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Recommendations for Tritium Science and Technology Research and Development in Support of the Tritium Readiness Campaign, TTP-7-084

DJ Senor

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TRITIUM TECHNOLOGY PROGRAM

Recommendations for Tritium Science and Technology Research and Development in Support of the Tritium Readiness Campaign

TTP-7-084

Revision 0

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Revision 0

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Recommendations for Tritium Science and Technology Research and Development in Support of the Tritium Readiness Campaign

Executive Summary

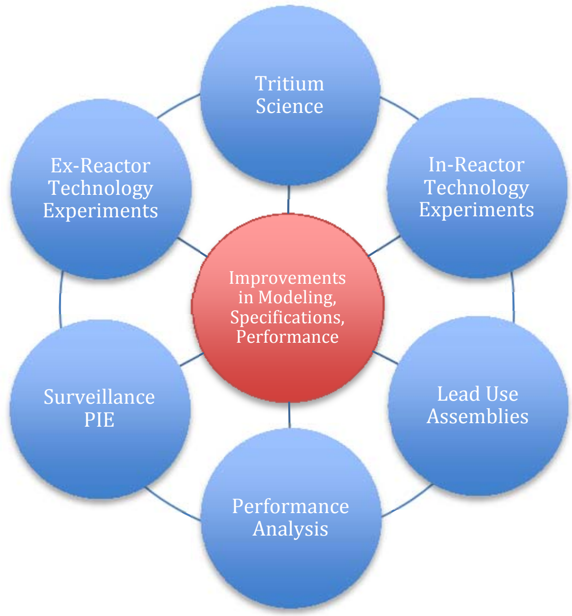
Between 2006 and 2012 the Tritium Readiness Campaign Development and Testing Program produced significant advances in the understanding of in-reactor TPBAR performance. Incorporating these data into existing TPBAR performance models has improved permeation predictions, and the discrepancy between predicted and observed tritium permeation in the WBN1 coolant has been decreased by about 30%. However, important differences between predicted and observed permeation still remain, and there are significant knowledge gaps that hinder the ability to reliably predict other aspects of TPBAR performance such as tritium distribution, component integrity, and performance margins. Addressing these knowledge gaps will provide numerous benefits to the Tritium Readiness Campaign, including the ability to:

- Explain and predict all aspects of TPBAR performance, leading to high confidence in repeatable results from cycle to cycle
- Reduce risk to TVA reactor operations and provide increased assurance of TPBAR reliability
- Adapt and interpret TPBAR performance as TVA changes reactor operating conditions and cycle schedules
- Ensure product specifications for TPBAR components control material properties and characteristics that influence in-reactor performance
- Evaluate and respond to changes in component suppliers and fabrication processes
- Make incremental design changes to improve TPBAR performance with high confidence

The TMIST and TMED experiments are large-scale, relatively applied studies addressing very specific aspects of TPBAR component performance. The experiments completed to date and the TMIST-3 experiment still underway provide significant data on in-reactor performance of liners, cladding, getters, and pellets that cannot be obtained in any other way. However, while they provide important quantitative data that is crucial to accurate TPBAR performance modeling, they are not designed to investigate the underlying mechanisms responsible for the observed performance. To address these fundamental mechanisms, studies of a type different from TMIST/TMED are required. The scope of such tritium science studies will vary depending on the phenomena being investigated, but in most cases studies of this nature will be smaller in scale and far less expensive than the TMIST/TMED experiments. In this way, tritium science studies will be more amenable to the challenging budget climate anticipated over the next few years. Despite limited budgets, progress toward improving fundamental understanding and modeling of TPBAR performance can still be made.

It is important to note that there are many aspects to a well-integrated research and development program. The intent is not to focus exclusively on one aspect or another, but to approach the program in a holistic fashion. Thus, in addition to small-scale tritium science studies, ex-reactor

tritium technology experiments such as TMED, and large-scale in-reactor tritium technology experiments such as TMIST, a well-rounded research and development program must also include continued analysis of WBN1 performance data and post-irradiation examination of TPBARs and lead use assemblies to evaluate model improvements and compare separate-effects and integral component behavior. The different aspects of the research and development program are graphically illustrated in the figure at right, showing their relationship to one another as well as to the common goal of improving performance models, component specifications, and ultimately TPBAR performance itself.



Graphical Representation of the Different Aspects of an Integrated Tritium Science and Technology Research and Development Program

Based on recommendations from recent Tritium Readiness Campaign workshops and reviews coupled with technical and programmatic priorities, the following high-priority activities are needed to address knowledge gaps. It is important to note that the near-, middle-, and long-term categories denote the time horizon during which the impact of the data obtained needs to be realized. That does not suggest that work should only be initiated soon on the near-term activities. In contrast, work should be started soon on all of the high-priority middle- and long-term activities because a significant amount of background study, scoping research, and planning can be accomplished even with modest budgets. Note that many of these activities, particularly the large experiments, near-term PIE campaigns, and lead use assemblies are already funded and underway, which significantly reduces the cost of new tritium science and performance analysis work that is needed to complement the existing studies.

- **Near-Term (3-5 Year) R&D Priorities**
  - Careful consideration of TPBAR impacts on core design, particularly as TPBAR quantities increase beyond the current 544/cycle. The creation of the Tritium Production Planning Group is a key aspect to addressing this issue.
  - Surveillance PIE comparisons of nominal and high/low production TPBARs within cycles and between cycles to better understand relationships between operating conditions and performance, and determine if the current tritium production limit is appropriate.
  - Irradiation of the most recently produced coated cladding in WBN1 Cycle 13 for comparison to the oldest coated cladding in inventory irradiated in previous cycles.

- Completion of the TMIST-3 in-reactor pellet performance experiment to better understand tritium release kinetics, better define burnup limits, and improve predictive models to avoid surprises in future WBN1 irradiation cycles.
- Continued improvement in the TPBAR tritium release attribution method to incorporate more realistic water movement data to increase confidence in TPBAR tritium release estimates and projections
- Completion of the component aging study to inform specification revisions or other actions necessary to ensure continued acceptable TPBAR performance.
- Computational analyses and leaching experiments to enable early diagnosis of a breached TPBAR during irradiation in WBN1
- Increase use of the TROD performance code as a diagnostic tool by implementing semi-empirical models with parameters that can be adjusted to match observed TPBAR tritium release behavior in WBN1.

- **Middle-Term (5-10 Year) R&D Priorities**
  - Refined LOCA calculations and selected experimental data such as burst tests to determine whether TPBARs can survive severe accidents intact so that WBN1 core designs can be optimized to reduce fuel costs significantly
  - Surveillance PIE of components produced by new manufacturers or new manufacturing processes to compare performance to historical trends, particularly with regard to pellets, getters, and liners.
  - Lead use rod irradiation of unique components and configurations to complement data from surveillance PIE.
  - An experiment to investigate irradiation effects on getter equilibrium pressure.
- **Long-Term (10+ Year) R&D Priorities**
  - A study on the effects of gaseous or surface impurities (C, CO, CO_2, CH_4, H_2O, etc…) on getter rate or equilibrium partial pressure over getters. A similar study on the effects of surface impurities on adsorption, decomposition, and recombination of hydrogen isotopes on the surface of the barrier coating is also of interest.
  - A fundamental study of pellet microstructural evolution as irradiation damage progresses to provide a better understanding of the mechanisms responsible for the behavior that will be observed in the TMIST-3 experiment.
  - Investigations into the mechanisms responsible for irradiation enhancements of various phenomena such as tritium permeation, solid-state diffusion, gaseous transport, isotopic exchange, and equilibrium partial pressures, including measurement of fundamental properties of interest such as solubility and diffusivity of tritium in pellets and coated cladding.
  - Radiation effects on gas composition within the TPBAR (e.g. radiolysis) including hydrogen isotopes and other impurity gases. This will also lend insight into the mechanisms associated with atomic tritium formation, transport, deposition, and permeation.
  - A feasibility study to investigate tritium production in small modular reactors.

- An investigation into modified or alternate barrier and/or cladding materials to reduce overall TPBAR permeation regardless of which mechanisms are dominant.
- A study of target design concepts to avoid gaseous tritium production or other revolutionary concepts to address longer operating cycles or other operational changes not yet envisioned. Such studies could also provide a starting point for evaluating tritium production options after WBN1 has reached the end of its operational lifetime.

1. Background

1.1 TPBAR Irradiation History

TPBARs have been irradiated in the Tennessee Valley Authority (TVA) Watts Bar Nuclear Unit 1 (WBN1) commercial power plant since 1997, starting with the 32-rod lead test assembly (LTA) and continuing from Cycles 6 through 12 as shown in Table 1. Planning is currently underway to insert 704 TPBARs in Cycle 13, and work has been started to increase TPBAR quantities to produce at least 1700 g by Cycle 16. It is notable that the TPBAR performance models available from Cycle 6 to Cycle 11 predicted a tritium permeation of approximately 0.5 Ci/TPBAR for each of those cycles. In reality, TPBAR tritium permeation has exceeded this rate and apparently varied considerably from cycle to cycle, as shown in Table 1. While there are some suggestive trends in the data, none of them are consistent and none indicate a clear phenomenological correlation to parameters such as total production, production rate, burnup, or time. This is primarily due to two facts: 1) the variability in the operating parameters over the five cycles is limited (25% variability or less), and 2) total tritium production, production rate, burnup, and cycle length are all correlated and not independent from one another. Thus, it is not surprising that tritium permeation shows similar trends as a function of tritium production, cycle length or Li-6 burnup because all three of those parameters are related. Because of this, it is not possible to deduce a causal relationship between tritium permeation and any individual parameter based on the available information. Thus, the data obtained during operation of WBN1 by themselves do not provide adequate insight into TPBAR performance to improve the accuracy of predictive models.

Table 1. Summary of WBN1 production cycle parameters and calculated tritium permeation values to date.

Cycle	TPBAR Design	Number of TPBARs	Nominal Assembly Avg Tritium Prod (g)	Peak Assembly Avg Tritium Prod (g)	Assembly Avg Tritium Prod Rate (g/MWD/MTU)	Li-6 Burnup (a/o)	Cycle Length (days)	Cycle Length (EFPD)	Number of Secondary Sources	Tritium Permeation During Entire Cycle (Ci)	Tritium Permeation During Last 365 Days (Ci)
6	Pencil	240	0.97	0.98	5.19e-5	43.3	490.3	482.0	1	3.8±1.0	3.4±1.2
7	Pencil	240	0.97	0.99	5.09e-5	43.2	525.0	490.1	2	3.8±1.0	3.3±1.2
8	Pencil	240	0.91	0.92	5.42e-5	40.5	436.8	432.5	2	3.0±0.8	2.9±0.8[1]
9	FLG	368	0.95	0.96	4.73e-5	44.8	545.2	515.0	3	3.8±0.6	3.4±0.6
10	FLG	240	1.00	1.01	5.01e-5	47.2	532.0	513.3	2	4.2±0.7[2] 3.7±0.7[3]	3.8±0.8[2] 3.4±0.8[3]
11	FLG	544	0.89	0.92	4.99e-5	42.8	480.4	458.7	2	3.5±0.4	3.4±0.5
12	FLG	544	1.00[4]	1.04[4]	5.09e-5[4]	47.4[4]	525[4]	506[4]	2	TBD	TBD

[1] Cycle 8 was short enough that the last 365 days encompassed all but the first 72 days of the cycle, when tritium release was essentially zero
[2] Derived using water movement data averaged over 24 hour periods
[3] Derived using water movement data averaged over 1 minute periods
[4] Projected values based on core design

The one significant design change implemented since the first production core was the change from the pencil design to the full-length getter (FLG) design in Cycle 9. This design change was implemented specifically to reduce the higher-than-predicted tritium permeation observed in Cycles 6 through 8. The impact of this design change on tritium permeation was evaluated based on the state of knowledge at the time regarding in-reactor performance of the TPBARs, which was largely derived from post-irradiation examination (PIE) of LTA and Cycle 6 (Lanning et al. 2002; Carlson et al. 2007; Carlson 2012) TPBARs. It is notable from the data in Table 1 that the design change did not improve tritium permeation. The inability to predict permeation demonstrated the limitations of relying exclusively on PIE results for insight into TPBAR performance. By its nature, PIE provides a snapshot at a moment in time (i.e. end of life) of integral TPBAR performance. What was lacking in the predictive models when making the change from the pencil to the FLG design was a clear understanding of the time-dependent separate-effects irradiation behavior of the various TPBAR components. After Cycle 9, the need for such understanding led to the creation of the Development and Testing (D&T) program of in-reactor and ex-reactor experiments to supplement the knowledge gained from WBN1 operational data and PIE.

