MDO-723-0048
December 9, 2005

The Manager
Schenectady Naval Reactors Office
United States Department of Energy
Schenectady, New York

Subject: The Evaluation of Lithium Hydride for Use in a Space Nuclear Reactor Shield,
Including a Historical Perspective, for NR Information

References: (a) NRPCT Letter: MDO-723-0049/B-MT(SPME)-22, to be issued
(b) Disney, R.K., "Status Report on the SP-100 Program Investigations of
Irradiation-Induced Swelling of Lithium Hydride Shield Materials," SP-GES-
93-0005, 1993
(c) Welch, F.H., "Lithium Hydride Technology: III. Properties of Lithium Hydride
For SNAP Shielding Applications," NAA-SR-9400, May 1, 1967

Enclosures: (1) A Perspective on the Use of Lithium Hydride in a Space Nuclear Reactor
Shield
(2) Summary of Lithium Hydride Material Performance and Issues in a Space
Nuclear Reactor Shield

Dear Sir:

This letter provides a summary of the Naval Reactors Prime Contractor Team (NRPCT) evaluation of lithium hydride (LiH) as a space reactor shield material. Furthermore, this letter is intended to aid future researchers studying LiH as a shielding material. This letter is submitted for NR information, and completes the NRPCT Prometheus Closeout Customer Commitment number 25209.

Summary:

LiH was one of the five primary shield materials the NRPCT intended to develop (along with beryllium, boron carbide, tungsten, and water) for potential Prometheus application. It was also anticipated that ¹⁰B metal would be investigated for feasibility at a low level of effort. LiH historically has been selected as a low mass, neutron absorption material for space shields (Systems for Nuclear Auxiliary Power (SNAP), Topaz, SP-100). Initial NRPCT investigations did not produce convincing evidence that LiH was desirable or feasible for a Prometheus mission due to material property issues (primarily swelling and hydrogen cover gas containment), and related thermal design complexity. Furthermore, if mass limits allowed, an option to avoid use of LiH was being contemplated to lower development costs and associated risks. However, LiH remains theoretically the most efficient neutron shield material per unit mass, and, with sufficient testing and development, could be an optimal material choice for future flights.

Literature was compiled and reviewed on various material properties of LiH, and its behavior under irradiation was investigated. An in-depth assessment of pre-1960s SNAP and Aircraft Nuclear Propulsion (ANP) irradiations revealed a pattern that cast (melted) and “out-gassed” (baked-out to remove gas) LiH showed superior irradiation swelling performance compared to cold pressed LiH that was not out-gassed. The presence of LiOH as an impurity in a pre-irradiated condition appears to be a cause of swelling, but other factors, like microstructural changes in cast LiH may be involved as well. Quantum mechanical studies of LiH irradiation are in process to explore this theory, and will be reported in final form in Reference (a). A further finding was that SNAP and ANP studies contained information that was not detailed in SP-100 reports (Reference (b)). A summary of this information is included herein as well as an annotated bibliography of several key documents.

Background:

Research dating back to the late 1940's has focused on irradiated material properties of LiH. SNAP, ANP, and SP-100 programs researched various LiH processing techniques (cast, cold pressed, etc.). A total of about fifty mixed neutron and gamma tests were performed in support of these programs that covered a broad range of temperatures and neutron doses, as well as several gamma irradiation tests, and tritiated (self-irradiating) tests. Conclusions from these tests indicate that swelling of LiH under irradiation remains a key uncertainty. Many of these tests were judged to be “failures,” including ruptured or leaking test capsules, excessive LiH swelling, or other issues; however, many were also judged to be “successes” (no swelling or other obvious damage). The successes as well as failures were studied by the SNAP and SP-100 programs. There appears to be interesting patterns in the performance of LiH related to process conditions that might be exploitable in future LiH materials development and testing.

Discussion:

Lithium hydride was among five “primary” materials planned for continued development. Due to design and material uncertainties, LiH and H₂O were maintained as competing hydrogenous material alternatives (see Reference (a)). The other three primary materials, beryllium, boron carbide, and tungsten were less developmental, and therefore less controversial. Isotopically enriched boron (¹⁰B) was identified as a promising emergent material, but hadn't received significant review at the time of the project redirection. Enclosure 1 provides a perspective on the various choices made for, and issues associated with, LiH.

In the case of LiH, irradiation-induced swelling appeared to be the key material uncertainty. There was also a judgment that significant research into a hydrogen containment system may be necessary to assure success of a LiH shield. Enclosure 2 provides: a summary of LiH research performed; a description of the historical research (SNAP, ANP, SP-100 and other studies) as well as new analysis of those efforts; quantum mechanical modeling results; an annotated bibliography; and a summary of an intended testing approach to supplement existing LiH data.

Summary of Findings

An analysis (including a statistical meta analysis) of historical mixed neutron and gamma irradiation tests identified that cast LiH or cold-pressed and (pre-irradiation) out-gassed LiH was unlikely to swell (many tests at various temperatures and fluences reported no swelling), whereas cold-pressed LiH without out-gassing was much more likely to swell. The results of this analysis led to consideration of, and planning for, conducting lower dose rate gamma testing, as well as mixed neutron and gamma testing at various doses and dose rates.

Gamma-induced swelling of LiH appeared to be a function of dose and dose rate, with SP-100 researchers measuring swelling up to 25% at doses and dose rates higher than expected in Prometheus (~20 times and ~1000 times, respectively). SP-100 used cold-pressed LiH, apparently without out-gassing, and all of the B-2A Test Series specimens tested in a mixed

neutron and gamma environment swelled considerably (~10 – 20%, with higher temperature specimens swelling less). Literature (References (b), (c)) concludes that swelling is gas-driven (hydrogen).

A common impurity in LiH is LiOH (often formed on the surface of LiH due to humidity), that subsequently reacts with LiH to form Li_2O and H_2 . This reaction may be increasing hydrogen inventories in LiH samples (especially samples made from LiOH contaminated LiH powder) during testing, accelerating swelling—opinions differ, and could not be resolved due to redirection of the Prometheus project. Alternatively, casting or out-gassing may be affecting LiH microstructure in ways that have not been reported in the open literature.

In addition to investigation of less accessible literature sources, “out of pile” testing was being considered as a next step in the development of LiH. The intended focus was on evaluation of the role of casting, out-gassing, and LiOH impurity in irradiation induced swelling prior to any further irradiation testing. Out-of-pile testing is judged to be high value and relatively inexpensive compared to irradiation testing. Further, fundamental (atomistic and quantum mechanical) modeling was planned to proceed concurrently with testing. Work of this nature is believed to have the potential to save significant time in development of LiH. Due to redirection of the Prometheus project, testing required to understand LiH irradiation performance was not pursued.

Conclusions:

LiH is a promising, although not fully understood, space reactor shield material, and should continue to be considered as a potential material for future applications. However, sufficient lead time is required to retire both material uncertainties, and design risks (thermal & nuclear).

A significant amount of research is documented in the historical record, including approximately fifty mixed neutron and gamma irradiations, and several gamma irradiation programs, and yet irradiation-induced swelling behavior of LiH remains uncertain. Additional risk and uncertainty may be retired by further investigation into less accessible literature sources that were not part of this investigation. The SNAP/ANP studies showed many successful cases where LiH did not swell as well as many failures. Patterns in swelling behavior were observed, but specific causative factors were not conclusively identified. Future research is required to complete these studies and qualify LiH for long-duration space shield use. However, it was found from these studies that pre-irradiation out-gassing, and fabrication by casting were strongly correlated to mixed gamma-neutron tests that did not show LiH swelling.

Concurrence and Acknowledgement:

The Manager, Space Materials (Simonson), the Manager, SPP Space Power Plant Systems (Schwartzman), the Manager, FSO-Shield Design Development (Collins), and the Manager, Space Plant Materials (Ohlinger) concur with this letter. Significant technical contributions to this letter were made by: Barri Gurau, Rose Lewis, Dr. Dean Poeth, and Dr. James Vollmer.

NR Action Requested:

This submittal is for information. No NR action is requested.

Very truly yours,

Brian Campbell, Manager
Fuel and Shield Technologies

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Enclosure 1 to MDO-723-0048:

**A Perspective on the Use of Lithium Hydride
In a Space Nuclear Reactor Shield**

**Author:
Brian Campbell**

**Reviewed by:
Barri Gurau
Rose Lewis
Dr. Dean Poeth**

The purpose of this enclosure is to provide insights to help future researchers understand key questions about lithium hydride (LiH) that they will face as they develop this material. Although no new LiH testing data was developed, LiH received the most study and debate of any shield material, and several observations were made during this analysis. This enclosure as well as Enclosure 2 were written with future space shield materials researchers in mind, as an attempt to save them time and resources, and both highlight the need to understand LiH thoroughly, and aid in the final choice of whether LiH is included in the shield.

The conclusions in this report are based on limited research, and therefore additional research, including testing and modeling will be needed to verify the conclusions and complete development of LiH as a space shielding material.

