer simulations of both clean salts and those with added fission and corrosion products most relevant for MSRs.

Ab initio molecular dynamics simulations have been performed to understand multi-component liquid solutions, in particular solubility of impurities and thermodynamic interactions in relation to the ionic-cluster structure of the fluid. We applied machine learning to regress from the simulation and experimental data in order to develop a fast-acting model that can handle molten salt with an arbitrary (≥ 10) number of chemical elements and be able to predict chemical potential as a function of composition and temperature.

This project resulted in a number of experimental and computer-simulation publications [1–6], a patent application [7], and numerous conference presentations (American Physical Society, American Chemical Society, and The Electrochemical Society [8, 9] among others). Multiple students and postdocs participated and collaborated on aspects of this project. This project seeded new collaborations between MIT and other institutions, such as the University of Massachusetts Lowell, the University of Illinois Urbana-Champaign, the University of California Berkeley, and Oak Ridge and Los Alamos National Labs. As such, this project has had a broad and lasting impact beyond its original scientific scope.

1 Summary of Project Activities

Each section below shortly describes a publication or a group of related publications that were supported by this project.

1.1 The atomic structure of chloride salts

In this section, we introduce our published works on measurements and simulations of chloride salts.

1.1.1 The complex structure of molten NaCl-CrCl₃ salt: Cr-Cl octahedra network and intermediate-range order

As MSRs operate, the composition and physical properties of salts change because of fission and corrosion. Since Cr is the principal corrosion product and NaCl is a common constituent, we studied the atomic structure of molten NaCl-CrCl₃ [1]. We found networks of CrCl₆³⁻ octahedra and an intermediate-range order with nonmonotonic temperature behavior in a remarkable agreement between measurements and ab initio simulations. Although the formation of octahedra and their chains is not unexpected for Cr³⁺ ions in NaCl, they have been studied here for the first time. In addition, we found a much lower-than-expected melting temperature and a broad metastable liquid-solid coexistence phase. Moreover, the availability of Cr isotopes with very different neutron-scattering properties makes Cr an ideal model multi-valent ion for experimental validation of new atomistic models such as neural network interatomic potentials.

The main findings are shown in Fig. 1. Although Cr impurities in real systems will be at a very low level, by studying high Cr concentration here we were able to validate computer simulations with high fidelity. Cr-ion concentration will be the highest near surfaces, where the impurity will affect the diffusivity, viscosity, and redox potential of the salt, thus affecting the corrosion rate directly. The interaction of corrosion products with dissolved nuclear fuel needs to be understood since Cr-Cl₆ octahedra are very similar to U-Cl₆ octahedra in U-containing salts. The coordination numbers of the metal ions are the same in both salts at similar concentrations, CN \approx 5.8. The difference between the salts is in the connectivity between octahedra, see Fig. 1. While the Cr ions tend to form multiple-octahedra chains, a vast majority of U-Cl₆ octahedra are in monomers. Therefore, it is conceivable that the presence of Cr ions in U salts could modify the structure and thus affect macroscopic physical properties, even though the corrosion will result in minute quantities of dissolved Cr.