1.2 Evolution of the Development and Testing Program

Irradiation testing of TPBAR predecessors began in the 1980s when the Contingency Program used a trial-and-error approach in the Advanced Test Reactor (ATR) to evaluate the tritium retention capabilities of a wide variety of configurations (Brizes 1986). Capsules with external helium sweep gas were used to monitor the tritium released from candidate targets and led to the selection of the getter-barrier concept as the most promising approach for producing tritium in a light water reactor. The Tritium Target Development Project adopted the getter-barrier concept and sought to refine the design by investigating scaling and variability in fabrication parameters and their effect on performance. Three closed-capsule tests in ATR were conducted in which tritium permeating into static water out of a 4-ft long getter-barrier target was monitored. In addition, the L-1 experiment in ATR simultaneously tested eight 4-ft long target rods in a flowing water loop that closely simulated the commercial PWR coolant and chemical environment. Tritium permeation from the L-1 targets was measured by the tritium concentration in the loop coolant. In the mid-1990s, the U.S. Department of Energy (DOE) funded the Tritium Target Qualification Project (TTQP) and irradiation of 32 TPBARs in the lead test assembly (LTA), which resulted in a target more amenable to commercial manufacturing than previous concepts. After the LTA, the Production Design was developed to further improve manufacturability while reducing fabrication costs.

It is significant to note that all of the testing preceding the first production core in WBN1 Cycle 6 was focused on measurement of the integral permeation of tritium out of a variety of target design concepts from short capsules to 4-ft target rods to full-length LTA

TPBARs. Integral permeation testing evaluates the integrated permeation resulting from the performance of the pellet, liner, plated getter, coated cladding, and end plugs of a target. Integral permeation testing is appropriate for proof-of-principle or validation of a design concept and predictive models but provides little insight into the processes occurring within the TPBAR. Before the D&T program, no separate-effects in-reactor testing had ever been conducted to address the processes that affect performance within the TPBAR.

An initial determination of data needs and prioritization was made in 2006 via a modeling maturity assessment (Senor 2006). This study focused on the impact of each available model on accurately predicting tritium release to the WBN1 coolant. The modeling capability at that time was focused on producing conservative estimates of performance and the models were primarily used as a tool to ensure the TPBAR design met all regulatory and operational requirements. To develop a best-estimate predictive capability that could be used to improve performance predictions, several of the models required experimental data to address irradiation effects on processes such as oxidation, permeation, and chemical reactions. The assessment concluded, based on the information available at that time, the least mature models from the perspective of best-estimate predictive capability were those for tritium (T_2O) reduction, tritium (T_2O, T_2, HTO, HT) transport, and tritium permeation. The report also identified other TPBAR phenomena that have less impact on tritium release to the WBN1 coolant, but still were not understood as well as they should be to generate best-estimate models, including pellet release speciation (i.e., T_2 versus T_2O release), the effects of isotopic exchange between tritium and ingressing protium (i.e., T_2O and H_2) on permeation, and the effects of nascent tritium permeation. Subsequent WBN1 operational data, TPBAR PIE campaigns, and D&T experiments have filled in some of these knowledge gaps, eliminated others from consideration, and generated additional ones.

A series of three workshops were held in 2006 and 2007 to identify the highest-priority data needs to improve TPBAR performance models (Hollenberg 2006, Senor 2007a, Senor 2007b). The workshops were attended by each of the organizations involved in the Tritium Readiness Campaign including NNSA, PNNL, Sandia National Laboratories-California (SNL-CA), Idaho National Laboratory (INL), Savannah River Site (SRS), Savannah River National Laboratory (SRNL), and WesDyne. During the course of these three workshops, plans were developed for six irradiation experiments and six complementary ex-reactor experiments to elucidate specific separate-effects phenomena associated with liners, coated cladding, plated getters, and pellets (Senor 2007c). Based on the modeling maturity assessment and the priorities defined during the workshops, the first two in-reactor and ex-reactor experiments began shortly after the workshops were completed. The TPBAR Materials Irradiation Separate-Effects Test-1 (TMIST-1) experiment on in-reactor oxidation and hydrogen uptake in Zr-base alloys was started first, followed closely by the TMIST-2 experiment on in-reactor measurement of tritium permeation through uncoated and coated cladding (Senor 2009a). While the in-reactor experiments were underway, the TPBAR Materials Ex-Reactor Development-1 (TMED-1) experiment on ex-reactor oxidation and hydrogen uptake in Zr-base alloys was performed to complement the in-reactor data collected by TMIST-1 (Senor 2008a). Shortly thereafter, the TMED-4 experiment on ex-reactor equilibrium partial pressure over Zr-base alloys and Ni-plated Zircaloy-4 (NPZ) getters was conducted (Senor 2008b). Execution of the various experiments was managed by PNNL, but work was performed in support of these four tests at PNNL (all four), INL (TMIST-1 and -2), SRNL (TMED-1 and -4) and SNL-CA (TMED-1 and -4), in addition to various commercial manufacturers that provided materials and components for specialized test specimens. As the tests were conducted, NNSA, TVA, and WesDyne were kept informed of progress, with specific attention devoted to implications for interpretation of TBPAR performance or possible future implementation in TPBARs. All program participants were actively involved in defining experiment objectives, priorities, and test matrices.

In 2009, as the TMIST-1 and -2 and TMED-1 and -4 experiments were well underway, a fourth workshop was held to review the D&T Plan in light of the information obtained in these studies and determine the next testing priorities for the program. Attendees included staff members from NNSA, PNNL, INL, SNL-CA, SRS, SRNL, WesDyne, Los Alamos National Laboratory (LANL) and TVA. The workshop identified pellet tritium release kinetics and speciation as the next priority for the D&T program. Accordingly, the TMIST-3 irradiation experiment focusing on separate-effects pellet performance was initiated shortly after the workshop (Senor 2010). At the same time, the TMED-3 development effort was started to produce specialized pellets for the TMIST-3 experiment (Senor 2009b). Table 2 provides a summary of the TMIST and TMED experiments that resulted from the first four D&T workshops and subsequent planning efforts.

Table 2. Summary of the TMIST and TMED separate-effects experiments resulting from the first four D&T workshops.

Experiment	TPBAR Component of Interest	Key Data to be Obtained	Number of Capsules/ Specimens	Irradiation or Ex-Reactor Testing Dates	Data References
TMIST-1	Liner	• In-reactor oxidation rate • In-reactor hydrogen uptake • Temperature and pressure dependence of oxidation and hydrogen uptake • Evaluation of candidate improved liner materials	4	May 2008 to December 2009	Geelhood and Cunningham (2011) Longhurst (2008) Senor et al. (2011a) Johnson et al. (2012) Senor et al. (2012)
TMIST-2	Bare and coated cladding End plug	• In-reactor tritium permeation rate • Temperature and pressure dependence of permeation rate • Evaluation of atomic tritium permeation mechanism	4	March 2009 to April 2010	Senor et al. (2011b) Luscher et al. (2012) Luscher et al. (2013b) Luscher et al. (2013c)
TMIST-3	Pellet	• Tritium release rate • Tritium release speciation (T_2 versus T_2O) • Temperature dependence of tritium release • Time/burnup/burnup rate dependence of tritium release • Effect of grain size and porosity on tritium release • Evaluation of candidate improved pellet materials	Test Train A: 22 Test Train B: 19	Test Train A: Spring 2014 to Fall 2015 Test Train B: Fall 2016 to Spring 2019	Senor and Luscher (2013)
TMED-1	Liner	• Establish ex-reactor oxidation rates and hydrogen uptake for comparison to in-reactor data from TMIST-1 • Evaluate thermogravimetric analysis as an inspection method for candidate improved liner materials	4 (identical to TMIST-1)	September 2008 to January 2009	Pitman and Senor (2010) Korinko and Imrich (2009)

Experiment	TPBAR Component of Interest	Key Data to be Obtained	Number of Capsules/ Specimens	Irradiation or Ex-Reactor Testing Dates	Data References
TMED-3	Pellet	• Develop specialized pellets for irradiation in TMIST-3 including large grains, small pores, large pores, thin wall, and four varieties of $LiAlO_2$/Zr cermets	16 types	May 2008 to September 2011	Telander (2012) Johnson et al. (2013)
TMED-4	Getter	• Partial pressure of H, D, and T over Zr, Zircaloy-4, and NPZ • Solid-state isotopic exchange effects	3 types	May 2008 to June 2011	Morgan and Korinko (2008) Korinko and Morgan (2010) Korinko et al. (2010) Korinko and Morgan (2011a) Korinko and Morgan (2011b) Korinko and Morgan (2011c) Morgan and Korinko (2012)

In 2011, with the TMIST-1 and -2 and TMED-1 and -4 experiments completed and the TMIST-3/TMED-3 experiments underway, an external peer review of the D&T program was conducted before a committee of four nuclear fuels and materials experts from LANL, Texas A&M University, University of Wisconsin, and University of California-Los Angeles (Meyer et al. 2011). The committee endorsed the systematic and thorough approach to research and development adopted by the Tritium Readiness Campaign, and they supported the prioritization of experiments identified in the earlier workshops to address the most pressing data needs. However, the committee observed that the D&T experiments to date were very focused on near-term applied technology issues, namely TPBAR performance modeling, and less attention was being given to long-term and fundamental tritium science issues.

After the external peer review, the fifth D&T workshop was held in 2011 to consider the question of tritium science data needs and prioritization. Attendees included tritium program participants from NNSA, PNNL, INL, SNL-CA, SRS, SRNL, WesDyne, TVA, and Southern Utah University. The workshop attendees identified the highest-priority data needs for both near-term and long-term issues facing the Tritium Readiness Campaign, including fundamental tritium science topics to improve the understanding of mechanisms behind phenomena observed in WBN1 operations, TPBAR PIE, and the various TMIST/TMED experiments. Shortly after this workshop, and before any of the recommendations could be implemented in the FY2012 planning process, significant budget cuts were imposed on the Tritium Readiness Campaign resulting in discontinuation of the TMIST-3 experiment after the design and capsule component fabrication phases were completed. In mid-2012, NNSA was able to provide additional funding to complete TMIST-3 capsule assembly and begin test train fabrication. In mid-2013, NNSA restored TMIST-3 funding to the project baseline budget beginning in FY2014. As of this writing, the first test train of the TMIST-3 experiment is scheduled to be inserted in ATR in spring 2014.

In late 2012, a sixth D&T workshop was held to reconsider Tritium Readiness Campaign priorities in light of the severe budget limitations first imposed in 2011. Attendees at this most-recent workshop included representation from NNSA, PNNL, SNL-CA, SRS, SRNL, WesDyne, TVA, Southern Utah University, and Texas A&M University. The attendees validated the earlier prioritizations of work, but realizing that budget challenges would limit large-scale irradiation experiments at least in the near-term, focused on identifying and prioritizing long-term fundamental science studies. Studies of this nature can be executed for a fraction of the cost of large in-reactor tests, and while they cannot replace the data provided by the TMIST experiments, they complement the TMIST studies by improving fundamental understanding of mechanisms occurring within TPBARs during irradiation. In this way, the tritium science studies contribute to the improvement in TPBAR performance models and maintain the progress resulting from the TMIST-1 and -2 and TMED-1, -3, and -4 experiments.

1.3 Results to Date from the Development and Testing Program

The principal purpose of the D&T program was risk reduction by quantifying the behavior of TPBAR components during irradiation, thereby improving predictive models and reducing uncertainty on performance projections. The lack of these data hinders the ability to reliably predict TPBAR performance, resulting in under-prediction of the permeation rate. The inability to predict TPBAR performance also has created difficulty interpreting tritium permeation trends at WBN1 during Cycles 10 and 11. Unexpected TPBAR performance since Cycle 6 has led to TVA decisions to limit TPBAR quantities, formal notifications of a licensing discrepancy to the NRC, and processing of Problem Evaluation Reports (PERs). Thus, it is important to be able to predict TPBAR performance accurately, but there are significant knowledge gaps that hinder the ability to do so reliably. In addition, there is uncertainty in current predictions of tritium distribution, component integrity, and performance margins. Addressing these knowledge gaps will provide numerous benefits to the Tritium Readiness Campaign, including the ability to:

- Explain and predict TPBAR permeation performance, leading to high confidence in repeatable results from cycle to cycle
- Reduce risk to TVA reactor operations and provide increased assurance of TPBAR reliability

- Adapt and interpret TPBAR performance as TVA changes reactor operating conditions and cycle schedules
- Ensure product specifications for TPBAR components control material properties and characteristics that influence in-reactor performance
- Evaluate and respond to changes in component suppliers and fabrication processes
- Make incremental design changes to improve TPBAR performance with high confidence

Between 2006 and 2012 the D&T program produced significant advances in the understanding of in-reactor TPBAR performance. Presentations, reports, and journal articles derived from the TMIST-/ TMED experiments are referenced in Table 2. Specific first-of-a-kind data obtained from these experiments include:

- **TMIST-1/TMED-1**
  - Quantified irradiation enhancement in Zircaloy-2 and -4 oxidation at low D_2O vapor pressure (~2X)
  - Quantified nascent deuterium uptake in Zircaloy-2 and -4 during irradiation (~20%)
  - Evaluated surface-modified Zircaloy-4 (candidate improved liner material) for oxidation kinetics and deuterium uptake
  - Observed differences between separate-effects (TMIST-1) and integral (TPBAR) environments
  - Improved understanding of the relationship between material characteristics (e.g. microstructural texture) and in-reactor performance providing greater confidence in specification requirements
  - Better fundamental understanding of TPBAR tritium transport and distribution
- **TMIST-2**
  - Quantified irradiation enhancement of tritium permeation through Type 316 stainless steel (~3X)
  - Confirmed pressure dependence of tritium permeation through Type 316 stainless steel of $p^{0.5}$, indicating a diffusion-limited permeation rate
  - Confirmed no effect of neutron fluence on tritium permeation through Type 316 stainless steel up to ~2×10^{21} n/cm^2
  - Confirmed no significant contribution to in-reactor permeation through Type 316 stainless steel from atomic tritium deposition and diffusion (<4%)
  - Benchmarking of ^{3}He concentrations in the stainless steel cladding after irradiation to evaluate a potentially valuable PIE tool for assessing tritium distribution and transport

- **TMED-4**
  - Observed differences in hydrogen partial pressure over Zr versus NPZ
  - Confirmed no unexpected isotopic exchange effects caused by introducing a hydrogen species (e.g. H_2) over a getter loaded with a different hydrogen species (e.g. T_2)

Incorporating these data into existing TPBAR performance models has improved permeation predictions, and the discrepancy between predicted and observed tritium permeation in the WBN1 coolant has been decreased by about 30%, as shown in Figure 1. However, important differences between predicted and observed permeation still remain; the most significant one being the time-dependence of tritium release from TPBARs during irradiation. It is important to understand time dependence of release because of the increase in release rate throughout an irradiation cycle that current models cannot explain.