1. Future Work: One purpose of this report is to document the progress the NRPCT made in reviewing LiH as a potential shielding material for Prometheus application (Enclosure 2). Another purpose is to provide a jump start for future researchers that take up where these efforts left off. Future researchers into shield materials are encouraged to start by reading this report, but this document is by no means comprehensive, nor sufficient in itself to provide the knowledge needed to choose or qualify LiH as a shield material. However, this letter provides useful information, e.g., LiH material properties, and should help guide future researchers in their first steps. Although the NRPCT did not test LiH, a literature review was performed, including the SP-100 literature (Reference (a)) and a more in-depth review of the Systems for Nuclear Auxiliary Power (SNAP) and Aircraft Nuclear Propulsion (ANP) LiH irradiations testing than can be found summarized in the SP-100 summaries (Reference (b)). The NRPCT considers the SNAP/ANP research important to the development of LiH, and recommends future researchers study many of the early references in detail. To facilitate this review, a summary of several of these key documents is included in Attachment 9 to Enclosure 2.
2. Scope of This Document: This report focuses on LiH in a space shielding application, and contains all of the findings from the NRPCT on this material, with the exception that some further insights into LiH swelling will likely be in a follow-on report (Reference (c)). In particular, integrated swelling rate modeling results using quantum mechanical modeling inputs are expected to be included in Reference (c).
3. Basic Status of Shield Materials Efforts: Five or six shielding materials were planned to be developed for potential shielding application. At that time of Prometheus project restructuring, the three foremost notional shield concepts included: a layered beryllium (Be), boron carbide (B₄C) shield; a potentially lower mass (than the Be/B₄C shield) SP-100-analog Be/B₄C/tungsten (W)/LiH shield (with increased thicknesses of Be/B₄C relative to SP-100); and a variant of the lower mass shield with water (H₂O) substituted for LiH. In some cases, LiH caps (or some other form of additional local shielding aft of the piping runs) were potentially required to shield neutron streaming through the primary coolant pipes. Late in the studies, an all ¹⁰B shield concept was determined to have a competitive mass with the above concepts, and therefore was planned to receive increased materials engineering review—not completed. The five primary materials (Be, B₄C, W, LiH, H₂O) plus ¹⁰B supported the pre-conceptual shield designs listed above.
4. Historical Perspective: Lithium hydride was selected for space applications in all modern shield studies and applications (SNAP, TOPAZ, SP-100) except for Prometheus, which did not complete a shield material down-selection. The LiH literature reviewed to date is judged not to be sufficient to allow final design of a LiH-based Prometheus shield. In the SNAP and ANP cases, after about 47 neutron irradiation tests with mixed results (Reference (b)), an overall shield test was performed for 10,000 hours “satisfactorily.” However, the background materials

testing leaves many questions unanswered. It appears that prior space shield design, e.g., SP-100, were severely mass-limited (e.g., SNAP-10A was 102 Kg), and chose LiH for mass savings. The NRPCT (in conjunction with ORNL, J. Johnson-lead) identified several shield concepts without LiH that were of comparable (if higher) mass (References (d), (e)). However, the Prometheus project was restructured before detailed shield designs were performed, and such issues as pipe routing, structural and thermal designs could significantly affect the final selected materials. Further, mass targets were not finalized for the Prometheus shield, which may impact shield material selection.

5. LiH Material Properties: A detailed review of LiH material properties recorded in the literature was made and included in Enclosure 2. This should serve as a starting point for designers and materials engineers. The primary uncertainty in the literature was the extent of LiH swelling under irradiation—especially neutron irradiation. The mechanical properties of LiH in the literature were limited; however the NRPCT may not have uncovered all of the useful data available. Mixed neutron and gamma induced swelling was considered a critical property, since Reference (b) reported “growth” ranging from “No” to “Yes” and “~1%” in 47 neutron irradiation tests (other early neutron irradiation tests reported higher swelling), and Reference (a) reported ~10 - 25% under neutron irradiation in the B2A test, and 0% in the ARMF test. A superficial assessment of this information could lead a researcher to conclude that LiH could swell significantly under neutron irradiation. The NRPCT cautions future researchers to study these results in depth. A key question is why many of the tests did not swell at all. High dose and dose rate gamma irradiation testing also reported swelling up to ~25%. However, again, this needs to be reviewed in detail. The high dose rate tests may be irrelevant to the actual conditions in the shield (~1000 times lower gamma dose rate). Still, swelling could lead to shield rupture and failure if improperly predicted, or excess mass if the conservative maximum values are used. Or, LiH could be eliminated as a shield material for the wrong reasons, or chosen and applied without sufficient engineering analysis.
6. Gamma and Neutron Irradiation Testing History: Based on SP-100 summaries (Reference (a)) the “general impression” regarding LiH was that no useful neutron irradiation data existed, however, gamma irradiation data was available and indicated that 25% swelling was possible. This led the NRPCT to immediately begin searching for alternatives to LiH, and down-playing the likelihood of its use in Prometheus. This delayed the NRPCT investing the appropriate time in researching the SNAP/ANP studies and beginning LiH development until the SNAP/ANP summary Reference (b) was studied. In fact, Reference (b) reported 47 neutron irradiation experiments, and the worst case gamma irradiation swelling data was likely not applicable due to the dose rate being orders of magnitude higher than what was expected in the Prometheus shield. As for the 47 reported neutron irradiations, they were apparently sufficient to support the use of LiH in the SNAP flight shield despite numerous tests being “bad” (the definition of “bad” is not clear, but seems to be a composite judgment by F.K. Welch (Reference (b)) as to whether the results support the use of LiH in SNAP or not). The NRPCT judges that significant further neutron and gamma irradiation testing is required to support the use of LiH in the Prometheus shield. To facilitate this, copies are being preserved and summarized in Enclosure 2 for future researchers to lessen the chance that this valuable information is overlooked or lost. As for the results from studies of the SNAP/ANP irradiations (both standard literature reviews, and a statistical “meta analysis”), certain correlations appear to exist concerning swelling, out-gassing of samples prior to irradiation or fabrication using the casting approach, and gas evolution during irradiation. These subjects are discussed herein.
7. Design And Materials Are Highly Interdependent: Three (Be, B₄C, and W) of the five primary materials for use in the Prometheus shield are believed to be relatively well characterized in thermal and physical properties, as well as behavior in an irradiation environment. Some

confirmatory irradiation testing should be completed before calling these materials qualified, but the NRPCT did not believe this was a high priority relative to H₂O or LiH. The hydrogenous materials, LiH and H₂O were considered unqualified at the end of the Prometheus work, with extensive testing necessary for qualification—especially if the H₂O contained dissolved poisons to improve thermal neutron absorption in the poison relative to the hydrogen to reduce gamma production and gamma shield mass. The scope and duration of the tests needed to ultimately select and qualify either LiH or H₂O were strongly dependent on the detailed design of the shield. For instance, if shield temperature was expected to be 600K or higher, H₂O would likely be non-competitive due to high pressures requiring a higher mass pressure vessel, whereas LiH might be in a minimum swelling range. Conversely, if temperature was expected to be 300 - 400K, H₂O might be advantageous due to potentially lower development and overall shield costs—and possibly mass. Since (1) prediction of the shield temperature is very difficult, (2) designs were fluid at the time of close out, and (3) the risk existed that either LiH or H₂O might not qualify for the Prometheus application, the NRPCT planned to develop both materials. If secondary systems such as coolers, heaters, piping, instrumentation, pumps, etc. were required for either H₂O or LiH, the extra mass and reliability issues would need to be considered. Conversely, shield designs without either LiH or H₂O were being considered, since both hydrogenous materials introduced developmental risks. Two contenders were: a Be/B₄C shield, and an “all” ¹⁰B shield, both with W gamma shielding. In the latter case, the idea was to simply make the shield from solid ¹⁰B metal with W, if required, for gamma shielding. There was consensus that if mass limits were met without LiH or H₂O, the risks of shield failure would be lower without them, and therefore they would likely be eliminated.

8. Temperature Range — Adequacy of 600 to 800K LiH Operational Range: One of the key questions about the use of either water or LiH in the shield is the temperature range that the designers must stay within. In the case of B₄C, W and ¹⁰B, temperature restrictions should not limit the shield design. Although not confirmed, Be was suggested as having a temperature limit in the vicinity of ~823K, but that may have been for structural applications. Peak shield temperatures were expected to be below 700K for all of the shield concepts discussed above. In the case of water, on the low end, temperature is limited by freezing and the necessary accommodations for the volume expansion. If freezing was to be avoided prior to start up of the reactor, an auxiliary heating system may have been needed. On the high end, the pressure of the saturated steam rises quickly with temperature above 450K. The higher the pressure, the higher the stresses on the containment system, which might require a thicker, higher mass, pressure vessel. Further, the H₂O pressure vessel would need to accommodate a relatively complicated corrosion environment for the life of the Prometheus shield. A certain minimum pressure vessel thickness would be required to handle launch loads; that thickness would handle some amount of pressure, and allow a certain maximum temperature without mass penalty. This was expected to be the case for Prometheus. Lithium hydride was believed to also require canning to prevent the thermodynamic and radiolytic conversion to Li metal, however, the pressure load on the vessel was expected to be negligible compared to the launch load. From the SP-100 summary (Reference (a)), the LiH was required to remain within the 600 to 800K temperature range, apparently based on the gamma irradiation data, which shows that gamma-induced LiH swelling drops abruptly at about 600K (Enclosure 2). The apparent focus on the gamma irradiation data (and resultant selection of a 600 to 800K temperature range), coupled with the assumption that the swelling under gamma irradiation represents the swelling under neutron irradiation, is judged to be inappropriate. SP-100 was performing mixed neutron and gamma irradiation testing at the time of close out to verify this. A future action is to explore the gamma irradiation performance below 600K to better characterize the effects of dose rate, dose, and composition/processing on swelling, as well as a full suite of neutron irradiations, likely using pre-irradiation out-gassed or cast stoichiometric LiH with minimal LiOH contaminate. The goal was to open the temperature range below 600K to

increase the design space and reduce the potential mission risks if temperatures were mispredicted or varied (e.g., low power coast mode), as well as complete the understanding of LiH swelling under mixed neutron and gamma irradiation.

Based on analyses of the information provided from the SNAP program underway during the Prometheus close out phase, it is not clear to the NRPCT that the gamma irradiation data, or the 600 – 800K temperature range (Reference (a)) makes sense or is relevant. The 47 neutron irradiations (most being mixed neutron and gamma irradiation due to typical test reactor conditions) during SNAP/ANP showed evidence (must be verified) of no swelling under varying neutron doses and temperatures, especially for “out-gassed” or cast LiH specimens¹ (discussed below). Since there is mixed gamma and neutron irradiation going on in any critical reactor irradiation test, this may indicate that the gamma-only irradiation testing is suspect; and therefore operating conclusions drawn from it (e.g., the 600K lower temperature limit) would be equally suspect.

9. Cast, Cold Pressed or Cold Pressed and Out-Gassed LiH: The SP-100 program chose cold pressing as the preferred method for fabricating the LiH portion of the shield--which allowed them to achieve a uniform 2% free lithium concentration in the fabricated LiH. Y12 performed the sample fabrication using supplies of “tails” from their in-house efforts. Cold pressed samples were also presumably readily machinable by Y12. No mention is made in Reference (a) about the chemistry of these samples, in particular, the LiOH content. Although initially presuming that cold pressed and sintered LiH was preferred for Prometheus, at the time of close out the NRPCT was not convinced of this from either a cost or performance standpoint. It appears from the SNAP research that cast LiH could be preferable from a swelling standpoint, and if not cast, out-gassing (or sintering) seemed very important. Reference (b) reported that the “full shield” 10,000 hour test using a cold pressed and out-gassed LiH slab did not grow after $\sim 2.5 \times 10^{18}$ n/cm² fast fluence. Further, casting could potentially accommodate piping runs and complex surfaces without expensive machining operations. However, if the cast LiH surface was flush against the shield walls, swelling could be more problematic.