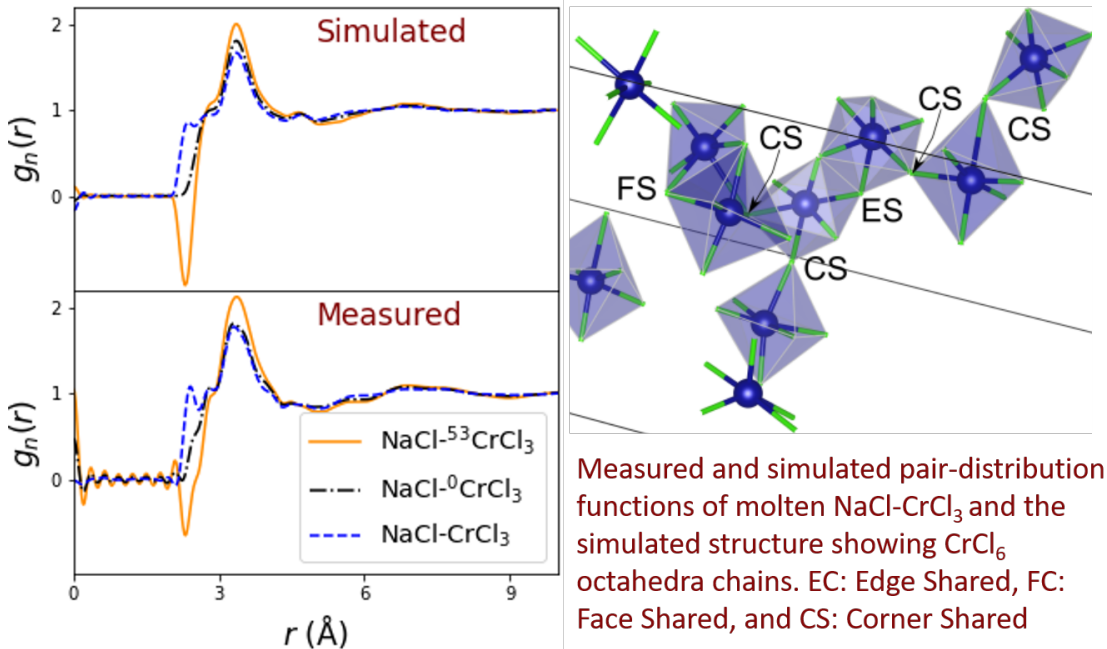


Figure 1: (Left) Neutron PDF measurement and simulation results in molten NaCl-CrCl₃ eutectic showing excellent agreement. (Right) The simulated structure shows CrCl₆ octahedra chains. EC: Edge Shared, FC: Face Shared, and CS: Corner Shared

To illustrate the level of insight that our studies can offer into the structure of molten salts,

we synthesize our findings in NaCl-CrCl₃. We showed that partial PDFs in the Na-Cl subsystem are unaffected by the presence of Cr. We found that in pure NaCl, the most popular coordination number is 6, which should correspond to an octahedral local structure considering that Cl-Na-Cl angles are mostly 90 degrees.[2] Considering the most likely Na-Cl distance is ~ 2.76 Å, the most likely separation between two opposite vertices of octahedra will be 5.52 Å. This number matches well with the observed secondary peak at ~ 5.5 Å in the Cl-Cl partial PDF of NaCl-CrCl₃ that appears also in NaCl at ~ 5.5 Å. It is worth noting that such detailed insight into the structure of Cr-containing melt is made possible by the availability of different Cr isotopes with both positive and negative neutron-scattering length, thus making isotopic substitution a very effective tool for probing the structure of the liquid. Given common structural motives between Cr and other multivalent cations (especially transition metals, but also rare earths and actinides), Cr could serve as a model ion to experimentally probe some of the structure and dynamics with high resolution.

The unexpected observation of the supercooled liquid and NaCl precipitation is important because the molten-salt chemistry in MSRs is normally approached within a chemical-thermodynamic equilibrium framework, assuming that chemical reactions and phase transitions are very rapid at reactor operating temperatures, up to 650 °C. However, this assumption may not be valid in a dynamic system such as an MSR. For instance, the fuel salt is going to experience temperature transients of about 100 °C within minutes as it circulates through the system, potentially leading to the formation of precipitates and out-of-equilibrium phases. Examples of non-equilibrium effects have previously been observed in molten salts systems, such as the formation of complex ions and changes in ion coordination may have caused a melting point depression in NH₄NO₃ salts with added metals (Li, Na, K, Ag, Ca, Sr, and Pb) [10]. Also, compound formation in a LiCl-Li₂O salt used in the production of uranium metal caused a lowering of the melting point and a co-vaporization of the LiCl-Li₂O salt [11]. However, a detailed analysis of non-equilibrium effects has not yet been done for molten salt systems relevant to MSRs, where nuclear reactions produce heat in circulating melts [12]. The idealized two-component salt studied here can be used to approach this problem since observations have shown a supercooled liquid 200 °C below the published equilibrium melting. Specifically, we have observed a supercooled liquid, where the intermediate-range order is stabilized with increasing temperature until the equilibrium melting temperature is reached [13, 14]. Such results are important for approaching the non-equilibrium phenomena arising due to temperature cycling relevant to operating MSRs.