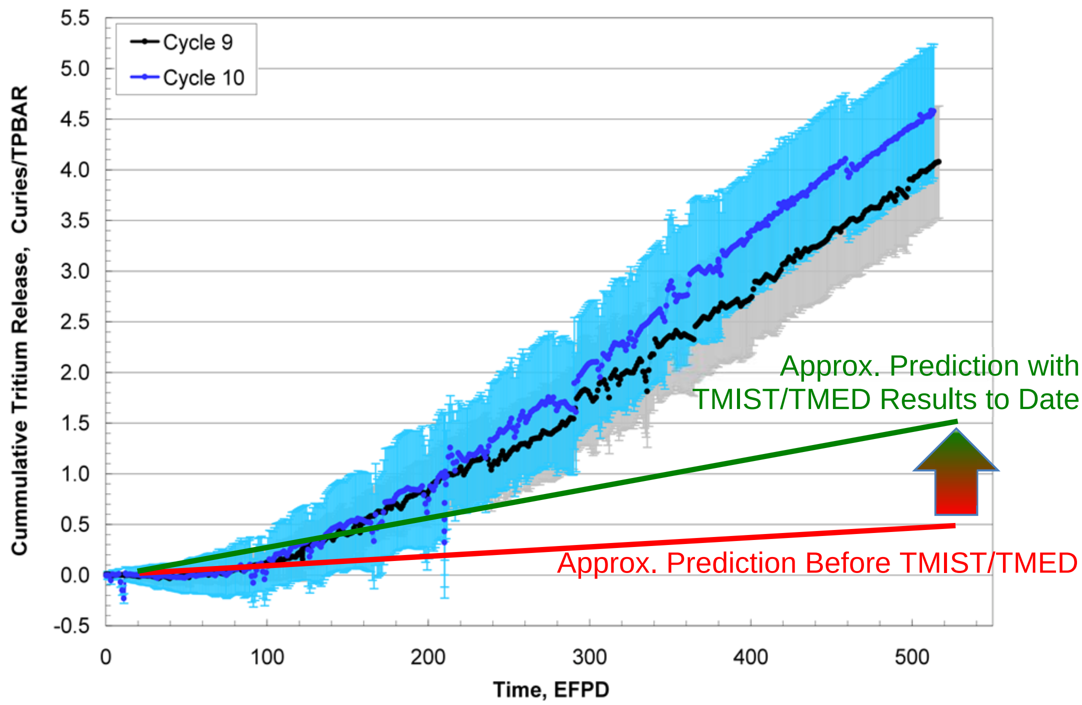


Figure 1. Improvement in TPBAR permeation predictions compared to observed TPBAR release after incorporating data from the TMIST-1 and -2, and TMED-1 and -4 experiments.

The TMIST-3 experiment is primarily focused on understanding pellet irradiation behavior to explain the time-dependence of TPBAR tritium release, as well as other related technical issues. Specifically, the experiment will provide TPBAR designers and modelers with data that will:

- Explain the time dependence of pellet tritium release to more accurately predict TPBAR permeation
- Define the relationship between host fuel assembly burnup and TPBAR permeation to improve understanding of reactor operating conditions on TPBAR performance
- Assess pellet performance beyond the current design burnup limit to better understand existing performance margins
- Determine whether low burnup TPBARs could be used to meet tritium production goals with overall lower permeation, requiring no change in TPBAR design
- Determine whether minor modifications to the pellets could improve TPBAR performance by increasing tritium retention
- Determine if more significant TPBAR design changes would significantly improve performance

1.4 Integrated Tritium Science and Technology Research and Development Program

The TMIST and TMED experiments described in the preceding section are large-scale, relatively applied studies addressing very specific aspects of TPBAR component performance. The experiments completed to date and the TMIST-3 experiment still pending provide significant data on in-reactor performance of liners, cladding, getters, and pellets that cannot be obtained in any other way. However, while they provide important quantitative data that is crucial to accurate TPBAR performance modeling, they are not designed to investigate the underlying mechanisms responsible for the observed performance (with some exceptions in TMIST-3). For example, a radiation enhancement in tritium permeation through stainless steel was observed in TMIST-2, but the mechanism responsible for the enhancement is not known and cannot be determined from the TMIST-2 data. Similarly, if TMIST-3 data show that tritium release speciation is affected by characteristics such as microstructure, burnup, burnup rate, or time, that knowledge will significantly improve TPBAR tritium release predictions and pellet product specifications, but the underlying cause of the behavior will likely not be apparent from the data. To address these questions of underlying mechanisms responsible for the observed behavior, studies of a type different from TMIST/TMED are required.

Fundamental studies designed to address underlying mechanisms are referred to in this document as “tritium science,” that is distinct from “tritium technology” as exemplified by the TMIST/TMED-type experiments. The scope of such studies will vary depending on the phenomenon being investigated, but in most cases studies of this nature will be smaller in scale and far less expensive than the TMIST/TMED experiments. Tritium science studies could consist of literature reviews, analytical or computational investigations, or experiments. In all cases, the experiments can be carried out in an ex-reactor setting, although the introduction of selected types of radiation via a source or an accelerator may be beneficial in some cases. Nevertheless, even when radiation is needed for a tritium science experiment, the magnitude of the undertaking will be significantly less than an in-reactor experiment. Thus, the tritium science studies will not only provide fundamental knowledge to underpin observations of in-reactor experiments, but they will do so at much less cost. In this way, the tritium science studies will be more amenable to the challenging budget climate anticipated over the next few years. Despite limited budgets, progress toward improving fundamental understanding and modeling of TPBAR performance can still be made.

It is important to note that there are many aspects to a well-integrated research and development program. The intent is not to focus exclusively on one aspect or another, but to approach the program in a holistic fashion. Thus, in addition to small-scale tritium science studies, small-scale ex-reactor tritium technology experiments such as TMED and the ongoing component aging study (Bagaasen 2011), and large-scale in-reactor tritium technology experiments such as TMIST, a well-rounded research and development program must also include continued analysis of TPBAR and WBN1 performance data and post-irradiation examination of TPBARs and lead use assemblies (LUAs) to evaluate model improvements and compare separate-effects and integral component behavior. Figure 2 is a graphical representation of the different aspects of an integrated tritium science and technology R&D program. As depicted in Figure 2, not only do each of the six categories of R&D enable improvements in TPBAR models, specifications and performance, they also complement one another by explaining mechanisms and providing data and/or validation.

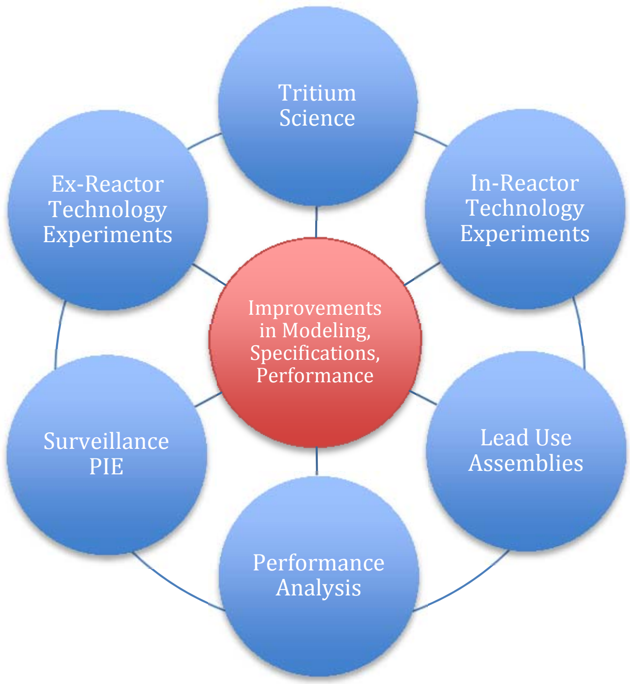


Figure 2. Graphical representation of the different, complementary, aspects of an integrate tritium science and technology R&D program.

There are many examples of worthwhile performance analysis, but the example WBN1 coolant analysis is illustrative. An external peer review of the methodology for attributing tritium to TPBARs was conducted in 2012 (Kurwitz 2012). The reviewer noted that many improvements to WBN1 coolant analysis have been made over the years and much insight into TPBAR (and reactor) performance has been gained as a result. It was analyses of this type that led to the discovery that secondary source rods, rather than fuel, contribute significantly to tritium concentration in the WBN1 coolant (Shaver and Lanning 2010). This realization ran counter to conventional wisdom in the nuclear industry, but had important consequences for attributing tritium in the coolant to TPBARs. There are a number of further improvements to this process that have been recommended and should be implemented to maximize this data source, such as finer time-scale resolution on water movement data during downpowers and shutdowns that could help explain non-physical step changes in tritium concentration that appear as data artifacts resulting from measurements at different times of tritium concentration and water movement.

There are two types of PIE studies that are currently being pursued within the Tritium Readiness Campaign, and both provide unique value. Surveillance of “nominal” TPBARs from each WBN1 cycle has been implemented since Cycle 11. The goal of this effort is to evaluate TPBARs irradiated at essentially the same conditions from cycle to cycle to determine if there are changes in performance that could be attributed to changes in manufacturers or manufacturing methods over time. In addition, surveillance PIE allows comparisons to be made between TPBARs irradiated to different conditions in different cycles to help elucidate the relationships between reactor operating conditions and TPBAR performance. Ideally, a greater spread in irradiation conditions than observed in the Cycle 6 and 9 PIE campaigns will be evaluated to determine if there are performance effects observable in PIE that can be correlated to burnup, burnup rate, irradiation time, or other operating parameters.

The second type of PIE is associated with TPBARs having unique component materials or configurations irradiated as part of LUAs. Lead use assemblies are currently being irradiated in Cycle 12 and are planned for irradiation in Cycle 13. These LUA campaigns will provide integral TPBAR performance data to evaluate various characteristics including pellet burnup, length, thickness, and microstructure, liner and NPZ cleaning methods, and gas transport pathways in the upper and lower plena. The performance characteristics and component features being evaluated in the LUAs cannot be duplicated in a smaller, non-prototypic reactor such as the ATR. As such, the LUAs are a vital complement to in-reactor tests such as the TMIST series.

2. Research and Development Recommendations for the Tritium Readiness Campaign

The following sections provide specific recommendations for each of the six aspects of an integrated tritium science and technology R&D program to support the tritium production mission, as described in Section 1.4 and illustrated in Figure 2. The recommendations resulted from previous D&T workshops, the Advisory Committee review, the tritium attribution metholology review, and LUA design reviews. Each workshop and review typically focused on one or two of the six aspects of the integrated R&D program. The priority of R&D activities within each category has been considered at previous meetings, and the results of those rankings are included in the sections below. However, to date there has been no comprehensive effort to rank technical and programmatic priorities among the different categories of R&D. Therefore, overall prioritization recommendations and a proposed path forward are addressed in Section 3 to provide a roadmap for planning purposes.

