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Roadmap for thermal property measurements of Molten Salt Reactor systems

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ABSTRACT

Thermal properties of molten salts, both with and without fissile and fertile material, are fundamental to modeling and simulation that supports design, construction, operation, and accident progression evaluation of molten salt reactors. This roadmap provides guidance to the research community on the types and amounts of required data for base, or carrier, salt systems, recommends simulated burnup fuel salt compositions to evaluate, and provides a technical foundation for a focused salt property evaluation matrix. The property values generated from both computation and experimental methods are used to develop models that constitute the Molten Salt Thermal Properties Database (MSTDB). While the building blocks of MSTDB are fundamental in nature, its data facilitates constructing engineering models that allow stakeholders to investigate the behavior of specific compositions of interest and supports broader modeling and simulation of MSRs through coupling to multi-physics, multi-scale mass accountancy tools.

1. Background

Molten salts have the potential to advance energy technology as heat transfer or energy storage media and as liquid nuclear fuels. Their thermal properties must be known for system design, engineering, and operation. Since many salt properties are not well documented, a major effort to measure them is underway funded by the Department of Energy (DOE) Office of Nuclear Energy Advanced Reactor Technology Molten Salt Reactor (MSR) Campaign. The DOE Nuclear Energy Advanced Modeling and Simulation (NEAMS) program is contributing computationally derived properties that can be more rapidly and economically generated. These are benchmarked to existing data. Those properties that have not already been studied experimentally must be validated with targeted measurements sufficient to develop confidence in the computational predictions.

A number of potential fluoride and chloride-based salts are being considered for several different MSR concepts. A challenge that must be addressed is understanding the variance in system properties with composition and temperature to support selection of a base (carrier) salt. Complicating the situation is the fact products are generated due to fission, transmutation, and decay. These will be referred to hereafter as FPs (fission products) for simplicity. Further, material is introduced due to corrosion may be or removed during operation, e.g. to control the redox potential. It is therefore important to understand the changes in salt behavior with varying amounts of minor constituents.

As will be shown, for the designs and operation conditions selected for the present analysis, the concentration of FPs remains low enough to minimally impact salt chemical properties. It is hypothesized that many of the physical properties will also not be affected significantly. However, it is recommended that this be confirmed through measurements of salt with simulated burnup, or simfuel. **It should be noted that if designs call for very high burnup and/or extensive operation without reprocessing, the FPs will likely build to compositions significant enough to affect the thermal properties and phase equilibria.**

The depletion calculations in this report have been performed using the MSRE (Molten Salt Reactor Experiment) [1] and SOFT (Salt reactor Onsite reprocessing Fast converter Task) [2] reactor designs to represent a thermal spectrum fluoride and chloride fast reactor respectively. The results serve as a starting point for identifying, prioritizing, and determining bounding compositions for studying salts with reactor operation products.

This report aims to give guidance to the research community on the amount of data that would be sufficient to develop models that reproduce the behavior of base salt systems, recommend simfuel compositions, and provide a foundation for a reasonable, focused test matrix for generating the necessary thermophysical and thermochemical properties. It is understood that specific compositions may be deemed proprietary by some developers. The purpose of this roadmap is to lay the foundation for understanding integral systems from a basic science perspective that will inform development of models that can interpolate within each system and extrapolate into multicomponent space. *These models will make up the Molten Salt Thermal Properties Database (MSTDB) to serve as a useful tool to developers by supporting industry efforts to design, construct, and operate MSRs; to the Nuclear Regulatory Commission (NRC) for making licensing decisions; and to the broader research community.*

2. Thermal properties and system selection

The thermal properties of interest for reactor performance and safety evaluations are those that impact its radionuclide retention, heat transfer, or fissile material carrying capacity - density (ρ), viscosity (ν), thermal conductivity (κ), specific heat (Cp), melting point (m.p.) and phase equilibria, as well as vapor pressures (p*)[1]. This report will focus only on elements that will dominate the *thermophysical* and *thermochemical* behavior and ultimately have the largest impact on its bulk molten salt phase. This is not the end-all-be-all list of important elements (or radioisotopes). For example, for the MSRE case study, outside of the base salt concentrations are well below 1 mole % for any element and iodine is among the lowest. While iodine may be important for safety evaluation, e.g. dose to the public [3], it will have a negligible effect on ρ, ν, κ, Cp, and m.p. It will be important to measure molten salt solutions with iodine, particularly p* of I_2 (and I bearing gas species, for example CsI) albeit at concentrations well above anticipated levels. This is necessary to extrapolate property behavior to realistic compositions to understand iodine behavior, for example activity coefficients for vaporization modeling for source term analyses. As with iodine, none of the other FPs are expected to impact any of the thermal properties. This hypothesis must be tested and an approach will be included in the test matrix summarized in 3.1.

Noble gases and metals can be ignored for the purposes of thermal property measurements of the molten salt solution phase because they do not chemically interact with it. This does not mean that insoluble solid precipitates and gas bubbles do not affect the overall thermal properties of the system; including those effects will be important for understanding integral MSR fuel behavior, particularly mass accountancy, heat transfer, reactivity feedback, etc. However, treating those physics is outside the scope of measuring homogenous molten salt thermal property and phase equilibria behavior. Therefore, it is only germane to the effort proposed here to consider the highest concentration soluble FPs, that is, the salt seekers [4, 5].

2.1 Molten Salt Thermal Properties Database (MSTDB)

The property data will be generated both experimentally and computationally, e.g. via ab-initio and classical Molecular Dynamics (MD), and be stored in a GitLab repository at ORNL. This raw data is used as inputs for development of the MSTDB by optimizing the adjustable parameters to either a Gibbs energy model or an empirical one for representing ρ, ν, κ, and Cp in temperature and composition (T-C) space. The MSTDB is subdivided into a thermochemical (MSTDB-TC) and a thermophysical database (MSTDB-TP). This is done because of the fundamental difference in how the two must be used. A Gibbs Energy Minimizer (GEM) is needed to calculate thermodynamic equilibria for predicting phase relations and other values like p*, Cp[2] and chemical potentials using the MSTDB. This can be done with commercial software like FactSage [6] or Thermocalc [7]. Thermochimca is an open source GEM that

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[1] Boiling point and emissivity are also of interest as properties but beyond the scope of this report.

[2] The specific heat or heat capacity is sometimes considered a thermophysical property. It is a thermodynamic property and can be calculated using Maxwell relations from the Gibbs energy.

can be used standalone or with other codes for multi-physics calculations. The NEAMS program is developing the Yellowjacket GEM written in C++ for coupling to other codes like SAM and Griffin for modeling mass accountancy in MSRs.

2.1.1 MSTDB-TC

The Calculation of Phase Diagram (CALPHAD) method [8] is the accepted approach for thermodynamic modeling and database development within the materials community. The highest value inputs for optimal development of MSTDB-TC are Cp, m.p., and p* as well as mixing (ΔH^{mix}) and formation enthalpy (ΔH^{f}).

The MSTDB-TC is developed from existing literature with a data package tracing the source of every model and/or the raw data used for its continuing development [9]. Currently, it accommodates at least 21 elements and models for 63 pseudo-binary (47 fluoride, 16 chloride) and 29 pseudo-ternary (28 fluoride, 1 chloride) molten salt solutions along with 26 solid solutions and 89 stoichiometric compounds. In addition, there are 5 higher order chloride systems assessed. With CALPHAD, the database can be built upon, or extended, to include more elements as more systems are studied. This will eventually include all the impactful elements, from a thermochemistry standpoint, that will exist during operation of a molten salt reactor to model the thermochemical behavior with burnup including additives and corrosion products.

In addition to the base salt and daughters from fission, transmutation, and decay; system components for alloys that contact the salt need to be included in MSTDB-TC. This is necessary so that phase equilibria and chemical potentials can be used as inputs for multi-physics codes under development in the NEAMS program for predicting mass accountancy in the salt loop including microstructure evolution and mass transport in structural materials.