1.1.2 Development of robust neural-network interatomic potential for molten salt

Efficient and accurate evaluation of salt properties from a fundamental, microscopic perspective remains a challenge. We applied artificial neural networks to atomistic modeling of molten NaCl to accurately reproduce the properties from ab initio quantum mechanical calculations based on density functional theory (DFT) [2]. The obtained neural network interatomic potential (NNIP) effectively captures the effects of both long-range and short-range interactions, which are crucial for modeling ionic liquids. Extensive validations suggest that the NNIP is capable of predicting the structural, thermophysical, and transport properties of molten NaCl as well as properties of crystalline NaCl, demonstrating near-DFT accuracy and 10³ higher efficiency in atomistic simulations. This application of NNIP suggests a paradigm shift from empirical/semiempirical/ab initio approaches to an efficient and accurate machine learning scheme in molten salt modeling.

We applied the Behler-Parrinello NN framework to develop a robust interatomic potential for a prototype NaCl molten salt system. Through proper design of the training dataset and minimizing a loss function considering both potential energy and atomic forces, our NNIP achieves a DFT-level accuracy in energy/force predictions and offers excellent stability of MD simulations under vari-

ous ensembles. Meanwhile, its computational cost is at least three orders of magnitude lower than AIMD. Extensive material property validations, including the structural/thermophysical/transport properties of molten NaCl and crystalline phase properties, demonstrate remarkable and consistent agreement between NNIP-MD and AIMD simulations. Furthermore, these NNIP-MD-based property evaluations also agree well with a wide range of experimental measurements, demonstrating the potential of NNIP for robust molten salt modeling. The workflow developed in this work has also been successfully applied to develop more complex fluoride molten salts [4]

1.2 The molecular structure and phase equilibria of molten fluoride salt with and without dissolved cesium: FLiNaK-CsF (5 mol%)

We demonstrate effects of Cs ions on the melting transition and molecular structure of molten FLiNaK (a eutectic mixture of LiF-NaF-KF) [3]. FLiNaK is a commonly studied multi-component model system, which represents the physical and chemical behavior of fluoride salts for nuclear energy applications. The dissolution of nuclear fuels leads to the formation of fission products directly in the molten salt. Cs is one of the most important fission products, due to its relative abundance, the long half-life, and potential environmental and health effects. Here, we determine the molecular structure and phase equilibria of dissolved Cs in FLiNaK by a combination of X-ray diffraction, X-ray total scattering, *ab initio* molecular dynamics calculations, and computational thermodynamics. Although Cs ions have a relatively large size, we did not find significant evidence that they disrupt the existing molecular structure of the liquid. We found good agreement between our simulated and measured structure factors and calculated that the coordination number of Cs is close to 10.