2.1 Tritium Science

From recent PIE campaigns, it has become clear that the chemistry within the TPBAR during operation is very complex. Carbon deposits have been found in numerous locations throughout the TPBAR on virtually every component. While the source of the carbon and the relevant transport mechanisms are still being investigated, it is also important to understand how carbon deposits of the type observed in surveillance PIE rods affect TPBAR component performance. A study on the effects of gaseous and surface impurities (e.g. C, CO, CO_2, CH_4, H_2O, etc…) on getter rate or equilibrium partial pressure over getters is therefore highly recommended. A similar study on the effects of surface impurities on adsorption, decomposition, and recombination of hydrogen isotopes on the surface of the liner, pellets, and barrier coating is also of interest. These studies would most likely take the form of combined computational/experimental investigations to evaluate the candidate chemical reactions separately and in combination in a parametric fashion. The results from such a study will help determine if carbon transport is ultimately detrimental to TPBAR permeation performance or not.

The fission and fusion reactor structural materials communities have been studying microstructural evolution of metals, alloys, and ceramics during irradiation for many years (Briec et al. 1988; Nishikawa et al. 1997, Griffiths 1988, Garner 1993). The $LiAlO_2$ pellets used in TPBARs survive 18 months of irradiation very well despite total Li burnup of approximately 12% (^{6}Li burnup of about 50%). However, there likely is a burnup limit on structural integrity of the pellets. Having a more complete understanding of the margin between existing pellet burnup and this limit would provide confidence in current functional requirements, and also possibly allow flexibility to increase the burnup limit if necessary to meet tritium production goals as TPBAR quantities increase in future core designs and tritium production per TPBAR decreases. To understand the fundamental nature of pellet structural degradation, a study of pellet microstructural evolution as a function of burnup is needed. A study of this nature would evaluate irradiation-induced defects from the atomistic scale to the meso-scale and would examine the size, location, and distribution of such features as dislocation loops, voids, bubbles, and second-phase precipitates using a variety of microscopy techniques. Such a study would complement the data that will be provided by the TMIST-3 experiment by enhancing understanding of underlying mechanisms responsible for the effects observed. While a study of this type will require irradiation to produce the desired damage, it might be possible to simulate neutron damage with protons or heavy ions produced in a small-scale accelerator. Because the focus of the study would be on microstructural features resulting from irradiation damage, very small samples could be used, with minimal instrumentation, which is consistent with an accelerator-based irradiation method and similar to many past fission and fusion materials studies (Was 2007).

Irradiation enhancement of various phenomena such as oxidation and diffusion has been reported in the literature for many years (e.g. Shirvington 1975; Lanning et al. 1989). The TMIST-1 and -2 experiments measured irradiation enhancement of Zr-base alloy oxidation and tritium permeation through stainless steel. However, the underlying mechanisms governing the observed enhancements are still unknown. Significant research into Zr-base alloy oxidation has been conducted over the past 30 years, and understanding of the mechanisms responsible for irradiation enhancement has been a primary topic of interest. However, research into other phenomena relevant to TPBAR performance such as tritium permeation, solid-state diffusion, gaseous transport, isotopic exchange, and equilibrium partial pressure has not received as much attention over the years. There is evidence in the literature that, under certain non-prototypic conditions, equilibrium pressure of hydrogen over Zr can be enhanced by radiation (Karasev et al. 1974). If true for TPBAR getters at prototypic operating conditions, this could explain much of the remaining discrepancy between predicted and observed tritium release from the TPBAR. This knowledge also would have significant implications for design options to reduce tritium release. Therefore, literature reviews to assess the state of knowledge and appropriate analytical/computational studies are recommended to improve the state of knowledge with regard to these processes. If a mechanism for the observed permeation enhancement can be identified, then changes to the composition or microstructure of the cladding and/or barrier coating can be implemented (or prevented) to ensure consistent TPBAR performance. Similarly, if fundamental research can better determine the likelihood of irradiation enhancement to getter equilibrium pressure (and its magnitude), then performance models can be significantly improved, and many other possible tritium release mechanisms to explain the discrepancy between predicted and observed TPBAR tritium release can be eliminated from consideration.

Researchers at SNL-CA have been investigating atomic tritium formation, transport, deposition, and permeation. The TMIST-2 experiment evaluated this mechanism and found only a minimal contribution to total permeation under the conditions that existed during the test. However, the possibility exists that conditions in a TPBAR could result in a higher concentration of atomic species that might cause a more significant contribution to total permeation. Therefore, continued fundamental computational and experimental investigations into the mechanisms associated with in-reactor atomic tritium formation and transport are warranted. Work at SNL-CA suggests that tritium barrier surface condition has a significant effect on the magnitude and time dependence of the atomic species permeation. The key piece of data needed to evaluate mechanisms of observed TMIST-2 or TPBAR performance data is the relative quantity of atomic species (e.g. H or T) to molecular species (e.g. H_2 or T_2) in ex-reactor tests as compared to ATR or WBN1. A related need is determination of the rate of formation of atomic tritium in TPBARs. It should be noted that atomic tritium formation is a permeation pathway that the Mark 9.2 design was not intended to address. Hence, if it is significant, it is a possible explanation as to why permeation of the production and Mark 9.2 designs was identical.

Modeling efforts to better understand tritium transport through the pellets and barrier/cladding system are hampered by a lack of fundamental data such as hydrogen isotope solubility and diffusivity. Therefore, fundamental measurements of solubility and diffusivity of hydrogen and tritium in $LiAlO_2$ and various aluminides are needed to enable better performance models of these components. With better knowledge of tritium transport within the pellets and cladding, the potential impact of candidate performance mechanisms can be evaluated computationally with higher confidence. These experimental studies can be conducted in an ex-reactor setting, and could begin with protium and/or deuterium to simplify test setup and operation.

Radiolysis effects are notoriously difficult to calculate because appropriate cross-sections are not particularly well known. Other uncertainties that make reliable calculations difficult include recombination and transport. Therefore, measurement of radiation effects on relevant gases that are likely present in TPBARs would provide valuable data. Gases of interest include H_2, T_2, HT, T_2O, HTO, CO_2, CH_4, and tritiated methane. Measurements of gas composition in the presence of ionizing radiation for single and multiple molecular species would be of interest. The measurements could be made using an appropriate gamma source and would not require a reactor experiment. The fundamental data that would result from such a study would provide input for a variety of gas transport and equilibrium pressure models, and would provide a basis for evaluating current model assumptions.

Because the effectiveness of the tritium permeation barrier on the TPBAR cladding directly impacts the release of tritium into the WBN1 coolant, recommendations have been made at several recent workshops and reviews to consider improved barriers for possible long-term implementation. Recent work suggests a number of technical possibilities, including a coating on the inner surface of the current aluminide (e.g. Be, Ni or Cu), co-extruded cladding with a structural alloy on the outer surface and a low-permeability material on the inner surface, a coolant-compatible coating on the outer surface of the cladding, a barrier coating on the outer surface of the FLG, and replacing the existing stainless steel/aluminide system with Zr-base alloy cladding or new materials such as SiC/SiC composites. An additional benefit of replacing the stainless steel cladding is reducing parasitic neutron capture, thereby potentially improving fuel economy and reducing fuel costs. It might be possible to develop a self-sealing cladding/barrier system to minimize tritium loss in the event of a breach such as a failed weld. Such a change to the TPBAR design would be challenging to implement, probably requiring ten years or more to develop and test, but steady progress toward this goal could be made even with relatively modest funding. Initial studies to establish the feasibility of candidate concepts would most likely take the form of literature reviews and analytical/computational efforts. The fusion materials community has evaluated many tritium barrier concepts (including some in-reactor) that could provide a starting point for a comprehensive literature review. This research would contribute to fundamental understanding of how tritium barriers work, and in the process improve knowledge regarding the behavior of the existing barrier coating. These studies could also point the way for future tritium production designs if the concepts were not suitable for implementation in WBN1 given cost and schedule constraints. Ex-reactor tests on cladding/barrier systems are probably not useful except perhaps as screening tools due to differences in permeation rate-limiting mechanisms between ex-reactor and in-reactor conditions as well as possible irradiation enhancement of permeation rates as observed in TMIST-2. A possible exception might be corrosion/erosion tests in PWR water conditions of candidate outer surface barriers. In-reactor tests ultimately would be required to evaluate revolutionary barriers, but there is significant fundamental research required before coating development or in-reactor testing is warranted.

2.2 Performance Analysis

Over the years, considerable improvements have been made in the attribution of tritium in the WBN1 coolant to TPBARs. The TPBAR source term models are relatively mature, and so most of the improvement to date has been with regard to reactor systems tritium source terms (e.g. secondary source rods, as discussed in Section 1.4). However, continued improvements in WBN1 coolant data analysis (e.g. better time-resolved water movement data) are needed to address discrepancies that still exist. One example is the apparent increase in TPBAR tritium release in Cycle 10. As shown in Table 1, preliminary calculations indicate that if the Cycle 10 tritium releases are estimated using minute-by-minute instead of daily water movement data, the tritium release curve shown in Figure 1 falls more in line with the estimated Cycle 9 curve. A recent external review of the tritium attribution methodology recommended a number of options to realize further improvements in the water movement model including 1) greater fidelity between calculated water movement and actual water movement between the primary loop and various tanks included in the RCS, 2) more sophisticated consideration of the interdependence of various uncertainties in the model, and 3) more extensive benchmarking of the model to plants without TPBARs (e.g. SQN) for which detailed tritium and water movement data are available (Kurwitz 2012). A higher fidelity tritium attribution method would also be beneficial in the event of an actual TPBAR breach because the anomaly would likely be identified earlier. Also, a better model, coupled with surveillance PIE, would provide more reliable indications of inconsistent TPBAR performance that may be related to manufacturing problems. More reliable tritium attribution estimates will reduce uncertainties associated with TPBAR performance, avoid unpleasant surprises related to computational artifacts, and provide higher confidence that TPBARs are consistently performing as designed.

Careful consideration of TPBAR impacts on core design is required, particularly as TPBAR quantities increase beyond the current 544/cycle. There are a number of reactor operations issues that have been discovered late in the core design process, in some cases prompting analyses or even changes to the core design only weeks before the refueling outage. Examples include the CRUD-Induced Power Shift issue identified just before Cycle 11 and concerns related to approaching the 1.2 g production limit for TPBARs in high power assemblies in Cycle 12. Both of these issues were managed without changes to plans for TPBAR loading, but this was largely due to the fact that quantities were still modest at 544. As TPBAR quantities increase, core designers will have less flexibility addressing issues of this nature. Thus, planning well in advance for future irradiation cycles needs to be implemented. The creation of the Tritium Production Planning Group (TPPG) during 2012 is a key aspect to addressing this issue. The TPPG has already proven its worth by evaluating core design scenarios to increase TPBAR quantities beyond 704/cycle and better defining reductions in tritium production per TPBAR as quantities increase. This advance planning will enable the program to seek appropriate license amendments from the NRC and produce the appropriate amount of tritium on a schedule that meets programmatic needs. This approach to core design will also provide flexibility to WBN1 core designers to produce a desired amount of tritium instead of dictating ^{6}Li enrichment and quantity of TPBARs while also maximizing production in each TPBAR. Such an approach could potentially reduce fuel costs while also possibly reducing overall TPBAR permeation if permeation turns out to be dependent on such things as host fuel assembly power.

The current path forward for increasing TPBAR quantities beyond 704/cycle in WBN1 includes the assumption that all TPBARs fail during a LBLOCA. This approach is consistent with the current licensing philosophy, and preliminary core design calculations suggest that it is technically feasible and can be implemented by WBN1 Cycle 14 to keep tritium production on schedule. However, the ability for the WBN1 core to accommodate the assumed loss of negative reactivity during a LBLOCA comes at a cost. To ensure adequate reserve shutdown margin, the core designers must increase fuel enrichment, increase the use of in-fuel burnable absorbers (IFBAs), and increase the number of fresh fuel assemblies per reload. All of this adds cost to the tritium production program. For WBN1 cycles after Cycle 14, more refined TPBAR failure calculations should be implemented to determine if margin can be found to demonstrate to the satisfaction of TVA and NRC that TPBARs will not fail during a LBLOCA. This will allow core designers to reduce reserve shutdown margin, which will reduce the overall cost of fuel to the tritium program and utilize supplies of unobligated fuel more efficiently. One necessary input to improved TPBAR failure analyses is burst test data at precisely-targeted temperatures and pressures that are relevant to LBLOCA conditions to replace conservative assumptions derived from less-relevant conditions that are currently used. Because TPBAR failure during a LBLOCA is a localized phenomenon, these tests can be conducted on short lengths of TPBAR coated cladding with appropriate end plugs and instrumentation. An existing induction furnace currently used to qualify TPBAR end plug welds can be employed to conduct these burst tests.