A deeper understanding of the costs and performance benefits of cast versus cold pressed, or cold pressed and out-gassed or sintered LiH is warranted. ORNL (Reference (f)) had also suggested hot pressing LiH samples as an alternative. The observation that the SNAP cast LiH could be preferable (have lower swelling) to the pressed alternative may be related to the presence of LiOH impurities in some of the pressed samples, the implicit purification during the casting process, or microstructural differences.

10. 2% Free Lithium or Stoichiometric: It is not clear that the SP-100 choice of including 2% free Li in the LiH was beneficial from a performance or cost standpoint. Fabrication of LiH samples with the deliberate addition of 2% Li is believed to be more expensive than not adding the metal. However, assuming the LiH remained below the melting point (~ 960 K), the NRPCT did not find any reason to deliberately add Li metal to the LiH, with the following exception. During the SNAP cast shield research, final cast LiH still included some minor cracks (Reference (b)). The SNAP researchers filled these in with Li metal, and reported that thermal conductivity and other properties improved.

The issue of thermal migration should also be considered. The NRPCT believed that sub-stoichiometric LiH was subject to thermal migration of hydrogen down the temperature gradient—whereas stoichiometric LiH was not. This could lead to the formation of a lithium phase at the hot side, which could result in expansion, reduced shielding effectiveness, and

¹ There were also samples that swelled, or were “bad.” However, if the “out-gassed” or cast samples are focused on, the above observation becomes apparent, if still unproven.

enhanced corrosion of the canning. As a simplistic example, in the classic shadow-shield, where the volume of “hot” LiH could be much smaller than the volume of “cold” LiH, thermal migration might be a serious issue, depending on LiH temperature gradients.

At the time of project close out, the NRPCT was not convinced that adding free Li was desirable, even at a cost savings, and intended to focus on stoichiometric LiH testing.

11. Natural Li versus Isotopically Enriched LiH: Studies were made of LiH shields with either more or less ^6Li than natural. Generally, some benefit in mass was obtained by changing the isotopic enrichment, but there did not appear to be justification to deliberately alter the enrichment from a performance versus cost standpoint. Again, if a source of isotopically modified LiH was available at low cost, shield studies should consider using it by performing trade studies. Otherwise, the NRPCT was intending to pursue materials testing on natural LiH. Further, should an isotopic form of Li be considered, which requires special security measures, e.g., special nuclear material controls, then those costs would need to be factored in, and could be overwhelming. Future researchers are cautioned to verify the isotopic content of any LiH they purchase, since there is some indication that recycled LiH depleted in ^6Li may be in the commercial market. Use of LiH depleted in ^6Li is feasible, but at both a cost, if enrichment is required, and mass penalty. Li could be enriched sufficiently in ^7Li to reduce the radiolytic decomposition rate due to the ^6Li (n, alpha) ^3H reaction, but this would increase the hydrogen capture gamma source and gamma shield mass required.
12. Selection of LiH as a Potential Shield Material: The NRPCT Shield Materials Down-Selection: NRPCT shield material screening efforts progressed to the point where a down-selection to a set of primary materials was planned (discussed in Reference (c)). Efforts to screen several promising alternate materials (e.g., ^{10}B metal) were planned to continue, but at a relatively low resource level, allowing focus on qualifying the primary materials. Reference (d) indicated that the shields containing hydrogenous materials seemed to be lower mass than the ^{10}B or other alternatives, however, mass limits had not been established for the shield at the time of Prometheus restructuring. The primary materials were expected to be sufficient to design Prometheus shields—excluding structural and insulating materials, which were not addressed in any detail. The NRPCT intended to proceed with development of: Be, B_4C , W, LiH, and H_2O , possibly with dissolved neutron-poisons. The material recommendations and general scope are summarized in Reference (c).

References:

- a) Disney, R.K., “Status Report on the SP-100 Program Investigations of Irradiation-Induced Swelling of Lithium Hydride Shield Materials,” SP-GES-93-0005, 1993.
- b) Welch, F.H., “Lithium Hydride Technology: III. Properties of Lithium Hydride For SNAP Shielding Applications,” NAA-SR-9400, May 1, 1967.
- c) NRPCT Letter: MDO-723-0049/B-MT(SPME)-22, to be issued.
- d) Bucholz, J.A., Blakeman, E.D., Johnson, J.O., “Radiation Transport Analyses to Support the Reactor Shield Materials Selection,” ORNL/LTR/NR-PROM1/05-21, August 10, 2005.
- e) Yugo, J.J., “Multi-layer Radiation Shield Optimization Studies and Simulations,” ORNL/LTR/NR-JIMO/05-03, February 4, 2005.
- f) Snead, L.L., Metals & Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, TN, personal communication, February 2005.

Enclosure 2 to MDO-723-0048:

**Summary of Lithium Hydride Material Performance and Issues
in a Space Nuclear Reactor Shield**

Authors:

Brian Campbell

Barri Gurau

Rose Lewis

Dr. Dean Poeth

Reviewed by:

James Nash

1. Introduction

This document summarizes the work completed in reviewing lithium hydride performance for the Prometheus shield application. The following attachments are included capturing additional information.

- Attachment 1 - LiH Material Properties for Project Prometheus
- Attachment 2 - Early (Pre- SP-100) Irradiation Experiments
- Attachment 3 - Meta Analysis of Early Irradiation Experiments
- Attachment 4 - SP-100 Irradiation Experiments
- Attachment 5 - Atomistic and Mechanistic Modeling of Irradiation Induced Swelling of Lithium Hydride
- Attachment 6 - X-ray Irradiation Testing of LiH
- Attachment 7 - Shield and Reflector Irradiated Materials Testing Laboratory at ORNL for Project Prometheus
- Attachment 8 - LiH Containment System
- Attachment 9 - Annotated Bibliography of LiH Related Resources

2. Background

Lithium hydride (LiH) has been selected as the shield material of choice on several previous space programs. The United States of America has investigated the use of lithium hydride in the shield on three major projects: the Aircraft Nuclear Propulsion Program, Systems for Nuclear Auxiliary Power, and the SP-100 Program. The Union of Soviet Socialist Republics (USSR) flew at least 30 TOPAZ-I systems that included lithium hydride reactor shields. Prior to the Prometheus program restructuring, the Naval Reactors Prime Contractor Team (NRPCT) was considering LiH, as well as Be, B₄C, W, and H₂O as primary shield material candidates. Several shield designs including a combination of these five materials were being evaluated for their ability to achieve design goals (e.g., attenuation, mass, etc.) and their ability to be manufactured.

The Aircraft Nuclear Propulsion (ANP) Program was operated by General Electric and contracted by the United States Atomic Energy Commission (USAEC) and the United States Air Force (USAF) from 1951 through 1961; a summary of the key milestones for the ANP Program are depicted in Figure 1. The use of a nuclear propulsion system for an aircraft had the potential to provide virtually unlimited range. The ANP power-plant concept included a direct air cycle turbojet, which included a lithium hydride shield (Reference (a)).

Figure 1: Summary of General Electric Aircraft Nuclear Propulsion Program

The shield work began in 1956, which focused on selecting an efficient neutron and gamma shielding material based on the per unit weight and its capability of high temperature (755-1144 K) operation under the thermal, mechanical and nuclear environment associated with the direct-cycle reactor power plant. LiH was selected by the ANP program as the primary shield material because of the combination of a high hydrogen density ($\sim 5.87 \times 10^{22}$ H atoms/cc), high melting point (~ 956 K), low density (~ 0.775 g/cc), high absorption cross section, and low molecular weight; all of which are ideal for use as a low mass, high efficiency neutron shield.

The ANP program performed fabrication studies on hot pressing, cold pressing, casting, sintering, and machining of lithium hydride. They also investigated metallic matrix materials to improve the strength and thermal shock resistance of the lithium hydride compact. Materials properties were investigated; the results of some of the experiments are discussed herein (Section 3). Chemical studies were performed to identify the handling requirements for LiH and compatibility with potential canning/structural materials. When the project was concluded, Baxter and Welch judged that lithium hydride had progressed to the point where shield sectors could be fabricated and the behavior under anticipated conditions could be predicted (Reference (a)).

The Systems for Nuclear Auxiliary Power (SNAP) program was initiated by the USAF in 1956, which included both reactor and radioisotope heat sources. The SNAP program included six reactor programs and several isotope programs. The first major milestone in the reactor programs was the

SNAP experimental reactor (SER) achieving criticality in 1959, just three years after inception of the program. The SNAP program continued on a similar pace, which included the launch and space operation of the flight system of SNAP-10A. In 1973 the last of the SNAP programs was terminated. Figure 2 depicts the major reactor systems and their respective power levels of the SNAP programs.

Figure 2: United States Space Reactor Power Trends (Reference (b))

Leading up to the launch of the LiH shield on SNAP-10A (45kW thermal power, 10,000 hour ground shield test), the program investigated the physical, chemical, mechanical, and nuclear properties, as well as the corrosive effects of lithium hydride. Several compositions (enrichment, addition of free Li, etc.) and forms were investigated for benefits. Since the SNAP reactors were designed to be maintenance free, hydrogen migration studies were performed to understand the requirements for maintaining a hydrogen partial pressure over the shield. Furthermore, shock and vibration and thermal cycle testing were performed on numerous shield assemblies. Welch (References (c) - (g)) summarizes the SNAP program, and some testing performed by ANP. These were by far the most extensive LiH development programs to date.

The lithium hydride shield, shown by Figure 3, was positioned directly below the reactor vessel and was contained in a stainless-steel casing to prevent hydrogen loss. A flexible mount was provided in the shield to support the lithium-hydride mass within the casing and enabled pre-launch thermal cycling of the system during thermal-vacuum acceptance testing. The choice of lithium hydride was based on available attenuation data and weight considerations. The shield assembly used a cold-pressed lithium hydride shielding material reinforced with stainless steel honey-comb. The shield was designed to withstand ten full thermal transients simulating reactor startup conditions with a maximum temperature of 712K at the attachment to the system support structure and a minimum temperature of 579K at the surface exposed to space. The shield assembly weight was 102 kg.

The development program demonstrated the adequacy of the shield design and established the effectiveness of the material for neutron attenuation through a series of neutron shielding experiments. The qualification test program demonstrated the integration of the shield and reactor structure attachments during launch shock and vibration loads and the ability of lithium hydride and

stainless steel honeycomb to withstand the radiation induced swelling and the thermal environment expected during orbital operation. The flight test data verified the significance of the scattering contribution to the total irradiation level for the shield design (Reference (h)).

