M&C 2017 - International Conference on Mathematics & Computational Methods Applied to Nuclear Science & Engineering,
Jeju, Korea, April 16-20, 2017, on USB (2017)

Retention of Radionuclides in Heavy Liquid Metal Coolants for Mechanistic Source Term Analysis

Ishita Trivedi[a], James Sienicki[b], Matthew Bucknor[b], Kostadin Ivanov[a]

[a] *Department of Nuclear Engineering, North Carolina State University, 2500 Stinson Drive, 3140 Burlington Engineering Laboratory, Raleigh North Carolina, 27695*
[b] *Argonne National Laboratory, 9700 S. Cass Avenue, Argonne, Illinois, 60439*
itrived@ncsu.edu, sienicki@anl.gov, mbucknor@anl.gov, knivanov@ncsu.edu

Abstract – *The information presented in this paper is the preliminary step towards the development of a Mechanistic Source Term (MST) for Lead Cooled Fast Reactors (LFRs) which realistically models the release and transport of fission products from source to the environment. The paper also aims to summarize the current state of art on retention and transport of various fission products in Heavy Liquid Metal Coolants (HLMC), specifically focusing on the liquid Lead (Pb) and Lead-Bismuth Eutectic (LBE) coolants used for LFRs. Fission products are assessed based on their element group to determine where the data are lacking.*

I. INTRODUCTION

The source term, which represents the release of radionuclides during normal operating conditions and accident scenarios, is a vital part of the licensing and operation of a commercial nuclear reactor. As per the U.S. Nuclear Regulatory Commission (NRC), source term assessment is anticipated to be a licensing requirement for advanced reactors. With several significant technical advancements, a Mechanistic Source Term (MST) is developed for new reactors which is a more realistic analysis compared to the deterministic approach taken in the past [1]. As explained in ANL-ART-3, MST is designed to model the release and transport of radionuclide from the source to the environment for a given scenario and, account for the retention or transmutation phenomena to any associated uncertainties [2].

With the above in mind, and the recent focus towards the advancement of Lead-Cooled Fast Reactor (LFR) technology, development of an MST for LFRs is a necessity that should be expanded on alongside core design and other technical and safety aspects. For LFRs, two types of Heavy Liquid Metal Coolants (HLMC) being considered are liquid Lead (Pb) and Lead-Bismuth Eutectic (LBE). Pb has a higher melting point of 327.45 ^oC and atmospheric boiling point of 1743 ^oC; and, LBE, composed of 45.0 at% Pb and 55.0 at% Bi, has a melting point of 124.5 ^oC and an atmospheric boiling point of 1670 ^oC [3, 4]. Further chemical properties of Pb and LBE can be reviewed in the Handbook on Lead-bismuth Eutectic Alloy and Lead Properties, Materials Compatibility, Thermal Hydraulics and Technologies, 2015 ed. [3].

The focus of this paper is to assess the current state of art on retention of fission products in Pb and LBE coolants, determine where data are lacking and identifying where these gaps could be filled experimentally. In addition, a study of Polonium (Po) generation in Pb and LBE is provided considering the behavior of Po as a hazardous alpha emitter if it were to be released into the environment.

Lastly, in an attempt to understand how fission products interact with liquid Pb under a true accident scenario, summary of information collected via email correspondence in regards to the investigation conducted at Chernobyl post-accident is also provided. The work presented in this paper is one of the preliminary steps towards development of an MST for LFRs.

II. LEAD AS REACTOR COOLANT

Pb and LBE as a choice for liquid metal reactor coolant can be traced to many of its advantageous properties such as the high melting and boiling points, high atomic mass, high density, retention properties for fission products such as Cs and I along with many other economic benefits [5].

A high boiling point of Pb and LBE allow the reactor to be operated at very high temperature without the risk for coolant boiling. This property is noteworthy from a safety perspective when using liquid metal coolants. Should a leak occur in the primary system, there is no risk of accidental loss of primary coolant because Pb does not flash or boil, which allows for adequate heat transfer by natural convection.

The high atomic mass of Pb promotes effective gamma ray shielding and minimizes energy loss along with limited neutron leakage from the inner core. Pb also acts an excellent reflector for the escaped neutrons. More importantly, since Pb does not interact vigorously with water or steam, the need to the intermediate cooling circuit comes into question as described in Tarantino, 2012 [5]. Without the need for the intermediate cooling circuit, the complexity of the plant design is reduced, and is more economical and reliable [5].