Detecting and interpreting indications of a TPBAR breach in WBN1 is a topic that has been repeatedly raised by TVA. While a low-probability event, it would have potentially dramatic consequences to the tritium production mission. The new 500,000 gallon water tank at WBN1 will provide some margin to deal with the problem, but in the event of an unambiguous TPBAR breach, it is possible the plant would be shut down within 30 days (long enough to order and receive standard burnable absorber rods) and all TPBARs would be removed for the remainder of the cycle. Possible lines of inquiry addressing this risk include evaluating manufacturing processes and inspection techniques to minimize the chance of manufacturing defects (primarily weld defects), maintaining an ongoing surveillance PIE program to ensure that all TPBAR components continue to perform as designed over time (particularly with manufacturer changes and the tendency for manufacturing process to "drift" over time), conducting leach tests to simulate the removal of tritium from a breached TPBAR so that the "signature" of a failed TPBAR could be clearly identified in the WBN1 coolant data at various times during the course of a cycle, and developing a set of procedures for how to identify a breached TPBAR from the coolant data and how to deal with it if it happens.

Part of the data analysis effort described in Section 1.3 for the TMIST-2 experiment involved using the TPBAR performance code (TROD) in which the steady-state (i.e. late in cycle) permeation rate from Figure 1 was used to back-calculate the tritium pressure required to produce the observed rate (assuming that pressure-driven permeation is the rate-limiting permeation mechanism). The results of the calculation provided some insight into possible mechanisms, including radiation-enhanced getter equilibrium pressure that could explain the shape of the tritium release curve shown in Figure 1. As such, this exercise demonstrated the value of using TROD not only as a predictive tool, but also as a diagnostic tool to help interpret TPBAR behavior. Semi-empirical methods such as these could be implemented with parameters that could be adjusted to match observed TPBAR (or experiment) tritium release behavior. Determining the value of empirical parameters that result in matching observed behavior lends insight into responsible mechanisms and can provide a guide for future experimental investigations. This approach is analogous to how the commercial nuclear fuel industry uses fuel performance codes to understand fuel behavior. A code of this type has been developed for use during irradiation of the TMIST-3 experiment to analyze in-situ pellet tritium release behavior and lend insight into the contribution of various operating parameters (e.g. burnup, burnup rate, time, temperature) or microstructural features (e.g. grain size, pore size, total porosity, open porosity) to tritium release.

Standard practice at WesDyne (as at most manufacturers) is the use of a first-in, first-out inventory system. Because TPBAR quantities irradiated each cycle in WBN1 have remained low compared to initial expectations, some of the components in inventory are approaching 10 years old. Attendees at past D&T workshops have raised the question of whether component aging could affect in-reactor performance. These concerns led to the aging study described in Section 2.5. However, that study cannot assess the impact of barrier/cladding aging on in-reactor tritium permeation. Therefore, recommendations were made to include the newest available coated cladding tubes in an upcoming irradiation. Accordingly, the newest coated cladding will be used when assembling the TPBARs to be irradiated in WBN1 Cycle 13. Comparison of the TPBAR tritium release estimates in Cycle 13 to earlier cycles, particularly with continued improvements in the TPBAR tritium attribution methodology described above, should provide some insight into whether barrier/cladding aging is a performance concern.

At WBN1, operations are dictated by electricity production needs as is appropriate for a commercial power plant. It would be instructive to consider optimizing reactor operations to accommodate tritium production to determine if there are inherent production, cost, or safety advantages to this approach. While probably not feasible at a commercial power plant, such an approach could be implemented in the post-WBN1 future if dedicated tritium production reactors are once again considered. A topic of this nature is ideal for partnership with a university, in which numerous reactor designs (e.g. small modular reactors, SMRs) could be evaluated for their suitability to produce tritium in a safe and cost-effective manner. For example, an ideal tritium production reactor would probably operate at lower temperatures, reducing concerns about permeability potentially by orders of magnitude. Another possibly attractive feature of a custom-designed production reactor would be the capability to remove tritium online during operation, similar to concepts for tritium breeding blankets proposed by the fusion community. Some of the fast reactor SMR concepts use liquid metal coolants, so perhaps a Li-based coolant could be used which would also serve as the target material. The proposed systems engineering study could start laying the groundwork for future, more detailed, investigations of future dedicated production reactor systems and it could highlight data needs that must be addressed before considering such concepts for tritium production in the future. It could also highlight operational parameters that have more or less impact on safe and cost-effective tritium production that could offer insight into current operations at WBN1.

There are a number of conceptual TPBAR design studies that could provide insight into methods to reduce tritium release. For example, target design concepts that minimize gaseous tritium production, switching the location of the liner and getter to sequester more tritium farther away from the cladding, or incorporating a liner material with higher nascent uptake. Concepts for minimizing gaseous tritium include cermet pellets such as those included in the TMIST-3 experiment or a spherical pellet that incorporates a hydride former as a matrix or a coating. Such pellets could even potentially be coated with a tritium barrier material (e.g. SiC), thereby taking advantage of TRISO fuel development experience for high temperature gas reactors (Grover et al. 2010). The TMED-1 and TMIST-1 experiments included surface-modified Zircaloy-4 and Zircaloy-2 samples that both demonstrated higher nascent uptake of tritium than the current Zircaloy-4 liners. Conceptual design studies such as these could utilize these data to help evaluate options and down select those with the best features. The studies would also identify the highest-priority areas for future work including material development and possibly extraction process changes (e.g. for pellets with an integral barrier coating). While such concepts may not be needed at WBN1 to reduce tritium permeation (assuming the necessary license amendments are approved) they would provide a valuable starting point for future designs if a dedicated production reactor is built in the future.

Because many of the material properties within the TPBAR have Arrhenius-type temperature dependence (e.g. cladding permeability), it is possible that TPBARs operated at lower temperature could reduce overall permeation. There are few options for providing extra cooling to the TPBAR given the existing fuel assembly design, but lower burnup pellets would lower temperatures slightly by reducing the (n,α) contribution to heating. Irradiation in lower power fuel assemblies would also lower cladding temperatures slightly, but as TPBAR quantities increase, the options for placement in the core diminish. Data from TMIST-2 along with core design data could help evaluate the effectiveness of this approach in a conceptual design study.

If the TMIST-3 experiment demonstrates a significantly non-linear relationship between pellet tritium release and burnup or burnup rate, it may be possible to reduce the upper limit of tritium production from 1.2 g/TPBAR to 1.0 g/TPBAR or less and reduce overall TPBAR permeation by more than a corresponding percentage. This idea is similar to the LoBAR concept that was considered previously. Such a change may have benefits in ensuring that TPBARs do not fail during a LBLOCA also. Therefore, depending on the results of TMIST-3, a design study to evaluate options for lower production TPBARs should be initiated to evaluate the potential benefits as well as the drawbacks (e.g. more TPBARs may need to be irradiated per cycle to achieve tritium production goals).

2.3 Surveillance PIE

An ongoing surveillance program for PIE on irradiated TPBARs was implemented starting with WBN1 Cycle 11 to evaluate component performance and material condition to ensure no detrimental effects from manufacturer changes or manufacturing process “drift” over time. For the Cycle 11 PIE campaign, three TPBARs were shipped to PNNL. Based on pre-Cycle 11 projections by the core designers, one of the rods was to have been a “high-production” TPBAR with about 1.05 g tritium, while the other two were to have been “average-production” TPBARs with about 0.99 g tritium. The average-production rod would have been compared to Cycle 9 TPBARs (also of the FLG design) to evaluate consistency in performance over time, while the high-production rod would have provided a difference of about 10% in production compared to previous PIE rods. This spread in production is of interest because all previously-examined rods had very similar production and therefore it was impossible to tell if any indications discernible in PIE were correlated to production (i.e. burnup). The third Cycle 11 PIE rod was to be irradiated to the same burnup as the average-production rod but included, for the first time, machined (instead of welded) cruciforms and FLGs manufactured from stock getter tubes produced by a new supplier. Surveillance PIE on the third rod was to be compared to the “average-production” rod to determine if there are observable performance differences that could be attributed to the new machined cruciforms or getter tubes.

Because of delays starting the cycle and unplanned outages during the cycle, the “high-production” TPBAR ended the cycle with an estimated 0.92 g tritium, while the “average-production” TPBAR produced about 0.91 g tritium, and the rod containing the machined cruciforms and new getter tubes produced about 0.86 g tritium (TVA 2013). Comparing these production values to the average and peak TPBARs from Cycles 6 through 10 shown in Table 1, it is apparent that the 0.92 g rod is similar to past average production, while the 0.91 g rod is only slightly lower than past average production. The

0.92 g rod can be used to compare nominal performance in Cycle 11 with past cycles, while the 0.86 g rod can be used to determine if there are noticeable performance trends discernible in PIE that could be correlated to burnup (albeit on the low side of the average instead of the high side). A possible complicating factor is the presence of machined cruciforms and new getter tubes in the 0.86 g rod. Careful consideration will be necessary if differences are observed between the 0.92 g rod and the 0.86 g rod to determine if they are due to the different components or the different production. Comparisons between the 0.92 g rod and the 0.91 g rod are probably not meaningful, but the 0.91 g rod can be used to supplement information from the 0.92 g rod if additional samples are needed for a particular feature. The Cycle 11 PIE Plan and cut plan will be revised to take into consideration the actual tritium production values in the three TPBARs.

Previous workshops and reviews have repeatedly recommended that PIE plans be developed with as few pre-conceived notions as possible so as to remain open to unexpected phenomena. In the past, when PIE observations were very focused and limited, later PIE campaigns revealed that important phenomena had been overlooked due to the sampling approach employed. The discovery of carbon deposits in the Cycle 6 TPBARs, later observed in Cycle 2 TPBARs after re-examining archive material using a different sampling approach, serves as an example. As a result of these recommendations and the Cycle 2 and 6 PIE experience, Cycle 9 PIE implemented a very broad sampling plan (Lanning et al. 2010), and the Cycle 11 PIE plan built on discoveries made during the Cycle 9 PIE campaign without focusing exclusively on these phenomena (Senor 2012). New analyses recommended by past workshops and reviews will be implemented in the Cycle 11 PIE campaign including 1) more detailed pellet and coated cladding microscopy to improve understanding of microstructural evolution with irradiation, 2) more extensive pellet chemistry to better characterize retained He, tritium, and oxygen, and 3) more quantitative analyses of carbon deposits, including depth profiles via Auger and x-ray photoelectron spectroscopy to provide insight into what molecular species might have transported the carbon and in what order the deposits were laid down.

Cycle 12 at WBN1 will include four lead use TPBARs with unique components and configurations that will experience the cycle-average tritium, currently projected to be 1.00 g/TPBAR (see Section 2.4), but the shipment to PNNL will also include one standard TPBAR with the same tritium production as the LUA rods. Surveillance PIE will be conducted on this TPBAR to evaluate performance consistency among Cycles 9, 11, and 12, and also as a basis for comparison to the performance of the four unique LUA rods.

2.4 Lead Use Assemblies

Four lead use TPBARs are being irradiated in WBN1 Cycle 12. Unique components in these TPBARs include 1) lower sealed getter, 2) full-length liner (FLL), 3) half-inch pellets, and 4) specially-cleaned liners and FLGs. All four TPBARs will be irradiated to similar burnup for comparability in PIE with one another and with a standard TPBAR (see Section 2.3). The science that the Cycle 12 LUA addresses is described below:

- **Lower sealed getter** - One way to eliminate transport of gaseous species such as tritiated carbon compounds to the inner surface of the cladding at the bottom of the TPBAR is by adopting the lower sealed getter design (Mark 11 TPBAR design). Evaluating the effectiveness of the sealed getter in the Cycle 12 LUA with respect to stopping carbon transport at the bottom of the TPBAR will be straightforward during PIE. However, PIE will not provide information on the impact to tritium permeation. The only way to do this short of a side-by-side irradiation experiment (e.g. a loop test at ATR) is to include a statistically significant quantity of lower sealed getters in a future WBN1 LUA, pending the results of Cycle 12 PIE, to see if there is a measurable difference in tritium release to the coolant. This concept is under consideration for the Cycle 14 LUA campaign.
- **Full-length liner –** Full-length liners were manufactured specifically for the Cycle 12 LUA in order to determine the viability of the concept as a method for simplifying TPBAR assembly and verify that there is no unexpected performance degradation. Two FLL variants were included in the Cycle 12 LUA with significantly different Zircaloy-4 microstructural texture (i.e. grain orientation). Comparisons between these two FLL types will provide further insight into the differences noted between liner behavior in separate-effects (TMIST-1) and integral (TPBAR) environments. Full-length liners were also included in the Cycle 13 LUA. Comparisons between the FLL and standard liners will enable an assessment of the FLL impact on internal gas transport.
- **Specially-cleaned FLLs and FLGs –** One possible source of the carbon deposits that have been observed in all irradiated TPBARs to date is surface contamination on the liners and getters resulting from lubricants used during thermomechanical processing of the tubes or from organic additives to the plating bath in the case of the FLGs. The FLL and FLG in this lead use rod were cleaned using specific solvents and methods to minimize surface carbon contamination.
- **Half-inch pellets –** One of the changes implemented when moving from the pencil to the FLG design was shortening pellet length from ~2 in. to ~1 in. At the time this design change was made, it was expected to contribute to an improvement in certain TPBAR performance characteristics. After Cycle 9, it was evident that shortening the pellets had little, if any, effect. Subsequent modeling studies have suggested that the pellets should be even shorter in order to observe a beneficial effect. Consequently, ~0.5 in. long pellets will be irradiated in the Cycle 12 LUA and compared to standard ~1 in. pellets to determine if a difference in performance can be discerned.