2.1.2 MSTDB-TP

The MSTDB-TP is a collection of empirical models for representing ρ, ν, κ, and Cp of molten salts as a function of temperature and composition. Currently there are 62 entries. Of them, 27 are pure compounds (14 fluorides and 13 chlorides), 8 pseudo-binary systems (1 chloride and 7 fluorides), 10 pseudo-ternaries (all of them fluorides) and 5 pseudo-quaternaries (all of them fluorides). The following details for each property are as follows:

- Densities have been established for 54 out of 62 of the compositions MSTDB-TP.
- Viscosity relations have been established for 48 out of 62 compositions. The majority of missing data are from actinide and lanthanide pure compounds.
- Thermal conductivity measurements have been performed for 25 entries. This is the property of greatest data need.
- For heat capacity, all pure compounds are represented together with 43 mixture compositions. Missing data ranges from pseudo-binary, pseudo-ternary and pseudo-quaternary systems.

2.2 Approach for data collection and modeling

The MSTDB must be populated with data for pure end members and pseudo-binary salts with temperature and composition. Extrapolating into multicomponent space based on these fundamental subsystems is an established practice within the materials community [10-12]. To a first approximation, a Redlich-Kister formalism [13], or similar expression [14-17], accounts for the interactions in binary systems that can be combined for predicting both thermodynamic behavior as well as density, viscosity, thermal conductivity, and specific heat in higher order systems. In this way, populating the MSTDB with pure end member and pseudo-binary mixture properties allows for data-based extrapolation into multicomponent space, i.e., properties of base salt with fission products. As phase equilibria becomes more apparent for down-selecting to specific salt assemblages, targeted compositional regions can be studied in more detail.

Figure 1 shows how the thermophysical and thermochemical properties are intertwined. For this example, the ρ of the pseudo-binary LiF-ThF$_4$ system [18] as a function of ThF$_4$ mole fraction is plotted in Figure 1(a) using Eqns. 1 and 2. In Figure 1(b), parts of the T-C space are colored in red due to the fact that this region is below the system liquidus. Thus, the relation generated does not hold there since both solid and molten salt co-exist. The phase equilibria, derived from thermodynamics, must be known to understand the bounding conditions for the thermophysical property relations.

$$\rho_{mix} = \frac{x_A mw_A + x_B mw_B}{x_A mw_A / \rho_A + x_B mw_B / \rho_B} + x_A x_B (L_1 + (x_A - x_B) L_2) \tag{1}$$

$$L_i = A_i + B_i T \tag{2}$$

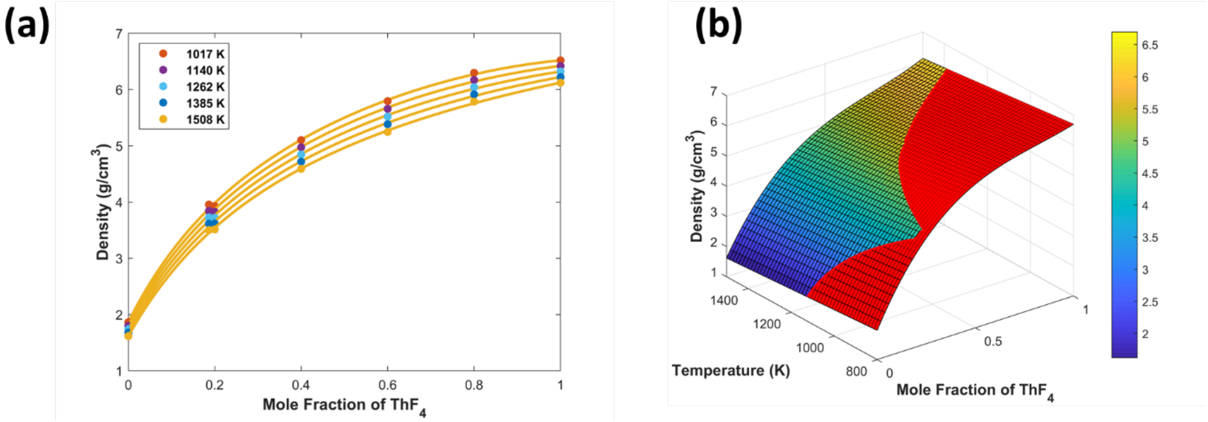

Figure 1(a) Density vs composition relationship for a series of temperatures and (b) ρ-T-C plot superimposed with phase space in red for which the model is not valid in the LiF-ThF4 system.

The coefficients in Eqn. 2 were fitted using a non-linear least squares approach with the Levenberg-Marquardt algorithm. The values, in g/cm^3 were found to be:

$$A_1 = 1.0565$$
$$B_1 = -8.8046x10^{-4}$$
$$A_2 = 1.2139$$
$$B_2 = -7.4044x10^{-4}$$

Computational techniques like ab-initio and classical MD have been demonstrated to effectively represent properties like ρ, ν, κ, and Cp for FLiBe (eutectic LiF-BeF$_2$), FLiNaK (46.5-11.5-42 mol % LiF-NaF-KF eutectic), and NaCl-UCl_3-UCl_4 compositions. This presents an opportunity to quickly populate needed meta-data for developing pure end member and pseudo-binary molten salt relations with temperature and composition. These data can then be validated through concurrent measurements and/or over refined T-C ranges of specific interest to stakeholders.

As FPs are generated, the fueled salt is an ever-evolving mixture of the elements with thermal properties that change with composition. However, it is important to understand what the major products are and their concentrations as a function of burnup. This is all highly dependent upon the reactor design and operation schedule. Therefore, depletion estimates are included here for a thermal spectrum fluoride and a chloride fast reactor to be as representative as possible to industry interests. The goal is to determine bounding compositions for the highest occurring and/or most impactful elements that are generated with burnup. The salt seekers are identified as they have the most significant influence on thermal properties. These are then classified into groupings, i.e. the Rare Earths (REs), that exhibit chemically similar behavior. For example, Nd, the RE of highest concentration, can be used to represent each trivalent RE. Cerium can be used to represent Pr as a mixed tri- and tetra-valent RE.

2.3 Thermal spectrum fluoride reactor systems

The base systems of interest to developers of thermal spectrum MSRs are LiF-BeF_2-UF_3-UF_4-ZrF_4, LiF-NaF-ThF_4, NaF-BeF_2-UF_3-UF_4-ThF_4, and LiF-NaF-UF_3-UF_4. As mentioned above, each of these should be understood starting with the fundamental pseudo-binaries resulting in 20 that should be studied systematically:

LiF – BeF_2
LiF – UF_3
LiF – UF_4
LiF – ZrF_4
BeF_2 – UF_3
BeF_2 – UF_4
BeF_2 – ZrF_4
UF_3 – UF_4
UF_3 – ZrF_4
UF_4 – ZrF_4
LiF – NaF
LiF – ThF_4
NaF – BeF_2
NaF – UF_3
NaF – UF_4
NaF – ThF_4
BeF_2 – ThF_4
UF_3 – ThF_4
UF_4 – ThF_4
LiF – BeF_2

The goal is to understand these systems from a basic science perspective and generate data for models that represent the properties over a sufficient T-C space. These models then become a tool for stakeholders to investigate specific compositions of interest.

For understanding the level of FPs that result from operation, a depletion data set was generated with the SCALE/TRITON continuous processing capability [19], which are derived from the ChemTriton tool [20, 21]. Parameters for the simulation of the thermal neutron spectrum MSRE [1] using a FLiBe carrier salt carrier are given in Table 1.

Table 1 Parameters used for simulating the isotopic inventory for the MSRE reactor.

Fuel type	35% enriched U^{235}
Carrier salt (mole %)	69.1 LiF – 30.9 BeF_2
Fuel chemical form	UF_4
Temperature (°C)	649
Salt Mixture (mole %)	65 LiF – 29.1 BeF2 – 5 ZrF_4 – 0.9 UF_4
Salt volume (m^3)	2.07
Fueling condition/rate	NA

The calculation was performed using the well-stirred pot assumption, which treats the entire primary loop fuel salt as a homogeneous mixture. This approach does not capture the spatial dependence of the fuel salt within the primary loop (e.g., core, piping, pump, and heat exchanger), which occurs over very short time periods of seconds to minutes. Instead, it generates the evolution of the fuel salt material over the months and years of reactor operation as FPs build up within the fuel salt. The results are presented in Table 2 and represented graphically in the Appendix.

Table 2 Composition of the highest yield products of fission, transmutation, and decay in the MSRE for 1, 10, and 30 years of operation. Any element persisting below 0.0048 mole % is excluded, including I.