Figure 3: SNAP-10A Reactor and Shield (Exploded View)

SP-100 Space Reactor Program was started in 1983 by NASA, DOE, DOD and DARPA (Defense Advanced Research Project Agency). Objectives of the SP-100 program included a focus on nuclear safety, evaluating the need for space nuclear power systems, developing space nuclear technology to fulfill military and civilian space applications, and initiating long range developmental efforts. Performance goals of the SP-100 reactor included 100 kW_e power output with 7 years full power operation with a physical constraint of 3000 kg (References (i) and (j)). A 1991 schematic drawing of the SP-100 reactor and shield is shown in Figure 4. The SP-100 Program was ended in 1993 due to a shift in funding.

Figure 4: SP-100 Reactor and Shield Schematic (circa 1991)

TOPAZ-I systems were initially created as a new generation of Ocean surveillance satellites, which included a LiH shield (Reference (k)). The USSR has launched over 30 nuclear reactor powered satellites from 1967 through 1988. The lifetime of the spacecraft ranged from 1 day to ~1 year (Reference (l)).

Each successive United States space reactor program made advances on lithium hydride. However, the SNAP program, which had the largest budget and the longest amount of time, provided the most significant progress. The NRPCT has studied the three previous space nuclear propulsion programs to build upon their knowledge of lithium hydride.

The NRPCT continued the study of the use of LiH in Prometheus shields including comparing LiH to several alternatives (e.g., rubbers, oils, plastics, water, carboranes, etc., Reference (m)). The NRCPT was considering several configurations and combinations of the hydrogenous (LiH and H₂O), non-hydrogenous (Be, B₄C), and high-Z (W) shield materials, as shown in Figure 5. Figure 6 displays a Prometheus shield concept next to the Prometheus gas-cooled reactor concept. Reference (n) provides further information on the Prometheus pre-conceptual shield design.

Figure 5: Early Pre-conceptual Prometheus Reactor Shield Configurations

Figure 6: Prometheus Reactor and Shield Assembly

3. Lithium Hydride Material Properties

Attachment 1 to this letter provides material properties for lithium hydride (LiH). A significant amount of literature review and analysis was performed to gather LiH material properties to support reactor design. To the extent possible, the available data, NRPCT-recommended equations, and competing equations are provided. However, more work remains to be done, both in terms of literature review and analysis to identify further data, and most importantly, further testing to generate new data. Two properties were not discussed in Attachment 1, due to lack of information: yield strength of LiH and Poisson's ratio of LiH. Some information is available related to the desired form and composition of LiH; however, it is not included in Attachment 1, which was originally created as a response to a design community request (Reference (o)) to provide material properties for beryllium, beryllium oxide, isotopically enriched boron carbide ($^{11}\text{B}_4\text{C}$) and lithium hydride to support reactor design efforts. Section 3.1 addresses whether stoichiometric LiH or LiH with 2% free lithium is desirable. Section 3.2 addresses whether enrichment of the lithium should be considered.

Since the majority of the data presented in Attachment 1 was obtained from open source literature, the measurement uncertainties in the data are not quantified. For example, it is commonly understood that the measurement uncertainty associated with thermocouples alone can be ± 0.5 to 1.0% . These and other uncertainties are not accounted for specifically in data presented herein. Statistical analysis and review included linear regression and curve-fitting techniques for the raw data, which provides some confidence, but is not a replacement for full understanding of the experiments. Therefore, the pedigree of the data is unknown. Since the recommended equations were generated using all available data from the literature, additional data may be required to validate these equations and relationships.

Prior to restructuring of the project, government approval to fabricate lithium hydride specimens for shield materials testing (Reference (p)) was obtained (Reference (q)). The primary goal of this testing was to determine the swelling properties of LiH; however other properties would be tested as well. Additionally, the NRPCT was investigating the applicability of quantum mechanical modeling and its ability to help in the understanding of swelling mechanisms. These results are included in Section 7. Both testing and analysis were expected to reduce the uncertainty associated with the use of lithium hydride.

The information provided in Attachment 1, has not been validated and is not sufficient to support final reactor design. Equations and correlations presented herein are not considered to be adequately qualified to be considered a final design basis. The material properties provided in Attachment 1 were independently checked, which included review of the calculations, methods used, and technical content. The information in Attachment 1, and generally included throughout this document, can be used in early analyses and pre-conceptual designs.

3.1. Stoichiometry

The four factors investigated to explore the benefit of adding free lithium to LiH were: pressure within the containment system, thermal conductivity, hydrogen migration, and corrosion. SP-100 chose to include 2% free Li in the LiH (Li/LiH), which was considered beneficial from a performance standpoint (Reference (r)). Nominally, the NRPCT was intending to study stoichiometric LiH. At the time of the project restructuring, this difference was not resolved.

3.1.1. Pressure

Reference (r) states that the presence of free lithium minimizes the partial pressure of hydrogen, and thereby reduces the can thickness and the amount of hydrogen lost by diffusion through the containment system. This was not expected to be the situation for a Prometheus shield. The LiH

minimum canning thickness for the Prometheus shield was expected to be dictated by launch load stresses, with the hydrogen pressure induced stresses likely negligible.

3.1.2. Thermal conductivity

Thermal design and management of the shield is difficult. SP-100 assumed a temperature range of 600-800K. Temperatures greater than 600K minimized gamma-induced swelling (and possibly neutron-induced swelling as well). Temperatures less than 800K minimized canning hydrogen pressure and thermally induced dissociation/swelling. The thermal conductivity, as seen in Figure 7 (References (s), (t) and (u), discussed further in Attachment (1)), increases with the addition of 2% free lithium. The benefit (relative to increasing thermal conductivity) due to the addition of free lithium is small (< 15 %) at 600 K and reduces with increasing temperature. Therefore, depending on which temperature limit the shield is closer to, additional free lithium can either enhance or exacerbate the thermal design.

Figure 7: Thermal Conductivity of LiH and LiH + 2%Li

At the time of issuance, it was not clear that the lower temperature limit of 600K was relevant to mixed neutron and gamma irradiated LiH. SP-100 appears to have chosen this limit based on gamma irradiation data, which the NRPCT believes may be irrelevant when ANP and SNAP neutron irradiation data is considered (Section 10). The irradiation effects on LiH thermal conductivity are unknown.

3.1.3. Hydrogen Migration within LiH

The advantage of LiH as a neutron shield material is dependent upon the total amount of hydrogen present and the uniformity of the hydrogen distribution. Since in sub-stoichiometric LiH hydrogen migrates against the thermal gradient leaving the hot regions depleted in hydrogen, the effectiveness of the LiH is directly related to the amount of free lithium present.

Hydrogen migration in non-stoichiometric LiH can potentially create streaming paths and/or less effective neutron shielding material. Consider a monolithic LiH with 2% Li shield. The thermal gradient induced by the reactor (along the axis of the shield) will cause the hydrogen to migrate to the colder

regions of the shield, as shown in Figure 8. The region closest to the reactor becomes less effective allowing neutrons to penetrate further into the shield and create gamma sources further into the shield. Complicate the same monolithic shield with coolant pipes running along the outside of the shield. The regions surrounding the pipes will be heated by the coolant, creating a radial thermal gradient. This could lead to an increased amount of the Li phase in the LiH, which is a less effective neutron moderator than LiH, potentially leading to a streaming path around the coolant pipes. Reference (e) provides an analysis of neutron streaming relative to the pipe configurations. The pipe configuration must be optimized to minimize the shield mass and still meet attenuation requirements, while meeting the thermal-hydraulic requirements of the reactor plant.

Figure 8: Potential Thermal Induced Migration Scenarios

Welch (Reference (e)) performed hydrogen migration studies, which concluded that the maximum change in H_2 concentration by thermal diffusion using dissociation pressure data is the percent of material not LiH. Therefore, if 2% free lithium were added, 2% of the hydrogen from the hot regions would seek to form stoichiometric LiH in the cold regions, leaving the hot region depleted in hydrogen. From a conservation of mass standpoint, if a large volume of sub-stoichiometric LiH is subject to a large thermal gradient, and the hot volume is small relative to the cold volume, a significant amount of Li metal phase may be created in the hot zone. This could lead to swelling (due to density differences), enhanced corrosion, or other detrimental effects. A region without the scattering capability of hydrogen can potentially lead to neutron and gamma dose limits being violated behind the shield.

3.1.4. Corrosion

Corrosion of the shield containment material(s) is a concern, especially with the inclusion of free lithium. SP-100 performed long term compatibility testing of LiH and Li/LiH with stainless steel. The degree of attack varies with temperature and Li stoichiometry, as displayed in Figure 9 (Reference (v)). Significantly more chromium and molybdenum leaching occurs with the presence of free lithium. However as Figure 9 shows, the rate of attack of stainless steel is low.

Figure 9: Corrosion of Stainless Steel with LiH Exposure

3.2. Enrichment of LiH

The SNAP program considered enriching the lithium hydride to improve the thermal management of the shield. Natural lithium ($^{\text{Nat}}\text{Li}$) is nominally comprised of ~7.59% ^6Li and ~92.41% ^7Li . Even though ^6Li is the minority component, the majority of the neutron captures occurs in ^6Li due to its large thermal neutron absorption cross-section (941 barns) (Reference (w)). Each ^6Li neutron capture produces a 2.1 MeV alpha-particle and a 2.7 MeV tritium, which results in a significant amount of heat (Reference (x)).

The impact of substituting ^7Li for $^{\text{Nat}}\text{Li}$, such that the LiH is composed of 99.99% ^7Li was evaluated. The thermal neutron absorption cross-section decreases from 71 barns for natural Li to 0.045 barns for ^7Li . The majority of the neutron captures in the lithium still occurs in the residual ^6Li , but is reduced by a factor of 750, reducing the heat generation due to the lithium neutron capture. However, the amount of neutron captures in the hydrogen ($\sigma_a=0.33$ barns) increases. Each hydrogen neutron capture produces a 2.23 MeV gamma. The increased gamma production eliminates one of the major advantages of natural LiH as a neutron absorption material, the near absence of capture gammas (Reference (c)). Additionally, the substitution of ^7Li for $^{\text{Nat}}\text{Li}$ increases the mass of the shield due to the higher mass of the ^7Li atom and the increased gamma shielding requirements, which may prove to be significant. Therefore, the benefits of ^7LiH do not appear to outweigh the disadvantages.