The WBN1 Cycle 13 LUA will include four rods to evaluate a number of additional unique components including 1) thin-wall pellets, 2) thick-wall pellets, 3) large-grain pellets, and 4) upper sealed getter. The thin-wall and thick-wall pellets will provide a range of burnups within the same TPBAR to further the understanding of pellet microstructural evolution with irradiation and its effect on pellet performance (specifically, retained tritium, helium, and oxygen). These data will complement the separate-effects data obtained in the TMIST-3 experiment (see Section 2.6) and will help enable (along with TMIST-3) the proposed pellet microstructure study described in Section 2.1. The large-grain pellets have the potential to delay tritium release from the pellets if intragranular diffusion is the rate-limiting step. Therefore, these pellets will allow the Cycle 13 LUA to determine (from retained tritium in these pellets) whether this mechanism is, in fact, rate-limiting. These data will complement those obtained from the TMIST-3 experiment. Finally, the upper sealed getter will lend insight into transport pathways at the upper end of the TPBAR, comparable to the information provided at the lower end of the TPBAR by the lower sealed getter in the Cycle 12 LUA.

Possible future lead use rod concepts include the following:

- Surface modified cruciforms and/or liners to validate their use if needed in the future to reduce water or other species at the upper and lower ends of the TPBAR. Surface-modified liners were irradiated in ATR in TMIST-1 and disks comparable to surface-modified cruciforms will be irradiated in TMIST-3, providing confidence for a lead use rod irradiation in WBN1.
- If tritium at the ends of the TPBAR contributes significantly to overall permeation, an integral test in a radiation environment would be needed using prototypic materials and geometry. An integral test could be designed using an ATR pressurized loop so that tritium permeation could be directly measured in the loop cooling water. However, another possibility is devising an appropriately-designed lead use rod that included witness samples at the TPBAR ends to provide some indication of tritium concentration (and therefore likely contribution to permeation) in these locations.
- To further evaluate the source of carbon transport in the TPBAR, labeling pellets or other components with ^{13}C is a possibility. Fabricating ^{13}C-labeled pellets is possible in principle, but development work is needed. The path forward for developing ^{13}C-labeled liners or getters is less clear. Preliminary evaluation of the carbon deposits in Cycle 9 TPBARs suggests that the $^{12}C/^{13}C$ ratio is comparable to natural carbon. Thus, activation does not appear to be a significant source of carbon. This implies that the use of ^{13}C as a tracer for carbon compound transport is possible (i.e. the $^{12}C/^{13}C$ ratio would be different than natural carbon and thus the source could potentially be identified). There are analytical techniques that could be used to measure the ^{13}C during PIE (see Section 2.7). While a lead use rod with ^{13}C-labeled pellets could provide information regarding the source of the carbon deposits, it would not by itself answer the question of whether carbon transport contributes significantly to overall TPBAR tritium permeation.

2.5 Ex-Reactor Tritium Technology Experiments

The majority of the components (e.g. pellets, liners, stock getter tubes) irradiated in TPBARs from Cycle 6 to the present were manufactured in a single campaign 10-12 years ago. These components have been stored under controlled environmental conditions at PNNL and WesDyne since they were produced. Over the years, questions have been raised regarding aging and possible irradiation performance impacts of these components. To evaluate these effects, a study was initiated in 2010 in which various components were exposed to aggressive temperature and humidity conditions to promote accelerated aging effects (Bagaasen 2011). To date, only pellets have shown any degradation under these accelerated conditions, and a series of pellet-specific tests at less aggressive temperature and humidity conditions has been started in recent years to better understand the relevant chemical reactions leading to pellet degradation and the associated kinetics. Ultimately, it is expected these tests will lead to more stringent requirements on environmental storage conditions for pellets. The component aging study and associated pellet studies are expected to run through 2015, and completing these tests has been highly recommended by several workshops and reviews.

To help determine the source of the carbon observed in TPBAR PIE, it would be useful to heat treat components individually or in an assembled TPBAR to determine which volatile carbon compounds are formed at temperature and in what quantity. There are archive TPBARs fabricated for every production cycle at WBN1 available at PNNL that could be dedicated to this effort. Ideally, the top or bottom end plug would be cut off and replaced by a valved fitting that would allow a vacuum pump to extract off-gas from the TPBAR as it is heated for sampling with a residual gas analyzer or other instrumentation. Alternatively, both ends of the TPBAR could be cut off in order to flow a carrier gas through the TPBAR for more efficient removal of off-gas. The fundamental studies on reactions and reaction rates described in Section 2.1 will provide valuable data to appropriately plan and design the TPBAR off-gas experiment described here.

An investigation into the possibility of tritium redistribution from hotter to cooler regions within the TPBAR (e.g. from liners to getters) would provide better understanding of the apparent discrepancy between the liner tritium uptake measured in the TMIST-1 separate-effects irradiation experiment and the integral environment of TPBARs. Such a study could be done in an ex-reactor setting, and if warranted, could proceed to an irradiation experiment later.

If carbon transport is determined to be detrimental to TPBAR performance, it would be useful to evaluate materials for their effectiveness at cracking compounds such as methane. In particular, it would be interesting to evaluate the effectiveness of the surface-modified Zircaloy-4 components for this purpose to determine if surface-modified cruciforms could be used not only to reduce water at the TPBAR ends but to crack carbon compounds as well. Similarly, it would be instructive to understand the behavior of Zr-base components (e.g. liners, cruciforms, spring clip) with respect to oxidation by CO or CO_2. The TMED-1 and TMIST-1 experiments provided significant data on oxidation behavior of Zr-base alloys in low pressure water vapor, but carbon species such as CO or CO_2 may be present in the TPBAR as well.

The liner and getter locations could be switched to keep higher concentrations of tritium farther from the TPBAR cladding, as discussed in Section 2.2. However, this puts the getter in a higher temperature location, where the equilibrium pressure will be higher, and it puts the liner in a lower temperature location, where the oxidation rates will be lower. The TMED-1 and TMIST-1 experiments provided data on liner oxidation over a range of temperatures. Similarly, evaluating getter performance at a range of temperatures above and below nominal TPBAR operating temperatures would help evaluate design options like this.

A complement to the study described in the preceding paragraph would be measurements of getter rate separately on the inner and outer surface, as well as at a range of T/Zr ratios between 0 and 2. Getter performance models would be improved if more detailed getter rate data were available. This would eliminate the need to extrapolate getter performance under any conceivable condition when evaluating TPBAR performance implications during extreme reactor operating conditions.

During TMED-4, work was done by SRNL to evaluate isotopic exchange of H_2 with tritium in the solid state in Zr-base alloys. Their work showed there was no unexpected T_2 pressure above the getter when H_2 was introduced. The original D&T Plan (Senor 2007c) envisioned an experiment to evaluate isotopic exchange of ingressing H_2 with T_2O generated in the TPBAR to determine how significant a source of T_2 that reaction might produce, particularly in the upper plenum. Such a test has not been done (either ex-reactor or in-reactor) and still has merit, but perhaps the test should also consider isotopic exchange between ingressing H_2 and tritiated methane or other carbon compounds. The test could be done initially in an ex-reactor setting to establish feasibility, configuration, and operational constraints (as originally envisioned for TMED-4 and TMIST-4 in the D&T Plan) before considering a much more expensive and time-consuming in-reactor experiment.

2.6 In-Reactor Tritium Technology Experiments

Completion of the TMIST-3 in-reactor pellet performance experiment will provide better understanding of tritium release kinetics (i.e. the last 400 days of the TPBAR tritium release curve in Figure 1) and improve predictive models to avoid surprises in future WBN irradiation cycles. In addition, the TMIST-3 experiment will provide valuable insight on 1) the chemical form of tritium release (T_2O versus T_2), 2) the impact of microstructural characteristics on pellet tritium release to provide guidance for new pellet manufacturing, 3) the ability of improved pellets to retain significant fractions of the tritium produced, and 4) the in-reactor performance of non-pellet components such as surface-modified materials and getters. Each of these areas will address significant existing knowledge gaps, improve predictive models, and help reduce uncertainty and surprises during TPBAR irradiation at WBN1.

The only major TPBAR component that has not yet been evaluated in a separate-effects irradiation experiment is the getter. There are data in the literature (for non-prototypic materials under non-prototypic conditions) that suggest the equilibrium partial pressure of tritium above the getter in reactor might be significantly higher than measurements made out of reactor, as in TMED-4. Further, analyses using TROD described in Section 2.2, based on TMIST-2 and TMED-4 data, suggest that such a mechanism could be responsible for the observed steady-state TPBAR permeation rate. If this is the case, it could explain much of the discrepancy between predicted and observed TPBAR permeation. It would also guide design efforts to address TPBAR permeation by focusing on appropriate solutions (e.g. lower permeability cladding/barrier coating). While radiation is necessary to evaluate this effect, the test may not need to be done in a reactor. It might be possible to devise an experiment using an appropriate radiation source or an accelerator, such as those available at the Idaho Accelerator Center, where tubing runs from the test to the instrumentation could be much shorter than in a test reactor (Luscher and Senor 2011). A source or accelerator also offers the possibility of evaluating the effect with a tailored radiation spectrum consisting of neutrons, gammas, or both. If the effect is primarily due to the gamma flux, it may be possible to use the gamma irradiation facility at the ATR canal, where even an instrumented experiment could be conducted much more economically than in the reactor itself. Another possibility for neutron flux only would be a beam tube at HFIR or a university reactor. An experiment to directly measure the partial pressure of tritium over the getter in a radiation field is very challenging, but there might be ways to indirectly determine the magnitude of the effect (or determine that the magnitude of the effect is not significant and can be ruled out as a significant contributor to higher-than-predicted TPBAR permeation).

2.7 New or Enhanced Analytical and Testing Capabilities

During the course of the Cycle 2, 6, and 9 PIE campaigns as well as the TMIST and TMED experiments, several new analytical capabilities have been used to better understand physical phenomena observed. Some examples include Fourier Transform Infrared Spectroscopy for measuring oxide thickness on liners and cruciform, radial gradient tritium assays in getters, and Auger electron spectroscopy for surface chemistry analysis. In each instance, new insight was gained into previously-observed phenomena, leading to a better understanding of the underlying mechanisms. This section describes a number of additional new or enhanced analytical or testing techniques that could further develop fundamental understanding of physical phenomena occurring in TPBARs during irradiation. These techniques could provide benefit to many of the proposed studies described in Sections 2.1 through 2.6, so are included separately in this section.

There is a significant need associated with techniques that can detect light elements such as isotopes of He and H in TPBAR components as an alternative or supplement to the current ^{3}He, ^{4}He, and tritium assays. Also of continuing interest are techniques that can provide gradient assays (or depth profiles) of light elements in irradiated TPBAR components. The most notable techniques recommended by previous workshops and reviews include:

- Secondary ion mass spectrometry (SIMS) could be used to evaluate carbon isotopic ratio and near-surface depth profiling, possibly even for hydrogen isotopes. Many SIMS units use heavy ion (e.g. Xe) sputtering for rapid depth profiling. Polished cross-sections could be used to obtain radial gradient information on various components.
- Nuclear reaction analysis was discussed as a possibility for assaying light elements (e.g. ^{3}He and tritium) in TPBAR components. Proper selection of the incident ion beam composition and energy could allow near-surface analysis of various isotopes, based on the available nuclear reactions of each. However, this technique could be problematic at low concentrations due to detector sensitivity limitations.
- Neutron elastic recoil detection (NERD) was discussed as another possibility for detecting light elements, including hydrogen, in metallic matrices. Using a 14 MeV neutron beam, depth profiles can be made up to several hundred micrometers. However, sensitivity for hydrogen is limited to ppm quantities.
- Scanning probe microscopy could be useful in identifying the surface composition and topography of thin films on TPBAR components.
- Transmission electron microscopy could be used to look for nano-scale features in irradiated barrier coating that could impact permeation resistance.
- The use of a focused ion beam (FIB) would be useful for sample preparation for many of these characterization techniques. Ideally, a FIB capable of use on irradiated materials would be of most value.