However, even with the above advantages, one of the major drawbacks of considering Pb as coolant is its corrosive nature towards structural material – predominantly at higher temperatures. Extensive research and development is required to determine the appropriate choice of materials [5].

III. FISSION PRODUCT GROUPS

Relevant fission products are assessed based on their element groups and a release fraction is determined from the original radionuclide inventory as shown in Table 1, which is reproduced from Guo, 2014 [6]. The radionuclide inventory shows the beginning inventory of the radionuclides released under an accident scenario for China LEAd-based Research Reactor (CLEAR-I) which is cooled by LBE and is based on an Accelerator Driven subcritical System**.** The fuel used in CLEAR-I is oxide fuel with Argon cover gas region with inlet and outlet temperature at 260 °C and 390 °C, respectively [6].

Table I. Beginning inventory and release of radioactivity post-accident in CLEAR – I [6].

Radionuclide	**Beginning activity (Bq)**	**Radioactivity released (Bq)**	
		0hr-2hr	**2hr-8hr**
Ar-37	2.42E+08	6.05E+07	1.82E+08
Ar-39	5.93E+05	1.48E+05	4.45E+05
Ar-41	9.61E+09	2.42E+09	7.25E+09
Kr-85	4.47E+11	1.12E+11	3.35E+11
Kr-87	2.94E+09	7.35E+08	2.21E+09
Kr-88	1.35E+10	3.38E+09	1.01E+10
Xe-131m	1.47E+09	3.68E+08	1.10E+09
Xe-133	2.06E+12	5.15E+11	1.55E+12
Xe-133m	2.60E+10	6.50E+09	1.95E+10
Xe-135	1.32E+11	3.30E+10	9.90E+10
I-131	2.87E+03	7.18E+01	2.15E+02
Cs-134	2.73E+03	6.83E+01	2.05E+02
Cs-137	3.24E+04	8.10E+02	2.43E+03
Hg-203	2.27E+05	5.68E+03	1.70E+04
Po-210	1.20E+06	3.00E+04	9.00E+04

1. Noble Gases

From Table 1, it can be seen that the largest amount of radioactivity released from the core is from Xe-133. Approximately, 25% of the beginning inventory is released within the first 2 hours post-accident. The radioactivity measured at 2 hours is 5.15E+11 Bq. Reaming 75% is released between 2 to 8 hours post-accident. The measured radioactivity after 8 hours is 1.55E+12 Bq.

After Xenon, the next major contributors of radioactivity are Krypton, Argon and Tritium. For all Noble gases, a release fraction of unity is assumed from the fuel pins. This data agrees well with the data presented on source term assessment for Experimental Thermal Demonstrator Reactor (ETDR) [7], presented in Fig. 1 and Fig. 2, where the normal operating temperature is 480 °C and is assumed to rise to 800 °C during the Unprotected Loss of Flow (ULOF) accident scenario.

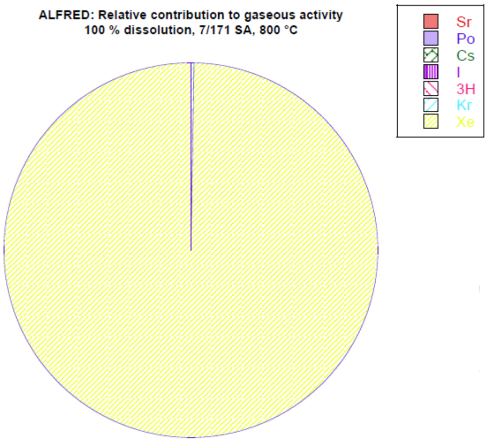

Fig. 1. Relative contribution to gas phase radioactivity 100% dissolution at 800 °C, reproduced from Jolkkonen, 2012 [7].

In regards to Trititum, although calculation from Jolkokonen, 2012 [7] show that 50% to 90% is soluble in Lead; this data is deemed to be insufficient based on the high pressures at which the data was collected. However, even with the conservative assumption that it primarily exist in gas phase, its production is not specific to LFRs. Therefore, Tritium production and release can be handled in a similar fashion as that in the currently existing reactors [7].