	Concentration (mol%)			
Constituent	**1st Year**	**10th Year**	**30th Year**	**Stream**
F	59.477	59.452	59.394	Fuel
Li	26.338	26.327	26.296	Fuel
Be	11.791	11.786	11.774	Fuel
Zr	2.025	2.036	2.059	Fuel
U	0.360	0.316	0.226	Fuel
Mo	0.001	0.011	0.032	Solid Waste
Nd	0.001	0.009	0.026	Fuel
Xe	0.001	0.008	0.023	Gas Waste
He	0.000	0.003	0.020	Fuel
Cs	0.001	0.006	0.018	Gas Waste
Ru	0.001	0.005	0.017	Solid Waste
Ce	0.001	0.006	0.016	Fuel
Ba	0.000	0.003	0.011	Fuel
Sr	0.000	0.004	0.009	Fuel
Tc	0.000	0.003	0.008	Solid Waste
La	0.000	0.003	0.008	Fuel
Pr	0.000	0.002	0.007	Fuel
Pd	0.000	0.001	0.006	Solid Waste
Cs	0.000	0.002	0.006	Fuel
Pu	0.001	0.005	0.006	Fuel

2.4 Chloride based systems

The base systems of interest to developers of chloride salt MSRs are $NaCl\text{-}MgCl_2\text{-}UCl_3\text{-}UCl_4\text{-}PuCl_3$, $NaCl\text{-}$ $ZrCl_4\text{-}$ $UCl_3\text{-}UCl_4\text{-}PuCl_3$, $NaCl\text{-}AlCl_3\text{-}$ $UCl_3\text{-}UCl_4\text{-}PuCl_3$, $NaCl\text{-}KCl\text{-}MgCl_2\text{-}UCl_3\text{-}UCl_4\text{-}PuCl_3$, $NaCl\text{-}KCl\text{-}ZrCl_4\text{-}$ $UCl_3\text{-}UCl_4\text{-}PuCl_3$, $NaCl\text{-}KCl\text{-}AlCl_3\text{-}$ $UCl_3\text{-}UCl_4\text{-}PuCl_3$, $NaCl\text{-}ThCl_4\text{-}PuCl_3$. As with the fluorides, each of these should be understood starting with the fundamental pseudo-binaries resulting in the following 27 to be studied systematically:

$NaCl – MgCl_2$
$NaCl – UCl_3$
$NaCl – UCl_4$
$NaCl – PuCl_3$
$MgCl_2 – UCl_3$
$MgCl_2 – UCl_4$
$MgCl_2 – PuCl_3$
$UCl_3 – UCl_4$
$UCl_3 – PuCl_3$
$UCl_4 –PuCl_3$
$ZrCl_4 – NaCl$
$ZrCl_4 – UCl_3$
$ZrCl_4 – UCl_4$
$ZrCl_4 – PuCl_3$
$AlCl_3 – NaCl$
$AlCl_3 – UCl_3$
$AlCl_3 – UCl_4$
$AlCl_3 – PuCl_3$
$KCl – NaCl$
$KCl – MgCl_2$
$KCl – UCl_3$
$KCl – UCl_4$
$KCl – PuCl_3$
$KCl – ZrCl_4$
$KCl – AlCl_3$
$NaCl – ThCl_4$
$PuCl_3 – ThCl_4$

As mentioned earlier, these systems are to be understood at a basic science level and the data is used to develop models to that are a tool for stakeholders to investigate specific compositions of interest.

For understanding the FPs that are generated with operation of an chloride fast reactor, SCALE/TRITON with continuous processing [19-21] was again used with the parameters in Table 3 which are based on the SOFT design [2]. The results are given in Table 4. See the Appendix for compositional plots over time with details for individual streams.

Table 3 Parameters used for simulating the elemental inventory for the SOFT reactor.

Fuel type	U/Pu
Carrier salt	NaCl
Fuel chemical form	$PuCl_3$, UCl_3
Temperature (°C)	537
Salt Mixture (mole %)	1 $PuCl_3$ – 8 UCl_3 – 10 NaCl
Salt volume (m^3)	107
Fueling condition/rate	Load depleted U to maintain overall salt density

Table 4 Composition of the highest yield products of fission, transmutation, and decay in the SOFT reactor for 1, 10, and 30 years of operation. Any element persisting below 0.05 mole % is excluded, including I.

	Composition (mol%)			
Constituent	**1st Year**	**10th Year**	**30th Year**	**Stream**
Cl	66.049	65.732	64.523	Fuel
Na	17.771	17.139	16.152	Fuel
U	14.207	13.560	12.574	Fuel
Pu	1.792	1.839	1.907	Fuel
Xe	0.020	0.193	0.550	Waste
Mo	0.018	0.187	0.533	Waste
Zr	0.017	0.167	0.477	Waste
Cs	0.017	0.172	0.465	Waste
Ru	0.019	0.159	0.440	Waste
Nd	0.012	0.139	0.398	Waste
Pd	0.010	0.121	0.356	Waste
Ce	0.012	0.091	0.250	Waste
Ba	0.004	0.056	0.187	Waste
Rh	0.005	0.054	0.156	Waste
Tc	0.005	0.049	0.138	Waste
La	0.005	0.048	0.135	Waste
Pr	0.004	0.044	0.124	Waste
Sm	0.003	0.035	0.111	Waste
Te	0.003	0.025	0.072	Waste
Sr	0.002	0.029	0.072	Waste

Table 5 Categories of major FPs. The soluble FPs (salt seekers) are those that are stable as halides and are expected to show some degree of solubility in the base molten salt.

Salt seekers	Noble gases	Noble metals
RE's (Nd, Ce, La, Pr)	Xe	Ru
Zr	Kr	Pd
Cs	He	Rh
Ba		Mo*
Sr		Tc*
Pu		
Cr		
Fe		
Ni		
Mo*		
Tc*		

Table 5 shows the categories of major FPs based on the results from both the MSRE and SOFT depletion calculations and what is expected from corrosion processes. The salt seekers are those that are stable as halides and are expected to show some degree of solubility in the base molten salt. Molybdenum and Tc are tagged with an asterisk and are expected to behave as noble metals. Strictly speaking, both can form halides. While it is hard to imagine a redox condition during normal and off-normal operations or even accident scenario in which this would occur, understanding the vapor pressures of some MoF_6 and TcF_6 gas species is important for mass accountancy modeling and predictions. Therefore, including them as a salt seeker for simfuel is a conservative approach for more precisely understanding the chemistry molten salts with burnup.

The NEAMS program and MSR campaign are coordinating with the University of South Carolina under a NEUP for further developing the MSTDB-TC. The systems currently being addressed are UF_3-UF_4, Ce-U-F, Ce-Na-F, Nd-U-F, Nd-Na-F, Zr-U-F, Zr-Li-F, Zr-Na-F, Zr-K-F, K-U-Cl, U-Mg-Cl, U-Na-Cl, Ce-U-Cl, Ce-Na-Cl and Ce-Mg-Cl. Cesium and I will be selectively modeled.

2.5 Corrosion products

For current MSR designs Cr, Fe, and Ni are major components of the alloys considered for the structural materials that will be in contact with the molten salt and are therefore included in Table 5. Another aim of the NEUP mentioned above is to include those elements that are anticipated to be major corrosion products. The specific work includes the general structural alloy elements of Cr, Fe, and Ni with major salt constituents of LiF-NaF-BeF_2-$UF_{3,4}$/ThF_4 and NaCl, KCl, $MgCl_2$, and $UCl_{3,4}$/$ThCl_4$. Corrosion mediated by contaminant levels of oxygen and OH will be considered as well. Some evidence suggests the Te plays a role in corrosion of structural materials [22]. However, Te concentration in the salt is not predicted to be much higher than 0.0027% and 0.072% by mole in the MSRE and SOFT based on the depletion calculations performed for this work. Tellurium is therefore presently neglected from inclusion for simplicity.

3. National Laboratory Plan

3.1 Experimental path forward

A major challenge for making property measurements is the chemical reactivity of salts with oxygen, water vapor, and container materials. This requires loading samples in inert environments as well as techniques for their transfer for analyses. No real system can be completely oxygen and moisture free. It will therefore be important to quantify the level of O_2 and H_2O contamination in samples used for property measurements. The MSR campaign has directed significant resources towards establishing the infrastructure and instrumentation needed to do this at several national laboratories. Others have leveraged separate funding sources to make use of existing facilities, e.g. LANSCE (Los Alamos Neutron Science Center) for establishing new ways for measuring ρ and ν of molten salts at high temperatures.