Reference (y) explored the potential Prometheus shield mass benefits of enriching the LiH in ^6Li . Generally, the mass of the shield (actually, a slab approximation of a shield) was lower than for natural LiH, however, only marginally so. The potential costs associated with enriching LiH in ^6Li could far out weigh the benefits, especially if the enrichment exceeds limits for classifying the material as a "special nuclear material."

4. Early (Pre SP-100) Irradiations

Lithium hydride performance in a radiation environment has remained a puzzle to researchers and scientists for decades. In many instances, prior experiments performed to characterize irradiation behavior were poorly designed, became contaminated, or the results were inconclusive (see Attachment 2). The judgment that the number of failed experiments should be interpreted as

indicating that “no reliable neutron irradiation data exists,” may be correct in the sense that a qualified set of neutron irradiation material properties does not exist, however it is flawed in the sense that key insights can not be gained from this prior research. In fact, the NRPCT judges that the ~47 SNAP (and earlier) neutron irradiations are highly valuable sources of insight into LiH’s suitability as a shield material. Based upon the compilation of ANP, SNAP, and SP-100 test results, atomistic (quantum mechanical) analysis, and the meta analysis (described in Attachment 3), several theories can be formed with some evidence (albeit not overwhelming) to support them. These insights are significant, and should form the starting point for both qualitative judgments on the suitability of LiH, and test programs to complete the qualification.

1. Out-gassing¹ specimens lessens or eliminates swelling.
2. Swelling is gas driven, i.e., gas build-up in the LiH, possibly related to LiOH presence, drives swelling.
3. Cast specimens evolve² less gas during irradiation than cold-pressed specimens--possibly due to 1 and 2 above.

Statistical significance can be found for the relationship between the color of the specimen (blackened) and growth as well as growth and gas evolution during irradiation. The correlation between growth and gas evolution is consistent with observations 1-3 above. The blackening is the result of color center formation due to radiation damage (Reference (z)).

These observations are based upon the potential performance indicators listed by Welch in Table 1 (reproduced from Reference (e) minus a few columns) [growth, blackening, and “results” of the experiment (a “good” or “bad” judgment by Welch, apparently depending on whether or not swelling, spallation, or other gross deterioration occurred)]. In addition to the compilation of information, Welch provides his observations and opinions on what the data implies (Reference (e)).

Out-gassing specimens prior to irradiation produces less swelling. It is not clear how this works. On a simple level, gas might be removed from the LiH, and therefore is no longer present to expand and drive swelling. Perhaps more likely, however, is that out-gassing removes LiOH, which is believed to evolve hydrogen through a chemical reaction with LiH. The evolved hydrogen can contribute to the swelling during irradiation if it is trapped within the LiH. The process by which LiOH is thought to be removed is given in Equation 1. LiOH might also simply escape un-reacted as a gas.

Baxter (Reference (a)) performed out-gassing studies. “It was evident that non-out-gassed lithium hydride continues to evolve hydrogen over a long period of time, whereas out-gassing the lithium hydride greatly reduces the amount of hydrogen released [during irradiation]. In addition, lithium hydride that is sealed and then out-gassed evolves less hydrogen than does lithium hydride that is out-gassed and then sealed.” The latter appears to imply exposure to atmosphere following out-gassing and before sealing, which the NRPCT believes will lessen the effectiveness of the out-gassing by allowing LiOH to reform due to (humid) air exposure. Baxter’s statement can lead to two theories: 1) out-gassing removes or reduces the amount of the lithium hydroxide (LiOH) formed during exposure to water vapor, given by Equation 2, because at elevated temperatures, LiOH reacts with LiH to produce hydrogen (H₂) gas (Equation 1); and 2) the amount of out-gassing is a function of the time the sample is exposed to atmosphere (i.e. the amount of LiOH formed).

¹ Out-gassing, is believed to be a pre-irradiation purification process, which drives off LiOH and other contaminants. This may not be true, and warrants further investigation.

² Evolution of gas is typically indicated by a pressure monitor indicating increased pressure during irradiation. It is important to note that the same pressure monitor also is employed to indicate a leak.

Equation 1 is believed to occur during out-gassing or during irradiation as the temperature increases after startup. This could be tested by measuring the amount of LiOH and Li_2O in a sample before and after out-gassing. Minushkin (Reference (aa)) confirms the reduction of LiOH and the creation of Li_2O with X-ray diffraction measurements that indicate the presence of lithium hydroxide prior to irradiation and the absence of LiOH and the presence of Li_2O and metallic Li post-irradiation.

Table 1: Summary of SNAP and ANP LiH Irradiation Data

	Identification	Temperature (oF)	Material Form	Constrained	nvt, Thermal	nvt, Fast	Out-gassed	Facility	Growth	Blackened	f/t Ratio	Gas Evolved	Duration (hr)	Results
1	Welch LTHxV2-3	200	P*	Uc*	4.4E+16	1.1E+16	Yes	LITR	No*	U*	<1	No	157	Good.
2	Welch STIR 2	237±14	Ct*	C*	1.3E+16	3.1E+17	No	STIR	-1%	Yes	>1	NM*	16	Bad. About 1% linear expansion.
3	Welch LTHx-6	160±15	P	Uc	1.1E+16	2.5E+16	Yes	LITR	U	In center	<1	Maybe	583	Bad. Soft under hard crust 1/16 in. Interconnected to LTHx-5.
4	Hamill-Waldrop	302-335	P	Uc	4.0E+15	1.6E+17	Yes	NARF	Yes	Yes	>1	Maybe	45	Bad. ~2.4% maximum expansion. Capsule leaked.
5	Minushkin No.5	100	P	Uc	1.6E+15	U	No	BNL	No	Slightly	<1	Yes	335	Good.
6	Welch Hx3-4	400	P	Uc	1.4E+18	U	Yes	X-pile	No	U	<1	No	444	Good.
7	Aitken and Henry	972	P	C	4.0E+18	1E+18	Yes	LITR	No	Slightly	<1	No	100	Good.
8	Welch LTHxV2-2	400	P	Uc	3.7E+15	9E+14	Yes	LITR	No	U	<1	No	130	Good.
9	Welch LTHxV2-1	560	P	Uc	2.5E+16	6E+15	Yes	LITR	No	U	<1	No	149	Good.
10	Welch LTHx-5	550±50	P	Uc	3.1E+18	3E+17	Yes	LITR	Yes	Yes	<1	Maybe	583	Bad. Leak Suspected. Powdered.
11	Aitken and Henry	1000	P	Uc	4.0E+18	1E+18	Yes	LITR	No	Slightly	<1	No	100	Good.
12	Minushkin No. 2	400	P	Uc	2.0E+16	U	No	BNL	Yes	Yes	<1	Yes	10-14 day	Bad.
13	Welch LTHxV2-4	800	P	Uc	4.1E+16	1E+16	Yes	LITR	No	U	<1	No	146	Good.
14	Welch Hx1-1	235-260	Ct	C	5.0E+17	U	Yes	X-pile	No	U	<1	No	155	Good.
15	Welch Hx1-2	235-260	Ct	C	5.0E+17	U	Yes	X-pile	No	U	<1	No	155	Good.
16	Welch Hx1-3	235-260	Ct	C	5.0E+18	U	Yes	X-pile	No	U	<1	No	155	Good.
17	Aitken and Henry	970	Ct	C	4.0E+18	1E+18	Yes	LITR	No	Slightly	<1	No	100	Good.
18	Welch LTHxV2-5	1000	P	Uc	3.3E+16	8E+15	Yes	LITR	No	U	<1	No	117	Good.
19	Welch LTHx-9B	790±10	P	Uc	8.5E+17	2E+17	Yes	LITR	No	U	<1	No	118	Good.
20	Welch Hx2-6	1000	Ct	C	5.9E+17	U	Yes	X-pile	No	U	<1	No	181	Good.
21	Welch LTHx-11	810	Ct	C	1.6E+18	4E+17	Yes	LITR	No	U	<1	No	149	Good.
22	Minushkin No.4	400-610	P	Uc	1.1E+18	U	No	BNL	Yes	Yes	<1	Yes	10-14 day	Bad.
23	Welch Hx2-2	800	Ct	C	5.9E+17	U	Yes	X-pile	No	U	<1	No	181	Good.
24	Minushkin No. 3	400-610	P	Uc	1.1E+18	U	No	BNL	Yes	Yes	<1	Yes	10-14 day	Bad.
25	Welch MTR	790±10	P	C	1.7E+18	4E+17	Yes	MTR	No	No	<1	No	100	Good.
26	Welch Hx3-1	250	Ct	C	1.4E+18	U	Yes	X-pile	No	U	<1	No	444	Good.
27	Welch STIR 3	237±14	P	Uc	1.3E+16	2.7E+17	Yes	STIR	-1%	Yes	>1	NM	16	Bad. About 1% linear expansion.
28	Welch LTHx-10	580±30	Ct	C	6.9E+17	1.7E+17	Yes	LITR	No	U	<1	No	148	Good.
29	Welch Hx3-2	250	P	Uc	1.4E+18	U	Yes	X-pile	No	U	<1	No	444	Good.
30	Welch LTHx-8	580±30	P	Uc	9.9E+17	2.5E+17	Yes	LITR	No	U	<1	No	118	Good.
31	Welch LTHx-4	400	P	Uc	2.1E+19	5E+18	Yes	LITR	Yes	U	<1	Maybe	744	Bad. Leaked.
32	Welch Hx1-2	300	Ct	C	5.0E+17	U	Yes	X-pile	No	U	<1	No	155	Good.
33	Welch LTHx-9	770±45	P	Uc	7.2E+16	1.8E+16	Yes	LITR	No	U	<1	No	150	Good.
34	Welch LTHx-12	1000	P	Uc	1.3E+19	4E+18	Yes	LITR	No	U	<1	No	155	Good.
35	Minushkin No.1	400	P	Uc	2.0E+16	U	No	BNL	Yes	Yes	<1	Yes	10-14 day	Bad.
36	Welch Hx2-5	400	Ct	C	5.9E+17	U	Yes	X-pile	No	U	<1	No	181	Good.
37	Welch STIR 1	237±14	Ct	Uc	1.3E+16	3.1E+17	Yes	STIR	Yes	Yes	>1	NM	16	Bad. Specimen spalled.
38	Welch Hx3-3	400	Ct	C	1.4E+18	U	Yes	X-pile	No	U	<1	No	444	Good.
39	ANL 4010	U	Crystals	No	U	U	No	CP-3	U	Yes	<1	Yes	240	Good. No change in appearance.
40	S10AFS3	775	P	C/Uc	1.0E+17	2.58E+18	Yes	S10A	ND	No	>1	No	10000	Good.
41	ANL 4208	U	Ct	C/Uc	8.0E+17	U	Yes	CP-3	U	Yes	<1	No	2160	Good.
42	NARF 8-10	ca 950	P	Uc	2e15 - 2e16	1E17 - 1E18	No	NARF	Yes	Yes	>1	Yes	350	Bad.
43	NARF No. 7	ca 951	P	C	1.3E+15	5.5E+16	No	NARF	Yes	Yes	>1	Yes	110	Bad.
44	NARF brick	ca 952	P	Uc	3.0E+15	1.4E+17	No	NARF	Yes	Yes	>1	Yes	220	Bad.
45	Welch STIR 4	237±14	P	Uc	1.3E+16	2.4E+17	Yes	STIR	No	No	>1	NM	16	Good.
46	Minushkin No.6	400-600	Crystals	Uc	1.0E+18	U	No	BNL	U	U	<1	Yes	10-14 day	U.
47	HW 10090	U	Ct	U	U	U	Yes	H-F pile	U	U	U	U	U	Good.