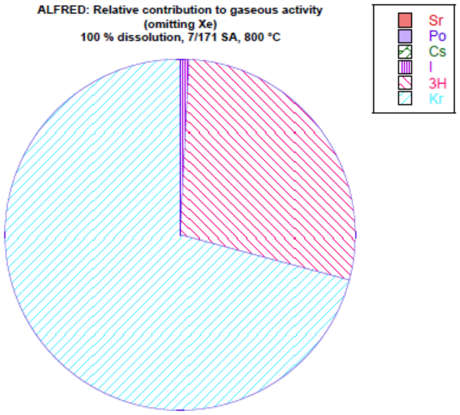

Fig. 2. Relative contribution to gaseous activity (omitting Xe) 100% dissolution at 800 °C, reproduced from Jolkkonen, 2012 [7].

As previously stated, all of the Noble gasses are assumed to be released from the reactor and due to their inert properties, are vented into the environment [6]. However, as these Noble gases travel to the surface through the coolant and are released into the cover gas region, there is a possibility that they may carry halogens and other volatile metals with them. This creates the potential for fission products to bypass the reactor coolant and be directly released into the cover gas region and possibly transport to the environment. Data gaps exist regarding what percentage of radionuclides travel to the surface entrained in Noble gas bubbles.

2. Halogens

In Fig. 3, Iodine is the largest halogen contributor of radioactivity from fission product release. Along with Iodine, retention of Bromine is also discussed as a secondary halogen contributor of radioactivity [7].

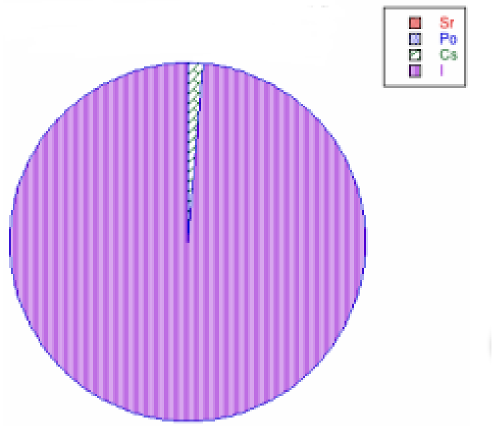

Fig. 3. Relative contribution to gaseous activity (omitting Xe, Kr, 3H) 100% dissolution at 800 °C, reproduced from Jolkkonen 2012 [7].

Iodine boils at a relatively low temperature of 184.3 °C [8] which means that Iodine present in the coolant is likely to be in a gaseous form. However, the important question is how much Iodine is retained in the coolant. In the phase diagram of Iodine in Pb (as shown in Fig. 4), it has been demonstrated that Iodine is mostly retained in Pb coolants [9]. This behaviour is attributed to formation of stable PbI_2 crystals with a high melting temperature of 408 °C and a boiling temperature of 1393 °C [3]. As seen in Fig. 4, a narrow region of solubility of PbI_2 crystals in Pb is seen up to 385 °C, after which a rapid increase in the solubitlity is noticeable [3, 10]. Further information of characterization of PbI_2 crystals can be found in Zhu, 2006 [10].

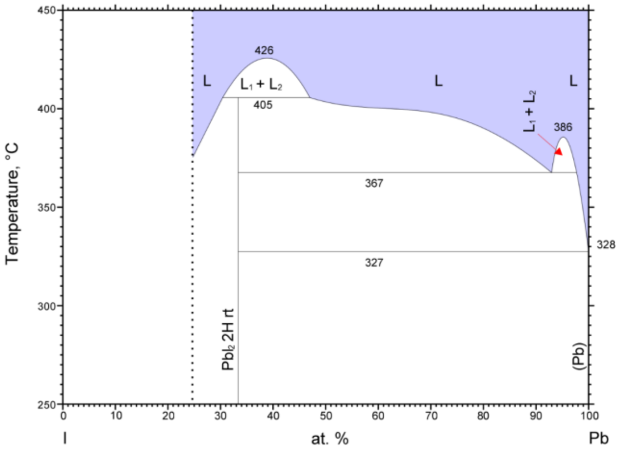

Fig. 4. Phase diagram of Iodine in Pb showing a narrow region of solubility of PbI_2 in Pb, reproduced from Argonne National Lab phase diagrams database [9].