Table 6 List of National Laboratories, measurement capabilities, and salts of focus.

Institution	Property measurement capabilities	Systems of focus
Oak Ridge (ORNL)	ρ, ν, κ, Cp, p^*, m.p, and compositional analysis	• U and Be bearing fluorides • U bearing Be chlorides
Argonne (ANL)	ρ, ν, κ, Cp, m.p, and compositional analysis	• Actinide and Be bearing fluorides • Actinide and Be bearing chlorides
Idaho (INL)	ρ, ν, κ, Cp, m.p, compositional analysis	• Actinide bearing chlorides • Irradiated salts
Pacific Northwest (PNNL)	ρ, ν, κ, Cp, p^*, m.p, $\Delta H^{f,}$ ΔH^{mix} and compositional analysis	• U and Be bearing fluorides • U bearing chlorides
Los Alamos (LANL)	ρ, ν, κ, Cp, m.p, compositional analysis	• Actinide and Be bearing fluorides • Actinide and Be bearing chlorides

While each national laboratory in Table 6 is technically capable of handling actinide bearing salts, including Pu, in practice, for the types of measurements discussed here, those are best performed at PNNL, INL, ANL, and LANL.

(a)

BeF_2	4 3					
UF_3	3 1	1 1				
UF_4	3 3	3 2	3 1			
NaF	4 4	4 3	3 1	3 3		
ZrF_4	4 2	2 1	2 1	3 1	4 2	
ThF_4	3 3	3 2	1 1	3 1	3 3	1 1
	LiF	**BeF_2**	**UF_3**	**UF_4**	**NaF**	**ZrF_4**

Key
1. No information
2. Partial information
3. Sufficient information
4. Complete information

Top left refers to thermodynamic data; bottom right refers to thermophysical properties

$MgCl_2$	4 3							
UCl_3	4 3	3 1						
UCl_4	3 3	2 2	2 2					
$ZrCl_4$	3 1	2 1	1 1	1 1				
$AlCl_3$	4 2	3 1	1 1	1 1	1 1			
KCl	4 3	4 3	4 3	3 3	3 1	4 2		
$PuCl_3$	3 1	3 1	4 1	1 1	1 1	1 1	2 1	
$ThCl_4$	2 2	2 1	2 1	2 1	1 1	2 1	2 2	2 1
	NaCl	**$MgCl_2$**	**UCl_3**	**UCl_4**	**$ZrCl_4$**	**$AlCl_3$**	**KCl**	**$PuCl_3$**

(b)

LiF	2 2	3 2	1 1	3 1	2 2	3 2	3 2	2 1	2 1	1 1	4 1	
ThF_4	1 1	3 1	1 1	2 1	1 1	2 1	2 1	1 1	1 1	1 1	1 1	
BeF_2	1 1	1 1	1 1	2 1	2 1	2 1	3 1	1 1	1 1	1 1	1 1	
NaF	2 1	3 2	1 1	3 1	2 2	3 1	3 1	2 1	2 1	1 1	4 1	
UF_3	1 1	1 1	1 1	1 1	2 1	2 1	1 1	1 1	1 1	1 1	1 1	
UF_4	2 1	3 1	1 1	3 1	1 1	1 1	2 1	1 1	1 1	1 1	1 1	
ZrF_4	1 1	1 1	1 1	3 1	4 2	1 1	1 1	1 1	1 1	1 1	1 1	1 1
	NdF_3	**CeF_3**	**CeF_4**	**CsF**	**BaF_2**	**SrF_2**	**PuF_3**	**CrF_3**	**FeF_2**	**I_2**	**NiF_2**	**ThF_4**

NaCl	3 2	3 1	1 1	3 3	2 3	2 1	2 1	2 1	3 1	1 1	4 2	
$PuCl_3$	1 1	1 1	1 1	2 1	3 1	2 1	1 1	1 1	1 1	1 1	1 1	
$ThCl_4$	1 1	2 1	1 1	2 1	2 1	2 1	1 1	1 1	1 1	1 1	1 1	
$MgCl_2$	1 1	3 1	1 1	3 2	2 3	1 1	2 1	2 1	3 1	1 1	4 1	2 1
UCl_3	1 1	2 1	1 1	2 3	1 1	1 1	1 1	1 1	1 1	1 1	1 1	1 1
UCl_4	1 1	1 1	1 1	2 3	2 1	2 1	1 1	1 1	1 1	1 1	1 1	1 1
$ZrCl_4$	1 1	1 1	1 1	2 1	1 1	1 1	1 1	1 1	1 1	1 1	1 1	1 1
$AlCl_3$	1 1	1 1	1 1	2 1	2 1	1 1	1 1	1 1	3 1	1 1	3 1	2 1
KCl	3 2	3 2	1 1	3 2	2 2	2 2	2 1	2 1	3 1	1 1	4 1	2 3
	$NdCl_3$	**$CeCl_3$**	**$CeCl_4$**	**CsF**	**$BaCl_2$**	**$SrCl_2$**	**$CrCl_2$**	**$CrCl_3$**	**$FeCl_2$**	**I_2**	**$NiCl_2$**	**$ThCl_4$**

Figure 2 (a) Test matrix of the pseudo-binary combinations for base salt system with an information status estimate. Each property ρ, ν, κ, Cp, p, should be measured from the liquidus to 1000°C (or as high as possible) spanning $0.00 \leq x \leq 1.00$ compositional regions. The phase equilibria should be characterized from 25 – 1000°C. The m.p. (solidus and liquidus) and the enthalpy of fusion are unique to T-C space. The enthalpy of formation is for STP. (b) Test matrix for the base salt and FP bearing constituent pseudo-binary endmember combinations. Properties are likely needed over the $0.00 \leq x \leq 0.10$ compositional region.*

An important aim beyond understanding property behavior of the fundamental subsystems, is to determine at what levels fission, transmutation, and decay products measurably affect individual thermal properties. As a first step, simfuel salt should be tested to determine ρ, ν, κ, Cp, p*, and m.p values using compositions at (or above) those given in Table 2 and Table 4. Loading simfuel with elements above those levels may be necessary as some, at least for MSRE, remain well below 0.1 mole % at any given time. The impact on the thermal properties should be verified to a first order with *additions* at or above the levels for 30 years of operation to understand bounding behavior and extrapolate into lower compositional regimes. Here, the term *additions* means amounts that are practical and measurable leading to a pseudo-simfuel composition. For example, it is highly unlikely there exists a capability for loading FLiBe base salt with Cs at 0.005 mole %. Therefore, the addition of Cs will likely need to be 0.1 mole % or higher.

As mentioned earlier, two other simplifications can be made and should be used to facilitate generating the necessary data for understanding molten salt behavior with nuclear reactor operation. Neodymium, is the RE of highest concentration for both the fluoride and chloride designs studied in this work. It can be used to represent each trivalent RE as a singular addition while Ce can be used to represent both Pr and Ce as a mixed tri- and tetra-valent RE. This approach serves two purposes. It reduces the number of additions and brings the concentration of both the RE^{3+} and RE^{4+} FPs to a potentially practical loading level. Finally, there is no substitute for verifying properties of actual fuel. The MSTEC (Molten Salt Thermophysical Examination Capability) facility is currently under development at INL. Measurements of ν, κ, Cp, p*, and m.p using irradiated salts with compositions given in Tables 7 and 8 should be performed to determine the influence of irradiation effects on these properties.

Table 7. Proposed salt compositions for thermal property measurements of MSRE pseudo-simfuel. Neodymium trifluoride represents NdF_3, LaF_3, and YF_3 while CeF_3 represents CeF_3 and PrF_3.