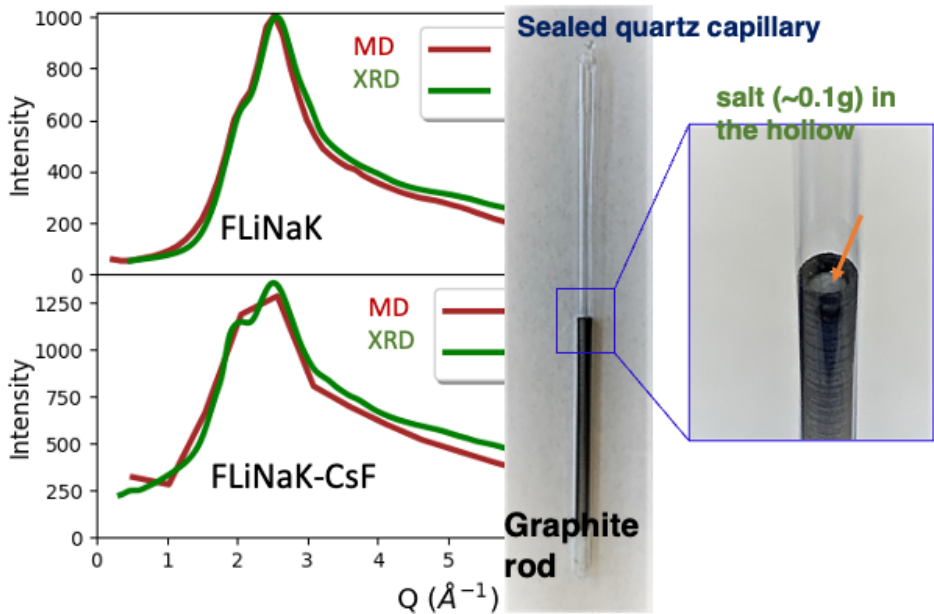


Figure 2: (Left) X-ray diffraction (XRD) and simulation (MD) results in molten FLiNaK and FLiNaK-CsF (5 mol%) showing excellent agreement. (Right) Sealed thin-wall quartz capillary with FLiNaK salt inside a graphite insert. The quartz capillary is ~ 3 mm diameter and 0.01 mm wall thickness. The insert is a 3mm-diameter HOPG (highly-oriented pyrolytic graphite) graphite rod (high purity, from SPI Supplies), further thinned to fit in the quartz capillary and machined a 2mm diameter hollow where ~ 0.1 g salt was filled. The quartz wool at the bottom of the capillary provides a space for the thermal expansion of graphite and protection of the capillary during assembly.

X-ray diffraction in combination with computational thermodynamics demonstrates that upon freezing Cs ions are captured into a CsLiF_2 compound, with a lower melting temperature than the FLiNaK mixture and much higher than that predicted for CsLiF_2 by computational thermodynamics. We also demonstrated a novel sample environment that we developed for X-ray measurements of molten fluoride or fuel salts. The major results of this work are summarized in Fig. 2. The experimental work described in this paper was supported by this project [3].

1.2.1 A Novel Design of High-Temperature Molten Salts Structure Analysis System (Patent application)

We designed a novel molten salt sample holder, shown in Fig. 2, for X-ray diffraction. This design combines the high-temperature stability and relative ease of sealing quartz with the excellent corrosion resistance of graphite. Sealed NMR capillaries (Wilmad-LabGlass, 3 mm diameter) prevent the exposure of molten salt to air while minimizing the background signal from X-ray scattering by quartz. (The capillary is sealed under a rough vacuum.) The graphite insert contains the salt while preventing corrosion damage to the quartz from molten salt at high temperatures. In addition, the graphite insert can be used to monitor accurately the temperature of the molten salt, as described below. High-energy X-rays used for total diffraction measurements penetrate the graphite rod with very little loss. This design has been successfully used for low-energy X-rays as well. The salt does not wet graphite, so the meniscus that forms by the molten salt can protrude above the graphite’s top edge. Thus, an X-ray beam of a few microns in diameter only penetrated the meniscus without interacting with graphite [3, 7].

1.3 FLiBe with impurities

Lithium fluorides, particularly $2\text{LiF}:\text{BeF}_2$ (FLiBe), are of considerable interest in nuclear systems, as they show an excellent combination of favorable heat transfer and neutron moderation and transmutation characteristics. The range of possible local structures, compositions, and thermodynamic conditions for nuclear salts presents significant challenges in atomistic modeling. Our simulation work was partially supported by this project [4]. We demonstrated that atom-centered neural network interatomic potentials (NNIPs) provide a fast method for performing molecular dynamics of molten salts that are as accurate as ab initio molecular dynamics. For LiF, these potentials can accurately reproduce ab initio interactions of dimers, crystalline solids under deformation, crystalline LiF near the melting point, and liquid LiF at high temperatures. For FLiBe, NNIPs accurately predict the structures and dynamics at normal operating conditions, high-temperature-pressure conditions, and in the crystalline solid phase. Furthermore, we show that NNIP-based molecular dynamics of molten salts are scalable to reach long time scales (e.g., nanosecond) and large system sizes (e.g., 10^5 atoms) while maintaining ab initio density functional theory accuracy and providing more than 3 orders of magnitude of computational speedup for calculating structure and transport properties [4].