Furthermore, Iodine is considered to be well retained in LBE from the data presented in Neushausen, 2006 (as seen in Fig. 4), where experiments were conducted to test the release of Iodine from LBE under Ar/7% H_2 atmosphere [11]. A temperature range of 428 K to 1223 K was tested. From short term experiment results, the maximum release fraction is 85% where the measurable amount is only seen at temperatures above 750 K. In LBE, Iodine is well retained up to 700 K due to strong chemical interactions with Pb and Bismuth (Bi). Further information on the experimental procedure can be found in Neuhausen, 2006 [11]. Additional data on chemical interaction of Iodine with Pb and Bi is well summarized in the Pb/LBE handbook [3].

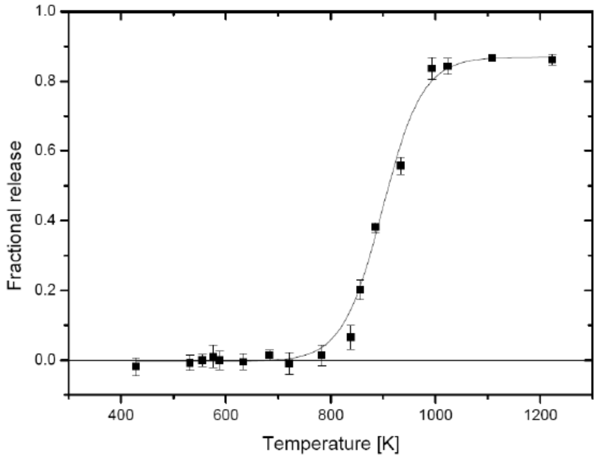

Fig. 4. Fractional release of Iodine from Lead, reproduced from Neushausen, 2006 [11].

Similarly, Bromine is also considered to be well retained in Pb based on the Gibbs enthalpy of formation of $PbBr_2$ and PbI_2 at 298 K of -261 kJ/mol and -174 kJ/mol, respectively [3]. Bromine has a relatively low boiling point of 59 °C and is almost exclusively present in gas phase. However, the strong interaction of Bromine and Pb should greatly decrease its volatility. Based on the enthalpy of formation, $PbBr_2$ is more stable than PbI_2. Therefore by comparison, since PbI_2 is well retained in liquid Pb, Bromine can also be expected to be effectively retained in Pb. Likewise, retention in LBE is confirmed via experiments performed at a laboratory scale at 250 °C [3].

3. Alkali Metals

Cesium (Cs) and Rubidium are the alkali metals that will be discussed in this section where Cs is the primary alkali metal contributor. Cs is quite volatile considering its relatively low melting point of 29 °C and boiling point of 671 °C. Retention of Cs in pure Pb is confirmed in the Pb/LBE Handbook, 2015 by proving high dilution of Cs in liquid Pb and retention by strong chemical affinity with Pb [3]. It is expected to have a lower vapour pressure in LBE based on strong chemical interactions with Pb and Bi as discussed in the handbook [3].

Retention in LBE is confirmed based on recent laboratory scale experiments studying evaporation of Cs from LBE from 450 °C – 750 °C [12]. The results were obtained by evaluating the activity coefficients which indicate that Cs is retained in LBE. It is worthy to note here the author's note in the Pb/LBE handbook regarding using conservative constant value of the thermodynamic activity coefficient for Cs based on the large scatter of the collected data and the need for a more reliable data [3].

In addition, Rubidium with a melting point of 39.5 °C and boiling point of 687.8 °C [13] is expected to be chemically similar to Cs, and is thus expected to be retained in LBE and liquid Pb analogous to Cs. This can also be seen in the similarities between the phase diagram of Pb-Rb and Pb-Cs [3].

4. Volatile and Noble Metals

Experimental data on interaction of Noble and volatile metals with Pb and LBE are sparse. The current state of art for these metals can be found in the Pb/LBE handbook. Although they are not considered a major contributor in radioactivity, it is worthy to track their interaction with Pb/LBE for further development of MST.