Constituent	**Mole % composition**
LiF	62.70
BeF_2	28.07
ZrF_4	4.91
UF_4	0.54
Mo	0.54
NdF_3	0.54
CeF_3	0.54
PuF_3	0.54
CsF	0.54
BaF_2	0.54
SrF_2	0.54

Table 8. Proposed salt compositions for thermal property measurements of SOFT pseudo-simfuel. Neodymium trichloride represents $NdCl_3$, $LaCl_3$, and YCl_3 while $CeCl_3$ represents $CeCl_3$ and $PrCl_3$

Constituent	Mole % composition
NaCl	48.36
U	5.07
UCl_3	32.58
$PuCl_3$	5.71
Mo	1.59
Zr	1.43
CsCl	1.40
$NdCl_3$	1.93
$CeCl_3$	1.12
$BaCl_2$	0.60
$SrCl_2$	0.22

Unlike for the MSRE which evolves to be very fluorine rich without processing and material removal, a chlorine balance using the depletion calculation for the SOFT reactor indicates significant halogen poor salt after 30 years of operation. This is supported with previous calculations from Robinson [23]. An analysis of the relative stabilities of the chlorides allows for specifying the chemical state of the constituents for the SOFT pseudo-simfuel. The Ellingham diagram in Figure 3 is a pictographic representation of this. It is used to determine the oxidation state and compositional values for each salt constituent in Table 8. All the Zr and some of the U are reduced to neutral. It is unknown whether these species will remain dissolved in the molten salt phase or precipitate out as metals. Studying the phase equilibria of the pseudo-simfuel will be important for answering that question.

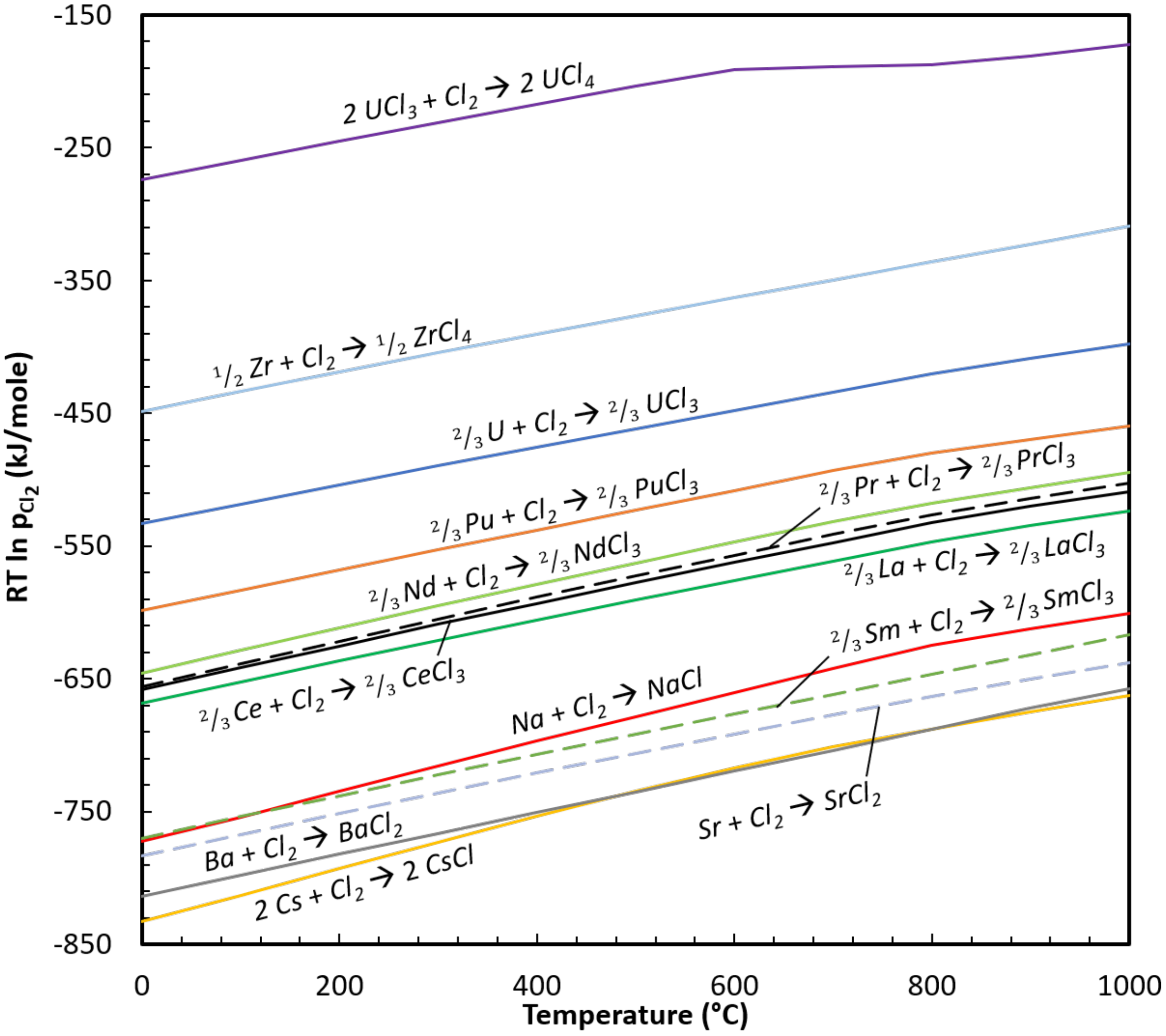

Figure 3. Ellingham of the salt seeking chloride fission, transmutation, and decay products.

3.2 Computationally derived salt properties path forward

The NEAMS program is developing the tools necessary for addressing modeling and simulation challenges associated with MSRs. Of particular importance for near term impact are ab-initio and classical molecular dynamics computational capabilities. Recently, both chloride and fluoride system properties have been calculated and benchmarked to existing data. Example results for NaCl, UCl_3, and NaCl-UCl_3 are shown in Figures 9-11 and compared to experimental data that is available in the literature. Agreement between simulations and measurements are very good for the pure salts. Mixtures show slightly higher deviations, but are still close to being within 5% of each other.

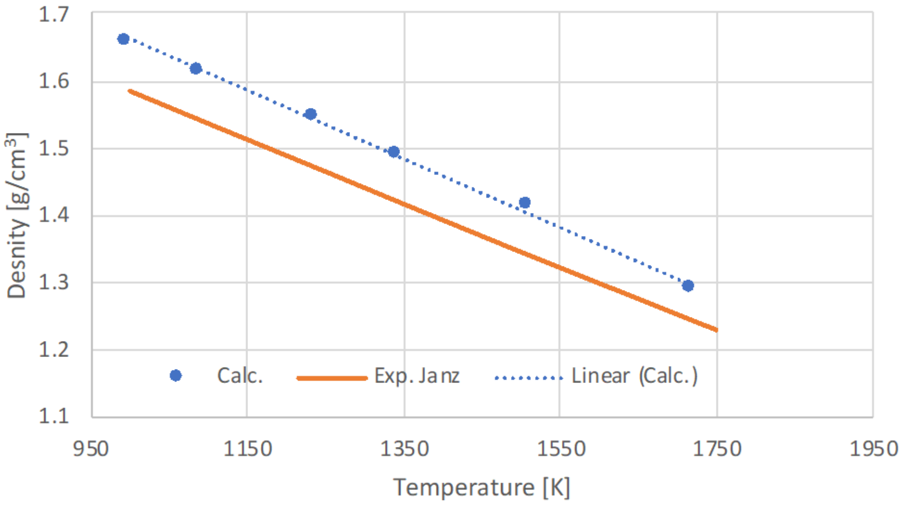

Figure 4 NaCl denity with temperature computed using AIMD compared to experimental measurments. The computational data set deviates from expereiments by less than 5%, which requiers inclusion of dispersion forces in the AIMD simulations.

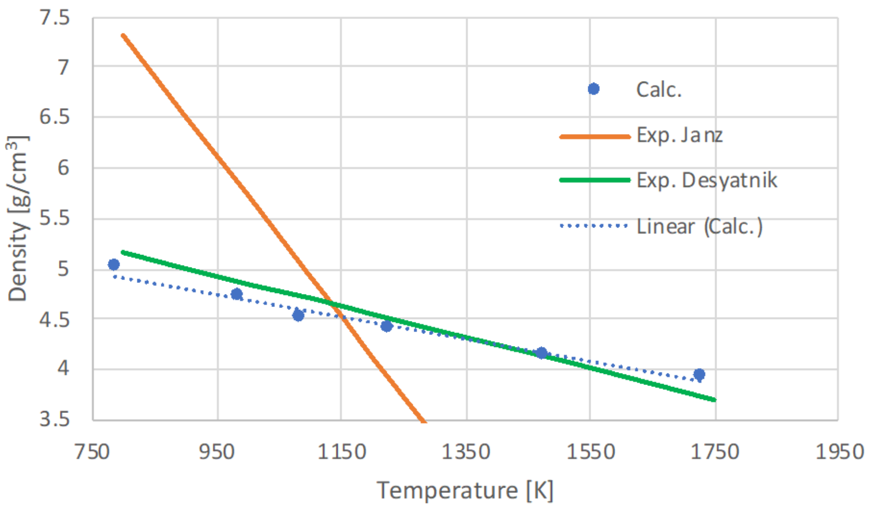

Figure 5 The density of UCl_3 with temperature computed using AIMD compared to experimental measurments from Janz and Desyatnik et al. The computational data set deviates by less than 5% from expereiment (Desyatnik). One of the experiemntal data sets is not reliable and deviates significantly from the computational densities..