2.8 Publication Plans

Publication of research and development results is a key component to the plan described in this document. The advantage of open literature publication to the Tritium Readiness Campaign is the interaction with researchers working on similar problems for other applications. There are many complementary science and technology efforts underway in the US and abroad that offer relevant data for the tritium program. While literature reviews provide one-way communication of external results of interest, much more can be gained by engaging in two-way communication. Such interaction can take the form of journal articles, presentations at conferences and workshops, and site visits. Communications of this type will stimulate new ideas (e.g. new analysis methods or test techniques), provide thorough peer review and validation of assumptions, methods, and results, and provide opportunities for collaboration with subject matter experts outside the tritium production program (e.g. universities). All of these interactions can lead to a diversity of viewpoints on a particular problem, resulting in research efficiencies that would otherwise be unavailable. Certainly, there currently are, and will continue to be, classified or otherwise sensitive results that must be properly protected. For these data, publication in classified reports is the best option. However, even these reports should be circulated as widely as possible within the Tritium Readiness Campaign to foster communication of data and ideas, stimulate discussion, thoroughly assess interpretation of results, and provide input for related work by other program participants. Opportunities for sharing classified results outside the tritium program should be sought whenever possible, such as the workshops organized by the Tritium Focus Group that brings NNSA tritium experts together periodically in a classified venue. Table 3 is a summary of recent and proposed near future open literature publication topics, their relevance, and references for those already published.

Table 3. Summary of recent and near future recommended open literature publications derived from activities conducted under the tritium science and technology research and development program.

Subject	Relevance	Reference(s)
In-reactor oxidation of Zr-base alloys and surface-modified Zr-base alloys (TMIST-1)	• Lends insight into oxidation and hydrogen uptake mechanisms • In-reactor data to improve liner performance models • In-reactor data to evaluate candidate higher performance liner materials	• Longhurst (2008) • Senor et al. (2011a) • Senor et al. (2012) • Future journal article
In-reactor measurement of tritium permeation through stainless steel (TMIST-2)	• Lends insight into tritium permeation mechanisms • In-reactor data to improve barrier/cladding performance models	• Senor et al. (2011b) • Luscher et al. (2013b) • Luscher et al. (2013c)
Post-irradiation examination of stainless steel subjected to tritium permeation (TMIST-2)	• Lends insight into tritium permeation mechanisms • Provides confidence in barrier/cladding specifications	• Luscher et al. (2012) • Future journal article
Ex-reactor tritium transport measurements and modeling	• Lends insight into tritium and tritiated water transport mechanisms and surface reactions	• Future journal article
Design of pellet performance irradiation experiment (TMIST-3)	• Provides interface with fusion community on irradiation testing capability relative to pellet tritium production and release	• Senor and Luscher (2013) • Future TMS paper
Benchmarking of Neutronics Models to Flux Wires in ATR I-Positions (TMIST-3)	• Improves understanding of ATR flux conditions and outer shim control cylinder movements on I-positions for future use • Strengthens collaboration between PNNL and INL/ATR	• Future ANS paper and/or • Future journal article
Lithium aluminate/Zr cermet pellet fabrication development (TMED-3)	• Provides interface with fusion and cermet fuel communities on cermet fabrication process development	• Future conference paper and/or • Future journal article
Hydrogen equilibrium pressure over Zr and Zircaloy-4	• Supplements existing data in the literature for hydrogen over zirconium and extends knowledge to Zircaloy-4	• Morgan and Korinko (2012)
Development of new PIE test methods	• Provides interface with fuels and materials PIE community to improve collaboration on measurement method development	• Baldwin (2008) • Hollenberg et al. (2008) • Carlson et al. (2013)
Ex-reactor oxidation of surface-modified Zr-base alloys	• Lends insight into liner and cruciform oxidation and hydrogen uptake mechanisms • Ex-reactor data to evaluate candidate higher performance liner materials	• Luscher et al. (2013a)
Lithium aluminate pellet hydriding and degradation (Aging Study)	• Lends insight into pellet chemical reactions with atmospheric water vapor and their kinetics • Provides basis for revised pellet storage specification requirements	• Future journal article
Ex-reactor pellet leaching	• Provides basis for leaching calculations supporting NRC licensing actions	• Future conference paper and/or • Future journal article

3. Prioritization and Recommendations

The recommendations in this section are an attempt to provide a comprehensive, integrated research and development program that addresses the most critical technical and programmatic needs of the tritium production enterprise. Near-term recommendations focus on data needs for the next 3-5 years and address R&D to support near-term issues associated with tritium production using the current TPBAR design in WBN. The middle-term recommendations focus on data needs with a 5-10 year horizon and address improvements in understanding potentially significant irradiation effects that could affect TPBAR performance, and minor changes to TPBAR design to improve performance. While the data from the middle-term R&D are needed in 5-10 years to facilitate design changes, work on the highest priority activities should be started soon to enable delivery of the desired data when needed.

In general, the long-term R&D priorities identified during previous workshops and reviews are items that either address fundamental scientific understanding of in-reactor mechanisms relevant to TPBAR performance, or long-range TPBAR component design evolution concepts. As such, they address data needs that have greater than a 10-year impact horizon. However, in virtually all of the recommended studies, the work could be started soon and conducted over an extended time period at relatively low levels of annual funding. This approach has the advantage of creating a robust and stable effort that will complement the near- and middle-term R&D needs while fundamentally improving the scientific understanding of TPBAR performance. A stable tritium science program, even funded at relatively modest levels, will create an environment that fosters rigorous thought regarding fundamental issues that can be sustained over long periods, unlike the near- and middle-term studies that tend to be focused on specific applied technology issues with sometimes severe schedule constraints. The results of the long-term R&D program, while benefitting ongoing tritium production at WBN1, will also position the tritium production enterprise for future possibilities such as new reactor types or altered regulatory requirements.

3.1 Technical Priorities

The drivers for obtaining data to support near-term needs of the tritium production mission include:

- Improving fundamental understanding of tritium transport and release mechanisms to ensure models adequately predict TPBAR performance to an adequate accuracy level
- Improving fundamental understanding of physical properties of components that affect TPBAR performance
- Improving TPBAR performance to the extent practical given the improved fundamental understanding

There are a series of phenomena that are potentially important for understanding and predicting TPBAR performance, but that currently have an inadequate knowledge base. These represent knowledge gaps that need to be filled in order to consistently predict TPBAR performance when material characteristics or reactor operating conditions change in the future. Tables listing the phenomena, questions that currently exist regarding the phenomena, motivation for understanding the phenomena, and testing options to improve our understanding of the phenomena are included in Appendix A. The three most significant knowledge gaps from the perspective of the TPBAR designer are:

- Pellet performance (tritium release rate and speciation) in an irradiation environment
- Getter performance (equilibrium pressure and getter rate) in an irradiation environment
- Effect of TPBAR internal chemistry (e.g. T_2O, C, H_2, etc…) and coolant chemistry on TPBAR performance

3.2 Programmatic Priorities

At the Sixth D&T workshop in 2012, NNSA outlined their programmatic priorities (Chambellan 2012). The highest priority activities identified by NNSA were the supplemental environmental impact statement (SEIS) and large-break loss-of-coolant (LBLOCA) safety analysis to support increasing TPBAR quantities beyond 704/cycle by WBN1 Cycle 14. Work continues on both of these activities at present. Another significant challenge faced by the program was providing unobligated fuel for WBN1 to facilitate production of tritium in the required quantities. Since the sixth workshop, this issue has been at least partially resolved via the tails enrichment arrangement (U.S. DOE 2012), but the cost will be significant, thereby contributing to the budget constraints that will be faced in the future. According to NNSA, the Tritium Readiness Campaign's principal challenges moving forward are:

- Maintaining production at TVA within approved environmental release limits and regulatory requirements
- Formulating a viable plan for sourcing unobligated reactor fuel
- Reconciling disconnects between funding targets and mission requirements
- Laying ground work for increased production via the SEIS, update of accident criticality safety analysis, and TVA license amendment request to the Nuclear Regulatory Commission
- Increasing understanding of TPBAR performance to adapt to future TVA operational changes
- Continue to change acquisition approach to reduce uncosted balances

While progress has been made in some of these areas since the sixth D&T workshop in May 2012 (e.g. identifying a source of unobligated fuel and minimizing disconnects between outyear funding targets and mission requirements) these challenges still exist, and a robust, well-rounded R&D program is critical to addressing most, if not all, of them.

Overall, the highest-priority near-term R&D need from the NNSA perspective is the capability to understand sufficiently TPBAR performance such that an acceptable operational envelope can be confidently defined, thereby avoiding surprises during irradiation at WBN1. To support this objective, the highest-priority research and development needs include (Chambellan 2012):

- Establishing a stable design that will meet mission requirements
- Better understanding of performance parameters to inform core design process and adapt to TVA operating parameter changes
- Performing surveillance of in-reactor TPBAR performance to address improved operational reliability and flexibility
- Gathering data to improve TPBAR predictive modeling results
- Identifying permeation mechanisms in the current TPBAR and the effect of potential design changes on permeation
- Maintaining a level of activity for lead use assemblies (LUAs) and lead test assemblies (LTAs) that will continue to exercise the design and post-irradiation examination (PIE) teams

3.3 Path Forward

Based on the technical value of the various proposed studies in each of the six categories discussed in Sections 2.1 through 2.6, coupled with the technical and programmatic priorities described in Sections 3.1 and 3.2, the following subsections provide a recommended path forward to address the most pressing concerns in the near-, middle-, and long-term time horizons while keeping in mind the reality of budget limitations that will exist for the foreseeable future. It is important to note that the near-, middle-, and long-term categories denote the time horizon during which the impact of the data obtained will be realized. That does not suggest that work should only be initiated soon on the near-term activities. In contrast, work should be started on many of the middle- and long-term activities soon because a significant amount of background study, scoping research, or planning can be accomplished even with modest budgets. Each of the identified activities is associated with one of the six categories of research and development to illustrate how all aspects of the R&D program work together to enable achieving the technical and programmatic goals of the tritium production mission. The order in which the recommended activities are listed is a rough indication of the priority within each of the three time horizons.

3.3.1 Recommendations for Near-Term R&D Priorities

In the near term (3-5 years), the principal objective for the Tritium Readiness Campaign is ramping up tritium production at WBN1. To do this successfully, on a schedule consistent with programmatic requirements, a number of things have to happen, including 1) integrating TPBARs seamlessly into WBN1 core designs as quantities increase, 2) addressing anticipated operating parameters for the next two to four WBN1 cycles, and 3) ensuring that the TPBAR design can support the desired tritium production levels at WBN1 (e.g. adequate production while satisfying LBLOCA and other criteria). To reduce risk over this time span and meet these objectives, TPBAR designers need to acquire the necessary knowledge to better support increasing TPBAR quantities in WBN1. The highest-priority activities to enable this goal in the next 3 to 5 years include:

- Careful consideration of TPBAR impacts on core design, particularly as TPBAR quantities increase beyond the current 544/cycle. The creation of the Tritium Production Planning Group is a key aspect to addressing this issue. (Performance Analysis)
- Post-irradiation examination comparisons of average and high/low production TPBARs within cycles and between cycles to better understand relationships between operating conditions and performance, and determine if the current tritium production limit is appropriate. (Surveillance PIE)
- Irradiation of the most recently produced coated cladding in WBN1 Cycle 13 for comparison to the oldest coated cladding in inventory irradiated in previous cycles. (Performance Analysis)
- Completion of the TMIST-3 in-reactor pellet performance experiment to better understand tritium release kinetics, better define burnup limits, and improve predictive models to avoid surprises in future WBN1 irradiation cycles. (In-Reactor Tritium Technology Experiments)
- Continued improvement in the TPBAR tritium release attribution method to incorporate more realistic water movement data to imcrease confidence in TPBAR tritium release estimates and projections (Performance Analysis)
- Completion of the component aging study to inform specification revisions or other actions necessary to ensure continued acceptable TPBAR performance. (Ex-Reactor Tritium Technology Experiments)
- Computational analyses and leaching experiments to enable early diagnosis of a breached TPBAR during irradiation in WBN1 (Performance Analysis)
- Increase use of TROD as a diagnostic tool by implementing semi-empirical models with parameters that can be adjusted to match observed TPBAR tritium release behavior in WBN. (Performance Analysis)

3.3.2 Recommendations for Middle-Term R&D Priorities

For the middle-term (5-10 years), TPBAR designers need insight into how production process changes and component aging have the potential to impact performance. Specifically, this includes addressing 1) aging of component inventories (e.g. pellets and barrier-coated cladding), 2) new component suppliers (e.g. pellets, stock getter tubes, liners), and 3) reduced throughput rate by the barrier coating vendor over the next few years as demand catches up to inventory. Timely test data is needed to have high confidence in the components available from new suppliers on a schedule to support the current WBN irradiation schedule. Much of these data can be obtained from ex-reactor studies such as the long-term storage study currently underway on pellets and other TPBAR components. However, as new vendors or new manufacturing processes are introduced, surveillance PIE on TPBARs irradiated in WBN will be crucial in assessing the performance of new components. The highest-priority activities for which data are needed within the next 5 to 10 years include:

- Refined LOCA calculations and selected experimental data such as burst tests to determine whether TPBARs can survive severe accidents intact so that WBN1 core designs can be optimized to reduce fuel costs significantly (Performance Analysis)
- Irradiation and PIE of components produced by new manufacturers or new manufacturing processes to compare performance to historical trends, particularly with regard to pellets, getters, and liners. (Surveillance PIE)
- Lead use rod irradiation of unique components and configurations to complement data from surveillance PIE. (Lead Use Assemblies)
- An experiment to investigate irradiation effects on getter equilibrium pressure. (In-Reactor Tritium Technology Experiments)

3.3.3 Recommendations for Long-Term R&D Priorities

Virtually all of the recommended tritium science studies fall into the long-term R&D prioritization because of the lead time involved in implementing the data obtained from fundamental investigations. With regard to the tritium science activities in particular, it is more important to maintain consistent progress, even if funded at relatively low levels. Therefore, the recommended tritium science studies are judged to be of the highest-priority within the long-term R&D prioritization because they need to start soon in order to guide later, more applied development.