Experimentally, we expanded on our previous measurements of FLiNaK-CsF by measuring FLiBe-CsF. Unlike FLiNaK, which does not contain multi-ion configurations (similar to other monovalent salts LiF, NaF, NaCl, etc.), liquid FLiBe has the presence of BeF_4 tetrahedra that are often connected into oligomers. These oligomers significantly affect thermophysical properties of FLiBe and the effect of impurities on them is important. Although we found again that Cs ions at 5 mol% level do not strongly perturb the liquid structure, we found the presence of clear Cs-Cs correlations, unexpected at such low concentrations. But such correlations resemble an earlier report of ion clustering of dilute Cr species in a chloride salt [15]. Interestingly, the addition of 5

mol% Cs completely changes the solid structure. No expected X-ray powder pattern of Li_2BeF_4 was found. We did find a signature of solid BeCs_2F_4 predicted by CALPHAD modeling of FLiBe-CsF (5mol%) below melting. These experimental results are being prepared for publication.

Another publication partially supported by this project was devoted to computer simulations of the impact of hydrogen valence on its bonding and transport in molten FLiBe [5]. In molten-salt nuclear-energy systems, the hydrogen isotope is of particular importance due to its ability to corrode structural materials as $^3\text{H}^+$ in fluoride salts, and its potential to cause significant radioactive release as diffusive $^3\text{H}^0$, which are cited as key barriers to technological deployment. Yet, the chemistry and transport behavior of the hydrogen species remain poorly understood due to the difficulties in handling toxic salts and radioactive materials. Using ab initio molecular dynamics, we conducted a coupled examination of hydrogen speciation in the most common prototypical salts, FLiBe and FLiNaK . Using extensively validated calculations on the local structure and dynamics, we found a significant difference between $^3\text{H}^0$ and $^3\text{H}^+$ transport behaviors that are usually overlooked. We find that $^3\text{H}^0$, which always exists as H_2 , diffuses 3–5 times faster than $^3\text{H}^+$, which can be ascribed to hydrogen bonding and complexation in solution. This work explains contradicting experimental results and provides useful species transport data for designing hydrogen capture and corrosion control systems for molten salts.

1.4 Towards in-situ corrosion monitoring in FLiNaK

Understanding and controlling the physical and chemical processes at molten salt-alloy interfaces is vital for molten-salt nuclear reactors. Corrosion processes in molten salts are highly dependent on the redox potential of the solution that changes with the addition of fission and corrosion products. Therefore, reactor designers develop online electrochemical methods of salt monitoring. But electrochemical spectroscopy relies on the deconvolution of broad peaks, a process that may be imprecise in the presence of multiple species in the solution.

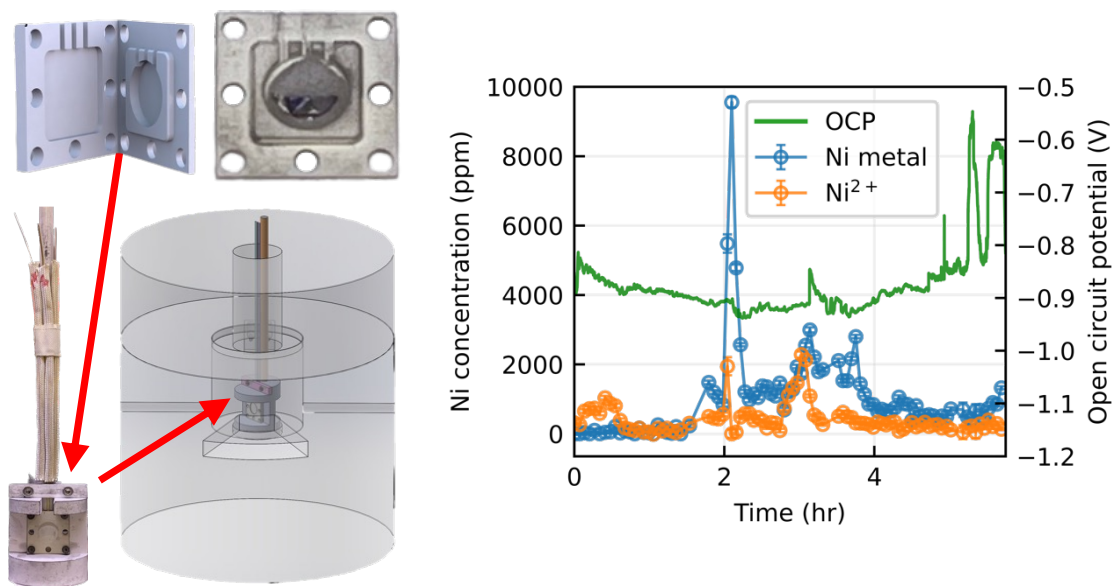


Figure 3: (Left) Photographs of boron-nitride sample cells for simultaneous X-ray absorption spectroscopy and electrochemistry (Right) Ni ion and metal concentration in FLiNaK and open-circuit potential in the same cell vs time.