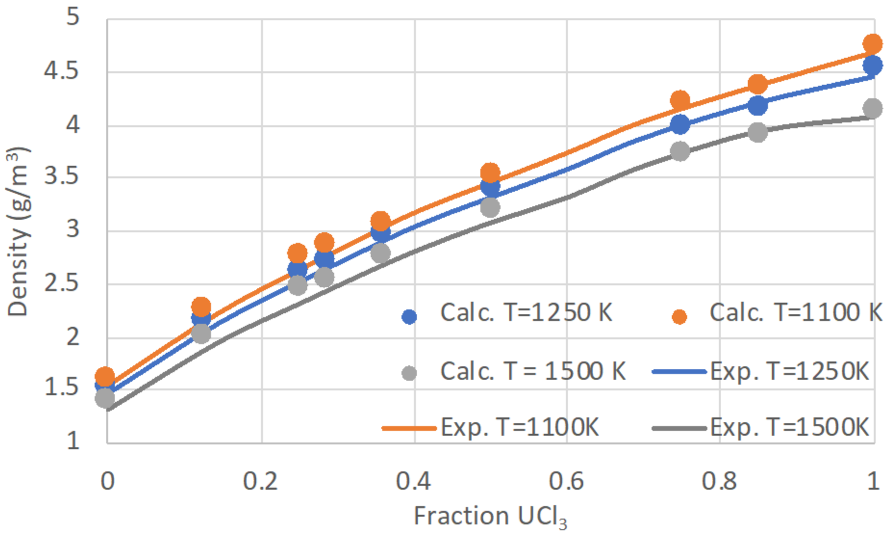

Figure 6 A mixture of NaCl-UCl_3 at 1100, 1250 and 1500K computed using AIMD and compared to experimental data from Desyatnik et al.

This molecular dynamics-based capability presents an opportunity to quickly populate the needed data set for MSTDB development through a synergistic computational and experimental campaign. Properties are calculated for pure end member compounds and pseudo-binary systems over an extensive, continuous T-C space; validated through targeted measurements; and implemented into MSTDB-TP. Once sufficient fundamental subsystem data exists, multicomponent assemblages are predicted. The MSTDB-TP empirical models can be further refined through subsequent targeted measurements.

3.3 Collaborators and contributors

As is evident in the test matrix presented in Figure 2, determining the required properties to address the systems relevant to industry as a whole is a significant one. In FY20, the Molten Salt Thermal Properties Working Group (MSTPWG) was convened to begin to attack this challenge. It is an informal confederation of national labs, academic institutions, and industry participants with the common aim of moving forward MSR technology through computational and experimental studies. An in-person meeting for the MSTPWG was re-scheduled due to the COVID-19 national emergency and held in a virtual setting, hosted by the University of South Carolina, on July 14 and 15, 2020. Attendees included representatives from industry, academia, other national laboratories, and governmental organizations, e.g. the US DOE and NRC; a detailed list is given in Table A.1. An in-person working group meeting is being planned for the next calendar year and interaction is ongoing.

This roadmap is a national laboratory defined plan for voluntary participation by MSTPWG members that are not directly supported by the MSR campaign and the NEAMS program. Relationships between researchers continue to develop and a community of scientists dedicated to advancing molten salt reactor technology is growing. The overarching goal is to experimentally generate needed data for database development and validate computationally derived molten salt properties defined herein. Due to the number of systems and properties that need to be characterized for MSTDB development, the hope is academia, industry, and other institutions can contribute in a timely manner by selecting systems to synergistically coordinate with the MSR campaign and the NEAMS program through the Gateway for Accelerated Innovation in Nuclear (GAIN), Nuclear Energy University Program (NEUP), and other funding vehicles.

4. Summary

Molten salt systems of interest to MSR developers were identified and the fission, transmutation, and decay product quantities were estimated for up to 30 years of operation using the MSRE and the SOFT reactor designs representing a thermal spectrum fluoride reactor and a chloride fast reactor respectively. Using this information, a plan is suggested for generating the data for the thermal properties needed to fully develop the MSTDB-TC and MSTDB-TP to predict thermal properties and phase equilibria into multicomponent space. Based on a review of the available, fundamental data [24, 25], it is estimated to require an effort spanning 5 years between multiple national laboratories, academic collaborators, and industry partners, costing around \$25M for experiments and \$10M for modeling and simulation.

A test matrix was formulated to cover the complete compositional range for an intended comprehensive understanding of fundamental molten salt subsystems. The goal is to understand the pseudo-binary behavior and generate property data for developing the MSTDB which has far reaching practical applications for MSR modelers, regulators, and developers. The approach is predicated on the concept that a multicomponent database can be built from the fundamental pseudo-binary and pseudo-ternary subsystems. The models in the MSTDB can then be combined for extrapolations into compositional assemblages of choice. The approach is the default first approximation method for thermodynamic modeling and should allow the thermochemical properties and the phase equilibria to be sufficiently reproduced and refined with targeted, follow-on validation measurements for multicomponent systems with the MSTDB-TC. The situation is the same for the empirical correlations that represent ρ, ν, and κ using the MSTDB-TP. The models in MSTDB then become a tool for stakeholders to investigate specific compositions of interest that may be subsequently viewed as business sensitive.

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APPENDIX

Table A.1 Institutions represented at the Molten Salt Thermal Properties Working Group meeting held June 14 and 15, 2020.

The US Nuclear Regulatory Commission (NRC)
The US Department of Energy (DOE)
Pacific Northwest National Laboratory
Brookhaven National Laboratory
Oak Ridge National Laboratory
Idaho National Laboratory
Los Alamos National Laboratory
Sandia National Laboratories
Canadian Nuclear Laboratories
The French Alternative Energies and Atomic Energy Commission (CEA)
Kairos Power
Flibe Energy
Elysium Industries (USA)
Elysium Industries Limited (Canada)
TerraPower
Slalom Consulting
The University of Florida
The University of Wisconsin
Gorgia Institute of Technology
Slovak Academy of Sciences
North Carolina State University
The University of South Carolina
University of Edinburgh
The University of Texas at San Antonio
The University of Connecticut
Brigham Young University
Ontario Tech
The University of Virginia
Virginia Polytechnic Institute and State University
The University of Utah
The University of California, Berkeley
Argonne National Laboratory
Virginia Commonwealth University
The Pennsylvania State University
The University of Nevada at Reno
Washington State University
San Diego State University
The University of Notre Dame
The University of Iowa