For the long-term (impact occurring 10 years or more in the future), TPBAR designers must develop a better fundamental understanding of key mechanisms, under in-reactor conditions, that have a direct impact on TPBAR performance, including 1) pellet tritium release characteristics, 2) getter partial pressure, 3) chemical interactions and molecular transport within the TPBAR, and 4) barrier performance. This fundamental knowledge will enable a fully mature modeling capability that can be used to make accurate and confident assessments of permeation performance can be made. This is a goal that has been aspired to and largely achieved by the nuclear fuels industry over the past 40+ years. The evolution of the TPBAR performance code, TROD, may be seen as analogous to that of the commercial fuel performance codes. To achieve this goal, test data are needed to permit development of appropriate mechanistic models that correctly predict TPBAR performance under all anticipated operational scenarios. The highest-priority activities for which data are needed beyond the next 10 years include:

- A study on the effects of gaseous or surface impurities (C, CO, CO_2, CH_4, H_2O, etc…) on getter rate or equilibrium partial pressure over getters. A similar study on the effects of surface impurities on adsorption, decomposition, and recombination of hydrogen isotopes on the surface of the barrier coating is also of interest. (Tritium Science)
- A fundamental study of pellet microstructural evolution as irradiation damage progresses. This could lead to a better understanding of the mechanisms responsible for the behavior that will be observed in the TMIST-3 experiment. (Tritium Science)
- Investigations into the mechanisms responsible for irradiation enhancements of various phenomena such as tritium permeation, solid-state diffusion, gaseous transport, isotopic exchange, and equilibrium partial pressures, including measurement of fundamental properties of interest such as solubility and diffusivity of tritium in pellets and coated cladding. (Tritium Science)
- Radiation effects on gas composition within the TPBAR (e.g. radiolysis) including hydrogen isotopes and other impurity gases. This will also lend insight into the mechanisms associated with atomic tritium formation, transport, deposition, and permeation. (Tritium Science)
- A feasibility study to investigate optimizing reactor operations for tritium production. The workshop attendees felt this idea would be ideal for partnership with a university, in which numerous reactor designs (e.g. small modular reactors) could be evaluated for their suitability to produce tritium in a safe and cost-effective manner. (Performance Analysis)
- An investigation into modified or alternate barrier and/or cladding materials to reduce overall TPBAR permeation regardless of which mechanisms are dominant. (Tritium Science)
- A study of target design concepts to avoid gaseous tritium production or other revolutionary concepts to address longer operating cycles or other operational changes not yet envisioned. Such studies could also provide a starting point for evaluating tritium production options after WBN1 has reached the end of its operational lifetime. (Performance Analysis)

Table 4 provides a summary of the recommended studies in each of the six categories and three time horizons. Note from the table that many of these activities, particularly the large experiments, PIE campaigns, and lead use assemblies are already funded and underway. It is the goal of this document to illustrate why each of these activities is needed and how each of them fits into an integrated and coherent R&D program. The objectives of each activity are interrelated, and progress addressing any one of them will further understanding needed for others. Conversely, without key pieces of the R&D program, other pieces will suffer from the lack of knowledge that would otherwise have been obtained. Such a holistic approach to research and development is the best path forward for reducing technical uncertainty and ensuring that programmatic objectives are met on the desired schedule.

Table 4. Summary of the recommended research and development studies categorized by type and time horizon when data are needed.

Recommended Study	Category	TPBAR Component(s) of Interest	Key Outcomes	Currently Funded? (Activity)
Near-Term (Data Needed in 3-5 Years)				
TPBAR impact on WBN1 core design	Performance Analysis	• All	• Better definition of tritium production per TPBAR • Define future required pellet enrichments • Better estimates of fuel costs • Improved understanding of normal operating and accident safety margins	Y (TPPG)
Irradiation and PIE of average and high/low production TPBARs	Surveillance PIE	• All	• Improved understanding of relationship between WBN1 operating conditions and TPBAR performance • Determination of whether the current production limit is appropriate	Y (Cycle 11, 12, 13 PIE)
Irradiation of recently-produced coated cladding	Performance Analysis	• Barrier	• Better understanding of potential barrier/cladding aging effects on performance	Y (Cycle 13)
Pellet performance irradiation experiment	In-Reactor Tritium Technology Experiments	• Pellets • Getters • SM cruciforms	• Improved understanding of TPBAR tritium release time-dependence • Improved understanding of tritium transport within TPBAR to better focus future R&D	Y (TMIST-3)
Water model enhancements	Performance Analysis	• All	• Better attribution of TPBAR tritium release • Higher confidence in TPBAR tritium release estimates and projections	Y (Core Follow)
Component aging	Ex-Reactor Tritium Technology Experiments	• All	• Improved confidence in component shelf life • Improved specification requirements for component storage	Y (Aging Study)

Recommended Study	Category	TPBAR Component(s) of Interest	Key Outcomes	Currently Funded? (Activity)
Analysis and testing to diagnose breached TPBARs	Performance Analysis	• All	• Better understanding of tritium, Li, or Al signature in the WBN1 coolant to enable early and confident identification of breached TPBAR	N
Use of TROD as diagnostic tool	Performance Analysis	• All	• Insight into possible irradiation enhancement mechanisms to guide future R&D • Improved understanding of performance prediction accuracy	N
Middle-Term (Data Needed in 5-10 Years)				
Refined TPBAR LOCA failure analyses	Performance Analysis	• All	• Improved TPBAR failure predictions • Increased likelihood of demonstrating TPBARs survive LOCA	Y (Burst Testing)
Irradiation and PIE of new components and components from new manufacturers	Surveillance PIE	• All	• Evaluation of new component performance • Evaluation of component performance fabricated by new manufacturers	Y (Cycle 11 PIE)
Irradiation and PIE of unique components and configurations	Lead Use Assemblies	• All	• Improved understanding of TPBAR internal operating chemistry • Improved understanding of TPBAR tritium release performance	Y (Cycle 12 and 13 LUA)
Getter equilibrium pressure irradiation experiment	In-Reactor Tritium Technology Experiments	• Getters	• Improved understanding of TPBAR tritium release magnitude • Better definition of future R&D needs	N
Long-Term (Data Needed in 10+ Years)				
Effects of impurities on getter and barrier performance	Tritium Science	• Getters • Barrier	• Improved understanding of the importance of carbon and other impurities on TPBAR performance	N
Evolution of pellet microstructure with irradiation	Tritium Science	• Pellets	• Improved understanding of importance of microstructural features to pellet performance to inform specifications	Y (Cycle 13 PIE, TMIST-3)

Recommended Study	**Category**	**TPBAR Component(s) of Interest**	**Key Outcomes**	**Currently Funded? (Activity)**
Fundamental investigation into radiation enhancement mechanisms	Tritium Science	• Pellets • Barrier • Getters	• Better insight into causes of radiation enhancement to guide future design decisions • Model improvements resulting from quantitative material property data	N
Radiation effects on TPBAR gaseous environment	Tritium Science	• All	• Improved understanding of tritium transport within TPBAR to guide future R&D and design decisions	N
Feasibility study for tritium production in SMRs	Performance Analysis	• All	• Initial feasibility assessment of the practicality of using SMRs for dedicated tritium production reactors	N (Done by TAMU with no funding)
Assessment of alternative barrer/cladding systems	Tritium Science	• Barrier • Cladding	• Identify promising alternatives for long-term consideration as candidate barrier/cladding systems to reduce TPBAR tritium release	N
Advanced TPBAR designs	Performance Analysis	• All	• Identify promising alternative TPBAR component configurations for future TPBAR concepts	N

3.4 Leveraging of Funding to Support R&D Priorities

Many of the tritium science and performance analysis R&D priorities lend themselves to collaborative efforts with universities, and thus might allow leveraging of funding sources more readily available to universities. For example, the evaluation of tritium production in small modular reactors described in Section 2.2 was conducted during the 2012-13 school year by four student teams as part of the senior-level design class in the nuclear engineering department at Texas A&M University. If appropriate topics can be identified each year, this is a way to conduct high-level feasibility studies at very little cost to the Tritium Readiness Campaign. In addition, it provides a connection to high-performing students that potentially could seek employment with one of the organizations involved in the tritium production mission.

Possible sources of external funding include numerous DOE-NE and NNSA programs that provide grants to university faculty as principal investigators, but that allow laboratory collaborators to work with the universities as consultants or mentors (e.g. NEUP within DOE-NE). Most of the tritium science R&D priorities described above are either largely or completely unclassified, and could be pursued by universities without the complication of dealing with classified data or materials. Universities also have access to radiation sources such as research reactors, accelerators, and isotopes. Some of the tritium science studies on radiation effects mechanisms proposed above could potentially take advantage of these sources in a more cost-effective manner than an irradiation experiment at the Advanced Test Reactor. Another possibility would be to propose an experiment under the DOE-NE Advanced Test Reactor National Scientific User Facility (NSUF). The principal investigator on these studies must be university staff or faculty, and no funding is provided directly to the PI or collaborators. However, an appropriately-designed experiment could be irradiated under this program at any of the NSUF partner facilities including ATR, HFIR, and MITR using NSUF funds and staff at INL, PNNL, ORNL or other NSUF partner facilities such as Westinghouse.

Many of the tritium science studies described in this document, and particularly those that do not require a radiation source, lend themselves to Laboratory Directed Research and Development (LDRD) funding sources at the national laboratories. Using LDRD funds to explore fundamental questions leading to larger NNSA-funded experiments is a valid and appropriate use of the LDRD funding mechanism.

Finally, there may be select opportunities to pursue cooperative long-term R&D activities with commercial entities. One possibility is R&D related to development of nuclear fuel cladding that might also have application as TPBAR cladding with improved tritium permeation performance. If beneficial to both parties, it might be possible for both NNSA and the commercial entities to provide funding and/or services or materials in kind to support such cooperative R&D efforts.

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Appendix A
TPBAR Design and Performance Modeling Knowledge Gaps

Topic Area	Specific Questions	Why Do We Care?	Opportunity to Learn More
Effect of reactor operating parameters on permeation	• Is there a correlation between permeation and cycle length, burnup, burnup rate, host fuel assembly power? • How does TPBAR placement in the core affect permeation? • How does water chemistry affect interpretation of TPBAR performance?	• Identify discrepancy between predicted and observed permeation • Improve predictability and eliminate surprises • Need to provide proper guidance to reactor operations and core designers • Potential power uprates or longer cycles	• Daily tritium and detailed water data from WBN1 • Assembly-specific analysis • Detailed temperature analysis • Surveillance PIE • C13 LUA • TMIST-3
Importance of microstructural features or mfg processes	• Do component specifications control all relevant material characteristics?	• Component performance could change with new vendors or new processes	• Surveillance PIE • C12 LUA • Future LUA
Pellet performance	• What is the time/burnup dependence of tritium release from pellets? • What chemical forms of tritium are released? • How does grain size and porosity affect tritium release? • What is the pellet burnup limit? • Could cermets improve tritium retention?	• Identify discrepancy between predicted and observed permeation • Better definition of pellet burnup limits • Better TPBAR permeation predictions • Improved pellet tritium retention • Improved LOCA performance • Optimization of TPBAR configuration	• TMIST-3 • C13 LUA

Topic Area	**Specific Questions**	**Why Do We Care?**	**Opportunity to Learn More**
Getter performance	• Does radiation increase equilibrium tritium pressure?	• Identify discrepancy between predicted and observed permeation • Better TPBAR permeation predictions	• Separate-effects test in radiation environment • TMIST-3
Carbon transport	• Where does it come from? • Where does it go? • How does it get there? • Does it affect permeation?	• Better TPBAR permeation predictions • Differences observed in LTA vs C6 vs C9 PIE	• C9 Rod 4 PIE • C11 PIE • C12 LUA • TMIST-3 • Future LUA
TPBAR failure diagnosis and consequences	• How would a failed TPBAR manifest itself? • What are the consequences for reactor operation? • How would a failed TPBAR be handled? • Can the chance of failure be reduced?	• Operational impact to WBN1 • Economic impact to TVA/NNSA • Programmatic risk going forward	• Analysis of failure scenarios • Selected leach tests • Weld inspection system improvements • WBN procedure development
Enhanced tritium permeation barrier	• Could modified or alternate barrier reduce permeation?	• Permeation improvement regardless of mechanism • Could reduce fuel costs	• Future separate-effects tests • Future LUA