*Definition of abbreviations:

P = Cold-pressed
Ct = Cast
Uc = Unconstrained

C = Constrained
U = Unknown
No = No visible change observed

ND = Not detected
NM = Not measured

Furthermore, a majority (69.77%) of the specimens listed in Table 1 that were out-gassed did not experience swelling, shown in Figure 10. Of the out-gassed samples, five (Hamill-Waldrop, STIR 1, STIR 3, LTH_x-4, and LTH_x-5) experienced swelling. All of these specimens have something in common: exposure to the atmosphere compromising the out-gassing. The Hamill-Waldrop chemical analysis on the irradiated blocks indicated a gross exposure to atmospheric moisture, ~11.2% LiOH (Reference (bb)). The chemical analysis on STIR 1 and 3, which were the control ("pure") specimens, revealed the hydroxide content to be 2.4 and 6.2 %, respectively (Reference (z)). Bauer indicates that although no rupture of the LTH_x-4 capsule occurred, the capsule developed a leak during the test (Reference (cc)). The pressure monitor indicated a leak in the LTH_x-5 canister, but it was never confirmed. Additionally, air was admitted to the capsule to help cool the test temporarily during a "reactor setback" (Reference (dd)). The hydroxide content in all of these specimens is far greater than ideal. Bauer concludes that the only two (LTH_x-4 and -5 out of the 23) specimens tested in the ANP Program to experience significant swelling or powdering were the two capsules that developed leaks during the experiment--thereby exposing the two specimens (LTH_x-4 and -5) to the air or water vapor, forming hydroxide (Reference (cc)).

Figure 10: META Analysis Results: Growth v. Out-Gas

**Figure 11: Dissociation Pressure of LiH
(Heating Without Irradiation)**

The test specimens listed in Table 1 all experienced heating simultaneous to the introduction of radiation, or at the very least the two effects are inseparable based on the results. However, Welch (Reference (c)) performed studies to identify the dissociation pressure of LiH, which separates the heating and radiation effects. At the onset of the heating cycle, a large pressure of 0.45 atm was observed. As the test continued, the pressure decreased with increasing temperature to 0.002 atm.

The pressure then increased linearly with increasing temperature, as seen in Figure 11. Welch explains the initial heating curve by considering the gas released by the reaction given by Equation 1. The reduction in pressure with continued heating is explained by the possible recombination of lithium and hydrogen. The minimum of the curve, the cusp point (~12 on the graph or 833 K), represents the dissociation pressure where the LiH thermally dissociates into Li and H₂ (gas). The increase in pressure as temperature increases beyond the minimum pressure point is believed to be due to LiH thermal dissociation. Below about 700K this experiment measures pressure increase due to gas evolution, not dissociation or radiation. This is consistent with the theory that the chemical reaction between LiH and LiOH produces H₂ (gas).

Test specimens that were subject to rigorous environmental controls did not experience swelling. Similarly, the specimens with limited or no environmental controls experienced swelling. The ANP Program was aware of the hazardous and toxic nature of LiH. The powdered LiH was always handled in a dry nitrogen or dry helium atmosphere. All of the machining performed on the cold-pressed specimens was done in a dry box with a dry nitrogen atmosphere. Consequently, only two of the twenty three specimens experienced growth, which was due to intentional contamination (Reference (a)). The LiH for the NARF experiments was canned in a standard shop that did not have any dry handling equipment. The S10AFS3, which was the full size shield tested for 10,000 hours, was pressed in a dry atmosphere containing less than 35 ppm of water vapor. The shield was then sealed in a stainless steel container where it was subsequently out-gassed to convert the LiOH to Li₂O. After out-gassing the container was then pressurized to 760 torr using He. After the 10,000 hours, the pressure was measured to be 430 torr, which is speculated to be due to either diffusion through the container or a slow leak to the vacuum chamber where the test was performed (Reference (z)). These tests support the hypothesis that a lack of environmental controls exposes LiH to water (humidity) that produces LiOH, and subsequently produces hydrogen when heated.

The LiOH/LiH chemical reaction occurs at the interface between the two phases resulting in a buildup of Li₂O and H₂. Therefore, the lithium hydroxide and lithium hydride must diffuse through the Li₂O buildup at the interface to perpetuate the reaction. This suggests that the effectiveness of out-gassing needs to be tested.

According to the quantum mechanics (discussed below), swelling is gas driven; the meta analysis indicated that samples that do not grow do not evolve gas (during irradiation) and samples that grow tend to evolve gas (see Attachment 3). Removing the gas or removing the source of the gas reduces the swelling in irradiated lithium hydride.

Three studies that experienced swelling also measured the change in the LiH lattice parameter (Figure 12). The lattice parameter did not increase dramatically (References (z) and (bb)). This is consistent with the belief that the majority of the swelling can be attributed to the formation of hydrogen bubbles. If the bubbles are governed by surface tension, then the pressure will increase with the absorption of additional hydrogen until the pressure exerted on the matrix is so large, the matrix will rupture or micro-crack. Microcrystalline fracturing was observed by Aitken and Henry (Reference (ee)) as well as Brasier Sr. (Reference (ff)) in tritiated LiH.

Figure 12: Lattice Spacing for Unirradiated and Irradiated LiH

Cast specimens evolve less gas during irradiation than cold-pressed specimens that were not out-gassed. Two theories for this behavior are as follows. First, the melting and zone refinement likely converts any existing LiOH into Li₂O, and moves it to the surfaces. Second, casting is performed under an inert atmosphere (likely hydrogen) with very little if any humidity, which limits LiOH formation (Equation 2). Subsequent to forming the specimen by casting, LiOH can form, but will be on the specimen surface. Then, upon heating, either the LiOH simply evaporates, or if it reacts via Equation 1, the hydrogen gas readily escapes. Second, casting can create a different microstructure than cold-pressing, which may facilitate the removal of any hydrogen built up within the specimen—this requires further research.

5. Application of a Statistical Meta Analysis to SNAP data

In 1967 F.H. Welch published a report entitled Lithium Hydride Technology III, Properties of Lithium Hydride for SNAP Shielding Applications (NAA-SR-9400 volume III page 103). This report included a compilation of data from various reports on irradiation experiments of lithium hydride (Table 1). This information is a complex collection of data from multiple sources, and clearly difficult to interpret. At the time of Welch's report (1967) statistical methods of data mining like a meta analysis did not exist, making correlations more difficult.

The relatively new statistical method of meta analysis provided an opportunity to mine Welch's table for usable information. Meta analysis is the statistical analysis of a large collection of results from individual studies for the purpose of integrating the findings. This analysis is described in Attachment 3. The results of this analysis show relationships between several variables of interest. The pairwise analysis showed that out-gassing and growth were correlated (if the LiH was out-gassed, it didn't grow), but not perfectly. No gas was evolved during irradiation with the cast material, whereas all of the crystal LiH (there were only two crystal specimens³) evolved gas. For cold pressed LiH, some specimens evolved gas and some did not. The dependent logistic variable, identified subjectively as "good" or "bad" by Welch, showed a relationship with gas evolved. Those specimens that were "good" generally did not evolve gas. Those specimens that were "bad" either evolved gas or it was possible

³ Crystal implies specimen fabrication techniques typically used to grow single crystals, although it's not known whether the researchers actually achieved single crystal specimens, or more likely, polycrystalline specimens with very large grains.

that they evolved gas. Gas evolved and growth were related, but not perfectly. Most of the specimens that did not grow also did not evolve gas during irradiation.

6. Review of the SP-100 program

Reference (x) details the SP-100 lithium hydride (LiH) literature review, LiH irradiation testing and analysis, and LiH swelling mechanisms and conclusions. The NPRCT finds the Reference (x) review of the SNAP and ANP literature, and the subsequent design of the SP-100 experiments (which should have built off of a detailed review of the SNAP and ANP testing) potentially flawed. In particular, the potential importance of casting and/or pre-irradiation out-gassing before irradiation testing appears to have been missed or ignored, and appears to be a key to the swelling of LiH (see Section 10). Lithium hydride was selected for use in the SP-100 shield based on mass minimization studies. SP-100 conceptual designs and LiH literature review identified a need for several irradiation tests focused on the swelling of LiH under various fluences, fluxes and temperatures. Detailed chemical and microstructural information is also not presented in Reference (x). Irradiation test temperatures focused on 600K to 800K full power operations and 400K to 500K for partial power operations.

The gamma testing performed during SP-100 was at far higher dose rates than prototypical of the Prometheus preconceptual shield (~1000 times). This was considered significant to the Prometheus shield (Section 10.1 and Attachment 1).

The SP-100 Program chose 600 to 800K as the design operating temperature range for the LiH. The NRPTCT believes the lower temperature limit, 600K, was largely chosen based on gamma irradiation testing whereas 800K was likely chosen to minimize hydrogen over pressure and thermal dissociation.

Attachment 4 provides further details and discussion of the SP-100 program irradiation testing and results.