In our most recent paper, which was partially supported by this project, we describe our developments towards monitoring the concentration and the chemical state of corrosion products in the melt by a combination of electrochemistry and X-ray absorption spectroscopy [6]. We placed NiCr foil in molten FLiNaK and found the presence of both Ni^{2+} ions and metallic Ni in the melt, which we attribute to the disintegration of the corroding foil due to Cr dealloying. Although extremely challenging, spectroelectrochemical measurements add a promising rich new data stream for online salt monitoring. The major results are shown in Fig. 3

1.5 Possible future directions

As we described above, this project enabled multiple collaborations, some of which are ongoing and some will require additional future funding. We would like to expand our work into high-resolution measurements of FLiBe and chloride salts with fission product impurities. In addition, we have started inelastic neutron and X-ray scattering measurements of diffusion of impurities and the microscopic dynamics in the liquid state. Another very interesting direction is the simultaneous X-ray absorption spectroscopy and electrochemistry that was started but has not yet been fully implemented.

2 Conclusions

There are multiple implications of our findings for Molten-Salt Reactors (MSR). We provided structural information that was and continued to be utilized for the experimental validation of atomistic models. We demonstrated a remarkable overall agreement between simulations and measurements of molten chlorides and fluorides.

In NaCl-CrCl_3 , we found the formation of CrCl_6 octahedra and their chains. Although this is not unexpected for Cr^{3+} ions in NaCl, we measured the details of the liquid structure for the first time with an exceptional resolution thanks to the use of isotopic substitution of Cr [1]. We made one of the first synchrotron X-ray PDF measurements of molten fluorides, FLiNaK and FLiBe, with fission product impurities (Cs) [3]. In addition to confirming simulation results, we found the formation of CsLiF_2 in FLiNaK and followed its melting transition. We confirmed the simulation results also in FLiBe-CsF (these results have not yet been published).

In parallel, robust and versatile Neural-Network Interacting Potentials (NNIP) have been developed for simulating molten NaCl, LiF, and an important nuclear salt FLiBe (2LiF-BeF_2) [2, 4, 5]. NNIPs have been shown to be highly adaptable to a variety of local environments while maintaining near ab initio accuracy. This feature is very desirable for applications to real systems, which involve many components and span wide thermodynamic conditions. Due to the ability to approximate an arbitrarily complex functional form, neural networks enable robust modeling of interatomic interactions of increasingly complex systems. Moreover, these potentials are able to accelerate property computations by orders of magnitude and far beyond the accessible time and length scales of ab initio methods while showing strong scaling efficiency with a large number of processors. As such, neural networks are demonstrated to provide a promising direction for multicomponent molten salts. In future work, these potentials will be applied to study more computationally challenging systems, which could enable dramatically accelerated screening and allow unprecedented interpolation across compositional and real operating space.

Next, we conducted the first simultaneous X-ray spectroscopy and electrochemistry measurements of in-situ corrosion in a molten fluoride salt. We discovered the presence of both Ni^{2+} ions and Ni0 (metal) in the molten salt due to the dissolution and disintegration of the test foil [6].

In addition to the structural and chemical information, we improved methods of data collection on molten salts, especially for X-ray diffraction and spectroscopy, where we developed sample cells for X-ray scattering and X-ray spectroelectrochemistry [3, 6].

The liquid state of matter is very difficult to fully understand and model. However, predictive modeling is necessary for the development of novel molten-salt reactors. Moving towards this goal was the objective of this project. We fulfilled the objective and gained crucial new knowledge about the molecular structure and dynamics of chloride and fluoride molten salts, to inform the design of new MSRs.

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