IV. POLONIUM GENERATION

Apart from the fission products release fraction, another major concern related to use of LBE as a coolant is the generation of highly volatile Po. The melting point of Po is 254 °C and the boiling point is 962 °C implying that it primarily exists as solid at room temperature. ^{210}Po is an alpha emitter with a half-life of 138 days and is produced as an activation product of LBE [4]. Under normal operating conditions, Po is well retained in LBE as PbPo [14]. However, under accident scenarios, if a significant amount were to be release to the atmosphere, it could pose serious radiological problems. On contact with moisture, the compound Polonium Hydride, H_2Po, is formed with a melting point of -36.1 °C and a boiling point of 35.3 °C [4]. Since H_2Po is highly volatile and an alpha emitter, it poses health hazards in terms of inhalation.

Two parallel mechanisms occur for the release of Po: formation of H_2Po (highly volatile) and direct evaporation of PbPo. PbPo has relatively low volatility as experimentally confirmed in Buongiorno, 2002 [14]. The partial pressure of PbPo was calculated according to equation 1 where χ_{PbPo} is the mole fraction of Pb-Po in a Pb-Bi bath [14].

$$P_{PbPo} = \frac{P^{o}_{PbPo}}{\chi_{PbPo}} \qquad (1)$$

The low vapour pressure of PbPo can be seen in Fig. 5 and is further discussed in Buongiorno, 2002 [14].

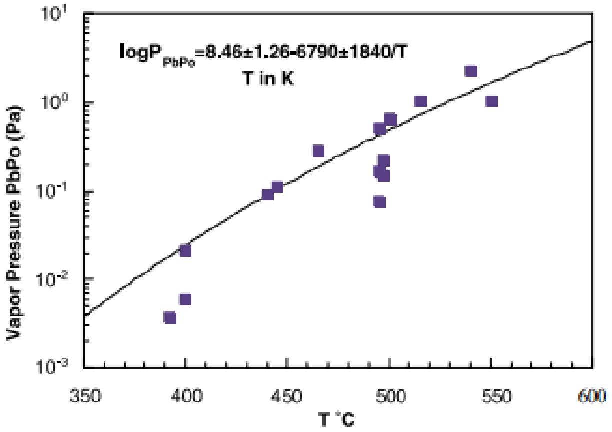

Fig. 5. Vapour pressure of PbPo as a function of temperature under Argon atmosphere, reproduced from Buongiorno, 2002 [14].

During the formation of H_2Po, two possible reaction pathways are provided in Equations 2 and 3 [14, 15].

$$PbPo_{(s)} + H_2O \Leftrightarrow H_2Po_{(g)} + PbO_{(s)} \qquad (2)$$

$$Pb + H_2O \Leftrightarrow H_{2(g)} + PbO \qquad (3)$$

In addition, the free energy of both reaction pathways was evaluated to understand the spontaneity of the reaction using Equation 4 [14].

$$\Delta G_{H_2Po} = -RT \ln K_{H_2Po} \qquad (4)$$

For both reaction pathways, shown in Equation 2 and 3, the $\Delta G>0$ implies both are non-spontaneous reactions. $\Delta G_{H2Po} > \Delta G_{PbO}$ indicates that Equation 3 is more likely and confirms the chemical instability of H_2Po as ΔG is positive [14].

Furthermore, the health hazards from release of Po under accident scenario become more concerning due to significant increase in Po gas phase concentration in presence of H_2O compared to Ar. This can be clearly seen in Fig. 6 and 7 which graphically confirm the increase in Po gas phase concentration independent of temperature changes [14].

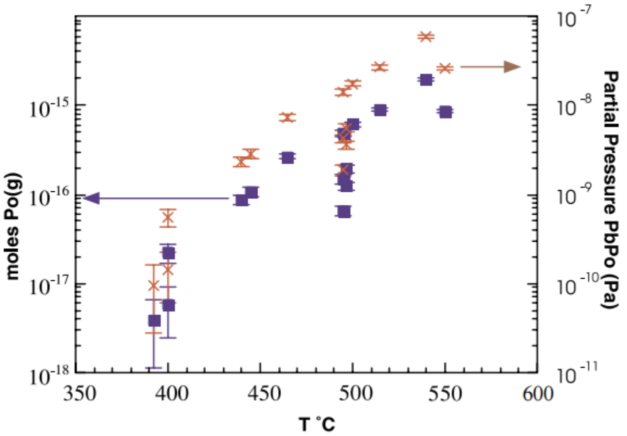

Fig. 6. Gas phase mol concentration of Pb as a function of temperature under Ar atompshere, reproduced from Buongiorno, 2002 [14].