7. Atomistic Modeling and Findings

In an attempt to better understand irradiation induced swelling of LiH, quantum mechanical methods have been used to predict the formation energies and migration rates for point defects that are expected to develop within LiH under irradiation. These methods have also been used to explore mechanisms for the formation of H₂ gas, which previous experiments (References (x), (z), (gg), (hh)) cited as the prime contributor to the irradiation induced swelling of LiH. These formation energies and rate predictions are the basic inputs required for a planned integrated rate model, which would attempt to predict the concentration of chemical species (H₂ in particular) as a function of temperature, time, and irradiation. Conditions that favor significant H₂ production could potentially lead to swelling of the LiH under irradiation. Due to the large number of competing processes that occur during irradiation of LiH it is not yet possible to make any conclusions on the rate of H₂ production without performing sensitivity studies with the planned integrated rate model, but some initial conclusions can be made based on the completed quantum mechanical results:

- It is predicted that less energy is required to knock Li ions off of their lattice (250 – 260 kJ/mol) sites to form vacancy/interstitial pairs than for the H ions (298 – 299 kJ/mol).
- Once formed, interstitial defects are expected to diffuse rapidly, with very low calculated barriers to diffusion (7 – 25 kJ/mol).

- The corresponding vacancies are expected to diffuse much more slowly, with much higher barriers to diffusion (43.7 – 57.1 kJ/mol for Li and 84.1 - 91.0 kJ/mol for H). The larger predicted barriers to diffusion for H are consistent with the larger radii for the H anions than for the Li cations.
- Two feasible mechanisms were identified for H₂ formation during irradiation: 1) reaction of adjacent H atoms across a Li vacancy, and 2) reaction between two interstitial H atoms to form an interstitial H₂ molecule. The predicted barriers to reaction are approximately 100 kJ/mol for both reaction mechanisms.
- An unusually favorable interaction energy was found for placing two H₂ molecules within the same LiH di-vacancy site.

The details of these analyses and additional findings are summarized in Attachment 5.

8. Strategic Approach to Lithium Hydride Qualification

Foremost, future researchers need to review the LiH literature, and perform out-of-pile tests and modeling prior to irradiation testing. The characteristics of the LiH samples appear to be a key to the swelling performance, and therefore should be carefully defined and controlled by the principle researcher, and not delegated to other organizations.

8.1. Unirradiated Testing of LiH Specimens

The unirradiated thermal testing of LiH with corresponding modeling work should precede irradiation testing. The NRPCT considers this very high priority, since this testing should help explain the role of LiOH and LiH microstructure. This work should include the following.

1. Explore the effects of LiOH on LiH prior to irradiation experiment.
2. Perform tests on cast, pressed and pressed and sintered/out-gassed LiH specimens.
3. Study the effect out-gassing has on well-characterized LiH specimens, and specimens exposed to controlled environmental conditions.
4. Perform microstructure, chemistry, and gas evolution tests.

Performing this work prior to irradiation testing will allow the researcher to determine the best use for the limited irradiation test space, and likely save time and reduce costs by limiting pointless testing.

8.2. Irradiation Testing of LiH Specimens

The NRPCT recommends irradiated testing of LiH under the following conditions in order to gather sufficient data to qualify LiH for use in a space reactor shielding application.

1. Mixed neutron/gamma irradiation should be conducted as close to the correct neutron/gamma ratio as possible to achieve prototypical LiH performance compared to the actual shielding application. Several irradiation dose rates should be tested to determine the effect. One dose rate should be less than 10x of the actual application rate, preferably using in-situ monitoring of swelling and gas evolution. Most tests, however, should be accelerated to achieve total predicted dose, similar to the successful SNAP/ANP tests.
2. The effects of neutron spectrum (fast-vs-thermal) must be understood relative to the source spectrum, and likely shifts in the spectrum within the shield.
3. Perform X-ray irradiation to quickly screen various parameters prior to gamma testing, e.g. dose, dose rate, impurities, temperature, processing, etc. (Attachment 6).

4. Conduct gamma irradiation to generate confirmatory data to compare with past gamma tests. Again, several rates should be tested including one rate less than 10x of the actual application rate.

Detailed chemical and metallographic testing should be performed to fully define the evolution of damage within the LiH, including with varying sample and test conditions.

The thermal testing as well as modeling should precede the first neutron insertions. Irradiations funding should be applied to the mixed neutron/gamma testing as a priority, with the remaining irradiation testing funds supporting the X-ray and gamma tests. This is also consistent with the typical lead times to begin a neutron irradiation test. Mixed neutron/gamma testing should be initiated as quickly as possible in order to provide the designers with LiH swelling predictions.

The NRPCT planned irradiation testing at ORNL, with the initial focus on generating mixed neutron/gamma irradiation data. The following points justify testing in the mixed irradiation field as the main priority.

- The mixed neutron/gamma historical testing data is the most variable, with some tests demonstrating no swelling and others showing up to 20% volumetric swelling.
- There is limited available data in the Prometheus flux and fluence range.
- The shield will be exposed to a mixed neutron/gamma irradiation field; therefore testing under these conditions will best determine how the actual shield will behave.
- The LiH swelling mechanisms (as discussed in Section 10) are not understood. A more prototypical test will allow using the results with some confidence of accuracy versus basing performance on non-prototypical spectrum testing (i.e. X-ray or gamma) alone.

The NRPCT planned cabinet X-ray irradiation testing of LiH specimens for the following reasons (detailed in Attachment 6).

- Cabinet X-ray testing advantages include the ability to obtain irradiation data rapidly and at low cost.
- Cabinet X-ray testing is less cumbersome than traditional irradiation testing equipment.
- This testing allows for an evaluation of dose rate and total dose effects over the entire operating temperature range of a spacecraft shield.

Attachment 6 describes an X-ray irradiation test to screen LiH irradiation variables prior to the more expensive and time consuming gamma or mixed neutron and gamma irradiation testing. The X-ray irradiation testing would be coupled with atomistic modeling and out-of-pile efforts. A rotating anode X-ray tube could be used to irradiate the LiH while being kept under an atmosphere of anhydrous hydrogen. The specimen could be heated during irradiation. A detailed statistical experimental design was created to perform the experiment. The attachment discusses the details of this irradiation testing plan.

Gamma testing at dose rates closer to those that are prototypical of the shield are recommended for the following reasons.

- The results can be compared to the existing gamma database (Attachment 1). Gamma dose rate affects swelling. All testing to date is accelerated and may over predict actual swelling in the shield.
- Gamma testing is inexpensive and relatively easy (compared to mixed neutron and gamma testing).
- The swelling mechanism in LiH due to gamma irradiation may be different than that from neutron irradiation (Section 10). Gamma testing, on sister specimens to the mixed

neutron/gamma specimens, will help separate swelling effects. In the case where the actual shield spectrum is different than the testing spectrum this will allow for a better prediction of actual shield performance.

- Testing in a gamma environment may contribute to better understanding of the swelling mechanisms in LiH overall by determining what swelling mechanisms are active in the gamma environment.

The NRPCT intended to recommend establishing a neutron/gamma irradiation test program at ORNL (HFIR). The CUF (Californium User Facility) at ORNL may also have been used to cover the lower fluence portion of the design space range; however use of the CUF was not clearly needed at the time of the project restructuring.

8.2.1. Space Irradiated Materials Laboratory

The NRPCT planned to fund Oak Ridge National Laboratory (ORNL) to modify an existing laboratory to carry out thermophysical property measurement on irradiated space materials, including LiH. Attachment 7 describes the NRPCT plan for the laboratory.

8.2.2. LiH Specimen Manufacturing

The following are some general guidelines for LiH testing.

- Pre-irradiation non-destructive testing of 100% of specimens. Approximately 10% of specimens should undergo destructive evaluation to establish unirradiated baseline properties. Reserve some unirradiated specimens for future testing needs.
- Tightly control LiH exposure to H₂O. As discussed in Section 10, the NRPCT believes LiOH may play a pivotal role in LiH swelling. Controlling every aspect of specimen preparation in regards to H₂O exposure is important to reliable test data.
 - Out-gas specimens before testing. This step will help ensure minimal LiOH remains in the test specimens and reduce swelling from the $\text{LiH} + \text{LiOH} \rightarrow \text{Li}_2\text{O} + \text{H}_2(\text{g})$ reaction. However, depending on the initial quantity of LiOH, a corresponding number of moles of Li₂O will remain as an impurity in the LiH. This needs to be evaluated.
 - Measure LiOH before out-gassing, after out-gassing and after testing. This information is important to understanding the role LiOH plays in swelling. Measuring LiOH before and after out-gassing will show the starting specimen purity and the effectiveness of the out-gassing step. Measuring LiOH and Li₂O after testing will identify if the specimen was exposed to a leak during testing and may explain anomalous swelling.
 - Measure gas released during out-gassing and during thermal/irradiation testing. The amount of gas released during out-gassing, along with a measurement of LiOH before will help verify kinetic modeling of the $\text{LiH} + \text{LiOH} \rightarrow \text{Li}_2\text{O} + \text{H}_2(\text{g})$ reaction.
 - Purposely vary the LiOH content in the specimens. Test specimens with several levels of LiOH (i.e. <0.1wt%, 0.5wt%, 1wt%, and ~6wt %) to determine how much that mechanism contributes to swelling. Compare this information with early swelling tests with higher levels of LiOH. The specimens purposely doped with LiOH should not be out-gassed, except as a comparison of out-gassing effectiveness.
- Prepare micrographs on unirradiated and irradiated samples to determine changes to structure caused by radiation. Look for bubble presence and location, i.e. intergranular vs. intragranular. Measure the void/porosity to determine the location of gas accumulation.
- Test control specimens in unirradiated environment under identical thermal conditions. This step will help separate thermal and irradiation effects.
- Test cast and pressed specimens for comparison to prior test results and to help determine

mechanisms. Destructive examination of these specimens is important.

8.2.3. LiH Testing Guidelines

As a minimum, testing should cover the following ranges:

- Temperature from 400 to 850 K.
- Neutron fluence ($E > 0.1$ MeV) from 1×10^{14} to 1×10^{19} n/cm² and higher if tests are successful.
 - The Prometheus neutron flux range is estimated to be 3×10^5 to 3×10^{10} n/cm²-sec. Ideally, prototypical fluxes and fluences would be used to perform testing, but that is often impractical. SNAP and ANP used accelerated tests, which are commonly employed in the irradiated materials field. Some testing near ten times accelerated should be performed (see table below) to ensure rate effects are characterized.
- Gamma dose from 0.01 to 3 G-rads.
 - The Prometheus gamma dose rate is estimated to be 3×10^{-11} G-rads/sec to 6×10^{-9} G-rads/sec. Complement the existing gamma testing with lower dose rate testing down to 10x prototypical and lower if possible (again, duration will be a practical issue, but in-situ monitoring could provide useful information during the test).