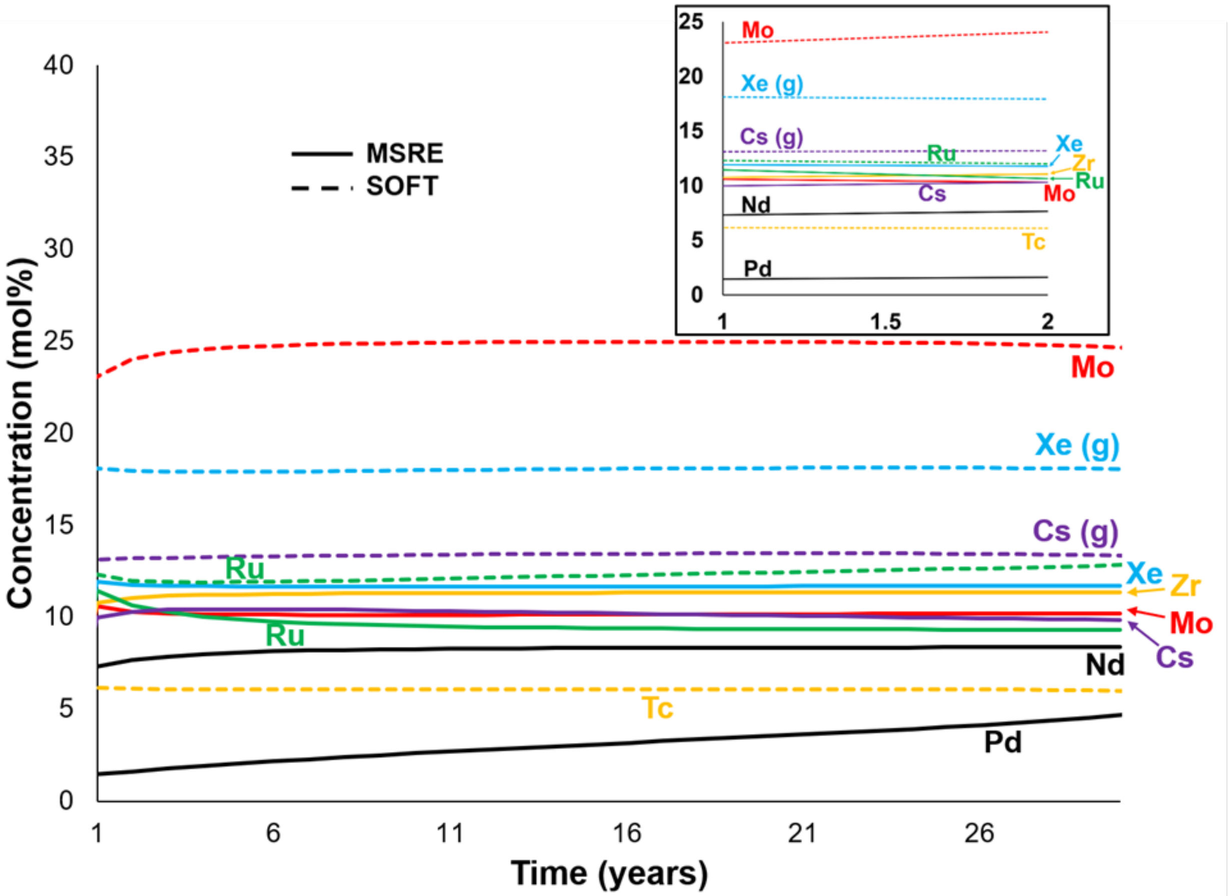

Figure A.1 Compositional make-up of the MSRE and SOFT waste streams over a 30-year operational time frame. The inset is over a 2 year period.

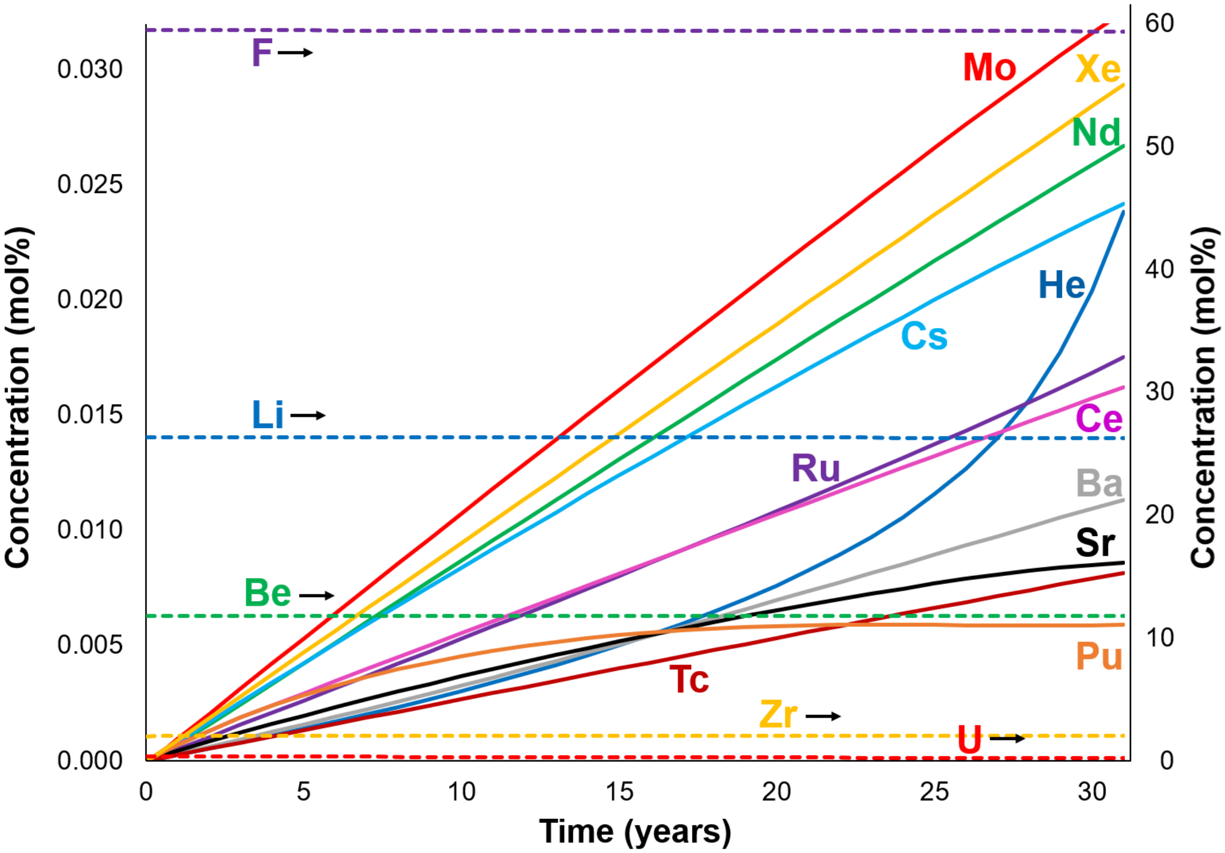

Figure A.2 Elements of highest occurring concentration in the fluoride based thermal spectrum MSRE reactor over a projected 30 year operational period.