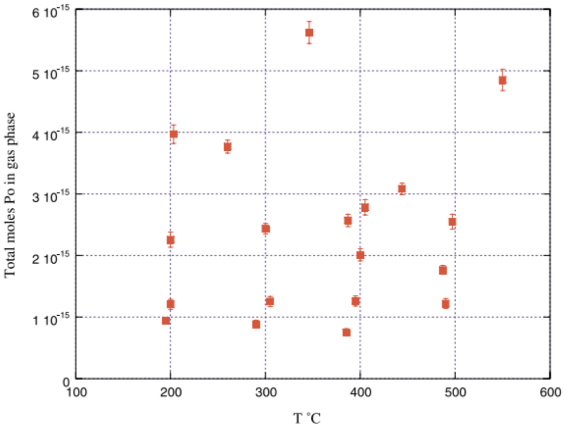

Fig. 7. Gas phase mol concentration of Pb as a function of temperature under Ar, H_2O and H_2 atompshere, reproduced from Buongiorno, 2002 [14]

V. LEAD DROPPED AT CHERNOBYL

In addition to understanding the current state of start on retention of fission products in Pb/LBE via recent studies and experiments, an attempt was made to find any viable data in regards to interaction of fission products with Pb from the Chernobyl accident. Most of the experimental data presented in this paper is from experiments conducted at laboratory scale. One of the advantages of Sodium-Cooled Fast Reactors (SFRs) over LFRs is the rich knowledge gained from previous full scale accidents. Therefore, information from Chernobyl accident, if any, could be vital.

After the Chernobyl accident, about 12000 tons of liquid Pb was dropped into the reactor vault in an attempt to prevent "China Syndrome" in Unit 4. However, so far, no lead had been discovered from the "lava" like substance discovered in unit 4. This implies that virtually no lead reached the vault. Thus, although brave, the attempts by the pilots to fill the reactor vault ended up to be futile [16]. This data was collected by direct email correspondence with the author [16].

VI. END NOTE

The information on the release fraction of various fission products from the HLMC presented in this paper is used to assess where data are lacking. Although appropriate information is available on Noble gases and Halogens, there are gaps for data availability of Noble Metals, Lanthanides and Actinides on their retention in Pb/LBE. Experiments are required to understand the chemical interaction between lanthanides and actinides with Pb/LBE at temperatures as high as 800 ºC, under accident scenarios. For instance, in the case of Halogens, experimental data for Bromine were collected on a laboratory scale at 250 ºC. Strong Br-Pb and Br-Bi interactions are shown; however, there is little or no information on how well these bonds will hold at temperatures as high as 800 ºC. Also, 100% release is assumed for Noble gases which goes back to the question on how much radioactivity is released from fission products in the coolant that reach the surface by being trapped inside Noble gas bubbles traveling from the fuel pin to the cover gas region following fuel pin failure. Data are also lacking on how various fission products interact once they enter the cover gas region.

In conclusion, it can be stated that although there are some data on how various fission products interact with the HLMC, it is insufficient and does not span the temperature ranges expected during accident scenarios. Table II provides a summary of the element groups along with an overview of where the data is lacking.

Additionally, a thorough literature review and supporting experiments are required for confirming some of the information presented in the Pb/LBE handbook such as that on retention of Rubidium in Pb [3]. Reviewing phase diagrams and understanding bond formations is not sufficient. The LFR research, although vital, lags far behind SFRs for source term analysis. This can partly be blamed on the relative absence of focus given to LFRs, and the subsequent scarcity of LFR accidents compared to SFRs. Therefore, a need for investment in experimental research to reduce these gaps is identified. Research focused on core design and fuel type for LFRs is already underway around the world. However, even with the advanced neutronics and other technical research, source term assessment is important for both the licensing process as per NRC regulations, and safe operation of the reactor. Further development of MST for LFRs is needed alongside other aspects of the LFR design.