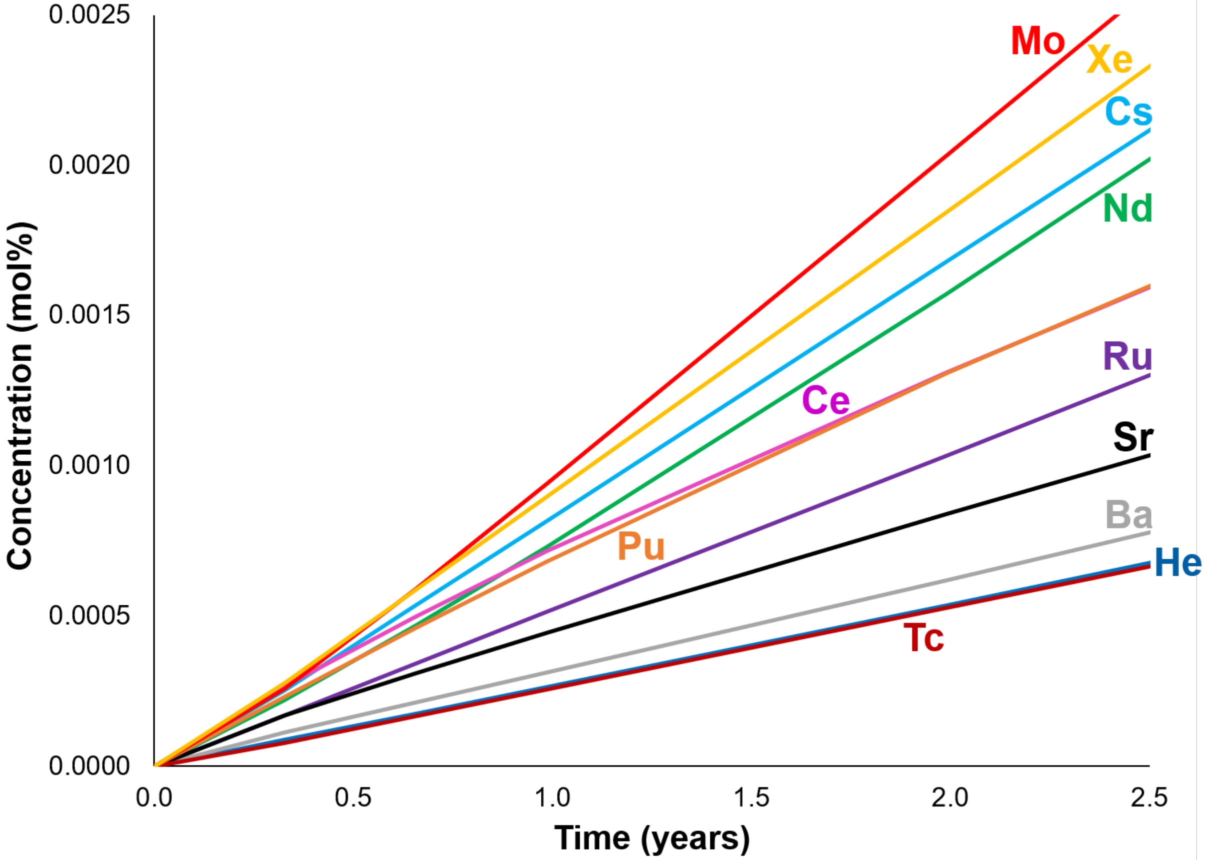

Figure A.3 Elements of highest occurring concentration in the fluoride based thermal spectrum MSRE reactor over a 2.5-year operational period based on the depletion calculation in this work.

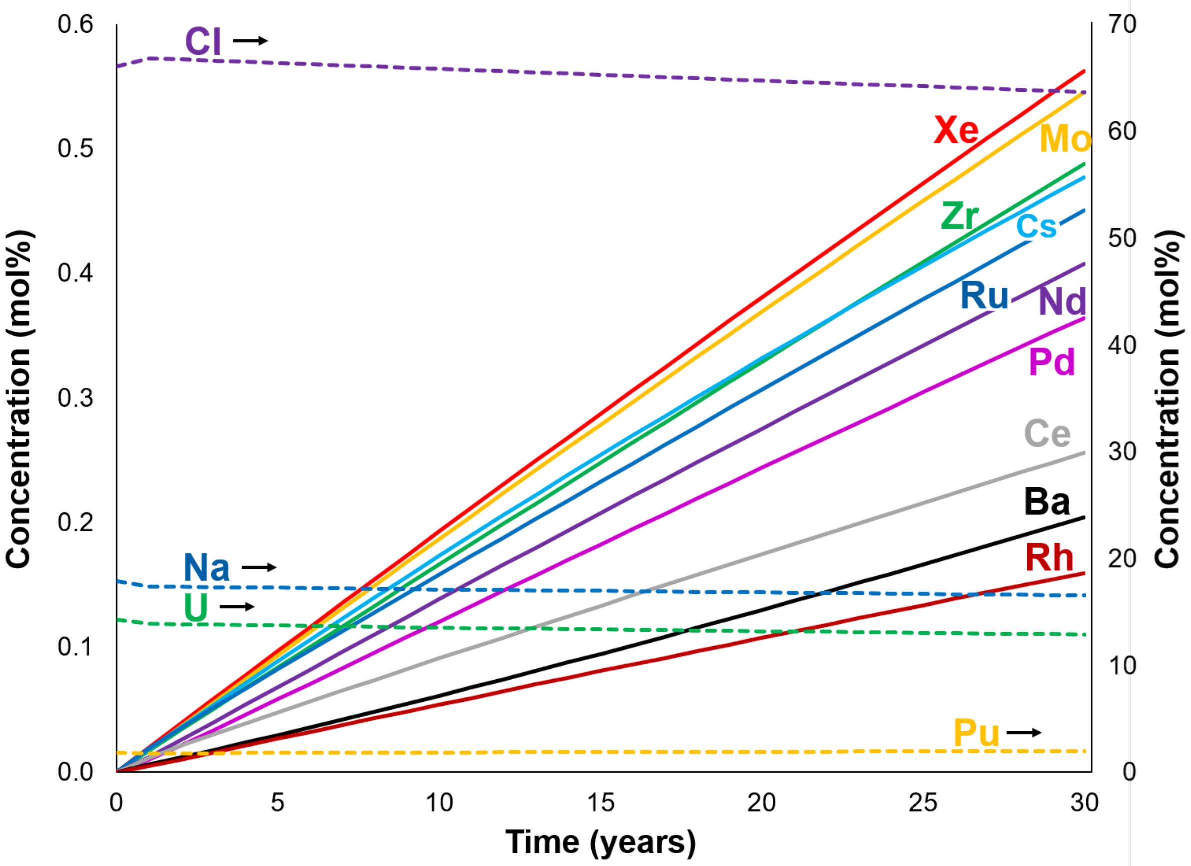

Figure A.4 Elements of highest occurring concentration in the chloride based fast spectrum SOFT reactor over a projected 30-year operational period.

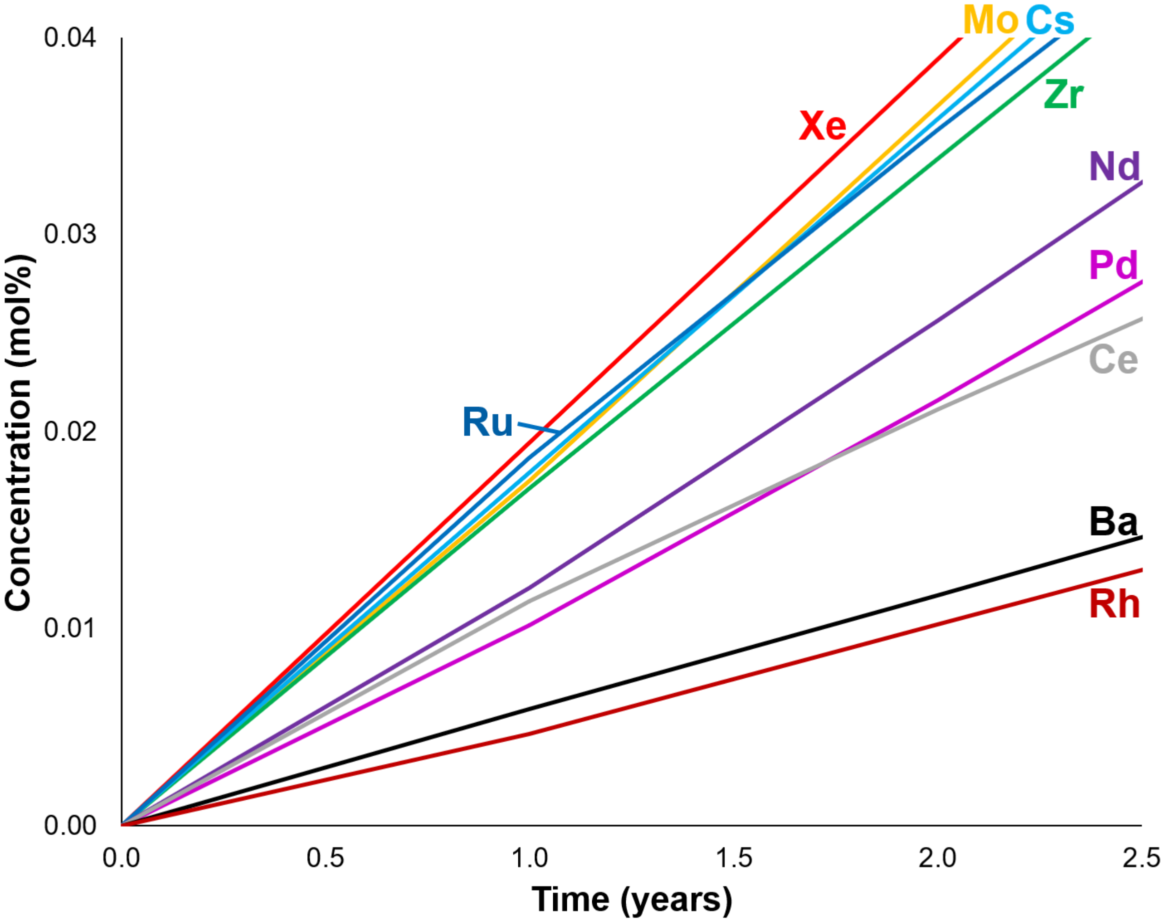

Figure A.5 Elements of highest occurring concentration in the chloride based fast spectrum SOFT reactor over a projected 2.5-year operational period.