Table II. Summary of retention and release of fission product groups

Element Group	**Details**
Noble Gases	
Major contributors:	Xe, Kr, Ar, 3H
Retention	100% release is assumed for Noble gases.
Gap	Data is lacking for fission products that by pass the coolant through Noble gas bubbles travelling from the source to the cover gas region.
Halogens	
Major Contributors:	I, Br
Retention	Iodine is expected to be retained in Pb pertaining to formation of stable PbI_2 with a high boiling point of 1393 °C. It is also expected to be retained in LBE up to 750 K. Br is expected to be retained in Pb based on strong enthalpy of formation of $PbBr_2$ and in LBE as demonstrated by laboratory scale experiments
Gap	Lack of data on how well Br bonds will hold at high temperatures of 800°C under accident scenario.
Alkali Metals	
Major Contributors:	Cs, Rb
Retention	Retention of Cs is confirmed based on strong chemical interactions with Pb and Bi. Rb is chemically very similar to Cs thus is expected to be retained analogous to Cs.
Gap	There is need for more reliable set of data for Cs due to the large scatter in the collected data for.
Volatile/Noble Metals	Data is sparse

For future work, the data analyzed in this paper will be used for the remaining steps of the MST development process, shown in Fig. 5, along with any associated uncertainties. This paper presents the preliminary analysis for step 1.

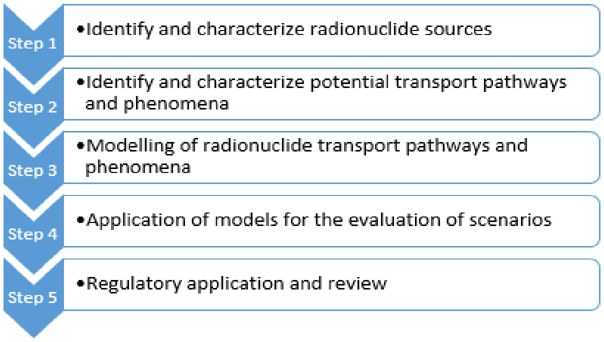

Fig. 5. MST development pathways [1].

REFERENCES

1. D. GARBASKAS, M. BUCKNOR, J. JERDEN. "Regulatory Technology Development Plan Sodium Fast Reactor: Mechanistic Source Term – Metal Fuel Radionuclide Release." ANL-ART-38. 2016.
2. D. GARBASKAS, A. BRUNETT, M. BUCKNOR, J. SIENICKI, T. SOFU. "Regulatory Technology Development Plan Sodium Fast Reactor: Mechanistic Source Term Development" ANL-ART-3. 2015.
3. *Handbook on Lead-bismuth Eutectic Alloy and Lead Properties, Materials Compatibility, Thermal-hydraulics and Technologies*. 2015.
4. J. SIENICKI, A.E. WALTER, D. R. TODD, P. V. TSVETKOV. “Lead-Cooled Fast Reactors,” Chapter 18 of Fast Spectrum Reactors, Springer, New York, 2012.
5. M. TARANTINO. “Lead-Cooled Fast Reactor (LFR) Development Gaps”. Italy, 2012.
6. Q. GUO. "Preliminary source term and consequence assessment of preimary cover gas leakage accident for CLEAR-I." *Progress in Nuclear Energy* (2014).
7. M. JOLKKONEN.. "Source term assessment for the EDTR." *LEADER Task 5.6*. 2012.
8. "Iodine." *NCBI*. U.S. National Library of Medicine, n.d. Web. 14 Oct. 2016.
9. "Phase Diagram of Iodine in Lead." *Phase Diagrams*. Argonne National Lab, n.d. Web.
10. X. H. ZHU. "Synthesis and Charaterization of PbI2 Polycrystals." *Crystal Research and Technology* (2006)
11. J. NEUHAUSEN. "Investigations on the thermal release of iodine from liquid eutectic lead-bismuth alloy." *Radiochim.* (2006): 239-242.
12. S. OHNO. "Test Results of Volatile Radionuclide Evaporation from Liquid Lead-bismith and Their Comparison with Test from Sodium Pool." *ICONE15*. Nagoya, Japan, 2007.
13. "Rubidium - Element Information, Properties and Uses | Periodic Table." *Rubidium - Element Information, Properties and Uses | Periodic Table*. Royal Society Of Chemistry, n.d. Web.
14. J. BUONGIORNO "Speciation of polonium released from molten lead bismuth." *Radiochim* (2002): 153-158.
15. S. OHNO. "Equilibrium Behaviour of Polonium and its Homologue Tellurium in Liquid Lead-Bismuth Eutectic." *Nuclear Science and Technology* (2006): 1359-1369.
16. Retention of Radionuclide in Lead." Private communication with the author. N.d. E-mail.