Fluence		Flux	10* flux	
1.00E+19	n/cm ²	2.64E+10	2.64E+11	n/cm ² -sec
1.00E+17	n/cm ²	2.64E+08	2.64E+09	n/cm ² -sec
1.00E+15	n/cm ²	2.64E+06	2.64E+07	n/cm ² -sec
1.00E+14	n/cm ²	2.64E+05	2.64E+06	n/cm ² -sec
Assume mission		12 years		

Perform pre-irradiation characterization of material properties relevant to the use of LiH as a space reactor radiation shielding material. As a target, the following properties should be evaluated in a dry⁴ inert environment in the range 400 to 850K:

- Chemical composition, including impurities, LiOH, hydrogen, oxygen, etc.
- Thermal conductivity
- Density
- Dimensional stability (and swelling)
- Li metal content and distribution
- Microstructure
- Heat capacity
- Yield, Ultimate Tensile Strength

9. LiH Containment System

The NRPCT did not study this to any significant extent due to early project restructuring.

A lithium hydride containment system will isolate the LiH from the surrounding environment, protect against loss of hydrogen, improve the mechanical performance of the LiH section of the shield, and play a role in the heat rejection from the shield. Other factors should be considered when designing a LiH containment system, which are not specifically addressed herein because the NRPCT did not study the containment system thoroughly. These factors include, but are not limited to, thermal

⁴ Note: the quantitative meaning of “dry” must be determined by characterization of the maximum allowable levels of water vapor, etc. to which LiH may be exposed without undergoing deleterious reactions.

management, swelling accommodation, and metallurgical compatibility. Attachment 8 discusses, in more detail, the requirements and design objectives of a lithium hydride containment system.

10. Potential Irradiation Swelling Mechanisms

This section does not provide a definitive description of the LiH swelling mechanisms, but instead provides a summary view as a starting point for future researchers.

From a LiH swelling mechanisms perspective, generally, the NRPCT has found the literature to be informative and reasonable in the area of gamma irradiation induced swelling (References (gg), (x) (Disney) for example), and more uncertain and questionable in the area of mixed neutron and gamma induced swelling (References (x), (e) (Welch) for example). The NRPCT recommends that future researchers develop a thorough understanding of both gamma-induced swelling mechanisms and mixed neutron and gamma induced swelling mechanisms for three reasons: 1) the ratio of gamma dose to neutron dose in the LiH portion of the shield varies significantly from front (reactor side) to back within any design; 2) designs are likely to change considerably as mass optimizations occur (including streaming through pipe and other penetrations, inclusion of a tungsten gamma shield or not, etc.) resulting in irradiation conditions that are very difficult to predict when irradiation testing is being proposed; 3) the incident neutron flux spectrum may be different from the test reactor spectrum (e.g., fast versus thermal), requiring mechanistic understanding and modeling to bridge the differences. For these reasons as a minimum, it is important to understand the mechanisms behind LiH swelling. The NRPCT recommends a balanced approach of literature review, modeling, out-of-pile experiments, and in-pile experiments (Section 8).

Gamma irradiation swelling shows distinctive swelling patterns versus temperature, dose and dose rate (Reference (gg)) that do not appear as evident in the mixed neutron and gamma irradiation literature presented by Disney and Welch. The NRPCT did not have enough time to do an exhaustive literature search, however, a key SNAP/ANP experimental result appears to have been overlooked by SP-100. In particular, a strong correlation exists between the pre-irradiation processing of the LiH and its swelling. If the test samples were either cast, or out-gassed, they had a high likelihood of not swelling in the SNAP/ANP tests. Exceptions exist to this generalization, e.g., failed test conditions (e.g., leaks) or the deliberate inclusion of LiOH in the specimen after casting (STIR 2, Welch). The NRPCT believed that the casting or out-gassing was largely eliminating the LiOH impurity in the samples, versus other specimens. Based on this, the NRPCT considered whether there might be a causal relationship between the elimination of LiOH and reduction in swelling under irradiation, however, there were concerns with this line of thought, and insufficient time to test this possibility. The SP-100 program indicated near close out that out-gassing specimens may be a way to lower swelling—as most of the SNAP tests that did not swell had done, either through out-gassing or via casting. The potential mechanisms behind gamma-only induced swelling, and mixed neutron and gamma induced swelling are discussed separately below. The resolution of the link between casting/out-gassing and LiH swelling, as well as the role of LiOH is left to future researchers.

NRPCT's view of the potential key variables affecting LiH swelling are:

- Radiation type: gamma only, neutron only (not discussed), or mixed neutron and gamma
- Neutron spectrum: fast, epithermal, thermal
- Temperature
- Dose rate: (gamma and neutron)
- Dose: (gamma and neutron)
- LiOH impurity level
- Processing Method (cast, cold-pressed, cold-pressed + sintered, hot-pressed)
- Stoichiometry

- Thermal Migration—as a function of stoichiometry
- Environment (hydrogen over-pressure)

10.1. Gamma Irradiation Induced Swelling

Swelling is believed to be driven by H₂ gas bubbles within the LiH. Generally, hydrogen gas (H₂) is believed to form due to gamma irradiation stripping electrons off adjacent H atoms in the LiH crystal lattice, allowing the atoms to bond to each other, forming relatively stable H₂ gas. The H₂ gas either stays in position, diffuses to form bubbles (or leave the sample), or recombines with Li to form LiH. The mechanisms of greatest interest to the shield design would be: 1) the formation of the H₂ gas, 2) the migration to form bubbles (driving swelling), and 3) the recombination to form LiH (reducing swelling). If the rate of recombination exceeds the rate of formation of the H₂ bubbles, presumably, the swelling would be reduced or minimized. Should LiOH be present, it will react with LiH to form additional H₂ gas. The kinetics are expected to be dictated by temperature and the proximity of the reactant phases.

Souers & Pretzel (References (ii), (jj), (z)) indicated that H₂ gas diffuses through LiH at all temperatures above room temperature. Bowman (Reference (hh)), who performed tritiated lithium (LiT) experiments noted that LiH traps a significant amount of H₂ (10 – 15% at ~350K), rather than simply releasing it. Souers measured (through microscopy) bubble sizes following gamma irradiation at temperatures as low as ~400K, below which, they believed the hydrogen either remained at its original site in the crystal, or formed bubbles below their capability to detect. The measured size of the bubbles increased from about 90 angstroms at 400K to about 1600 angstroms at 550K. Above approximately 400K, recombination of the remaining Li atoms with H₂ gas is believed to become significant. Prior gamma irradiation testing in the range of ~3 to 15 Mrads/hour (Souers) suggests that the rate of recombination exceeds the rate of H₂ bubble driven swelling at approximately 500K. By ~600K, swelling is essentially eliminated under these dose rates.

Another observation in the SP-100 literature (Reference (ff)) was that below 600K, some LiH samples showed significant microcracking, but above 600K, there was no such microcracking. The work performed by these researchers was terminated at the end of the SP-100 project, but appeared promising. Again, this was at very high dose rates compared to Prometheus shield applications.

The NRPCT judges that the gamma irradiation induced swelling of LiH in the literature (primarily Souers & Disney) is informative and reasonable. However, the experimental dose rates were far in excess of the dose rates predicted for Prometheus (~1000 times higher). Based in part on these high dose rate tests, SP-100 concluded that a minimum temperature of 600K was needed in the LiH. The NRPCT was concerned that this lower temperature limit would unnecessarily restrict the design space for Prometheus, perhaps making LiH unattractive compared to a Be/B₄C or all ¹⁰B shield. However, SP-100 also believed that the extent of gamma induced swelling at a given temperature (nominally > 400K) would be a function of dose rate (the lower the dose rate, the lower the swelling), since, for instance, the recombination of lithium and hydrogen (reducing swelling) would compete more favorably at a lower dose rate. Given that the swelling appears to be a rate balance between H₂ bubble formation and lithium recombination with hydrogen, the former primarily a function of dose rate and temperature (Reference (hh)), and the latter primarily a function of temperature (kinetics), the dose rate is judged to be a critical parameter to test in the lower temperature ranges, e.g., 400 – 550K. Therefore, the main inadequacy the NRPCT finds in the literature is that the testing was at far higher dose rates than is applicable for Prometheus. Gamma induced swelling testing at dose rates closer to prototypical Prometheus rates (accelerated perhaps only 5 – 50X) appear to be warranted to determine whether the apparently simple mechanisms are in fact accurate (Section 8). This

information would need to be combined with mixed neutron and gamma irradiation swelling information in support of shield design.

10.2. Mixed Neutron and Gamma Irradiation Induced Swelling

The basic mechanisms of neutron scattering, and absorption and subsequent reactions in LiH, as well as gamma interactions with matter are commonly understood and thoroughly explained in the literature. Disney provides a general review of these processes, and Pretzel et al. (Reference (z)) provides a useful review of radiation damage in LiH from a crystallographic perspective. The NRPCT assumes future researchers review this material as well as the other references included in this document, and then review the information presented in this section to better understand LiH swelling and plan future testing.

Mixed neutron and gamma irradiation induced swelling of LiH is complicated, and difficult to fully explore within a practical irradiated materials test program. As an example, one variable is the fraction of dose due to gamma versus neutron irradiation, as well as the combined interactions. In the Prometheus shield, this was predicted to be ~1:100 (gamma dose : neutron dose, both in rads) in some sections of the shield, but this varies through the shield and may not be the same in future applications. Another example is temperature dependence. From the SNAP & ANP literature, a clear temperature dependence on swelling was not obvious, however, a loose correlation is evident in the SP-100 irradiations, and gamma irradiation shows a clear dependence with temperature. SP-100 intended to use LiH in the 600 to 800K range to minimize swelling, but the NRPCT is not able to concur with this limit, since this design choice seems to be based largely on high dose rate gamma testing, and not on the full breadth of mixed neutron and gamma testing. Further, the NRPCT preferred a broader design temperature range to limit design and analysis issues and extra design changes or support systems (e.g., heaters) to maintain this range. There is a general sentiment that the mechanisms for neutron and gamma induced swelling should largely be the same—and therefore gamma testing would make up most of the irradiated materials testing program. The NRPCT has mixed opinions on this point, which will not be resolved due to the Prometheus Project being in the restructuring phase. The approach to testing is discussed in Section 8.

Fortunately, Welch and Disney report numerous mixed neutron and gamma irradiations of LiH, focused largely on swelling, which provide a significant advantage to future researchers. The NRPCT was not able to perform LiH testing. However, a limited review of the literature was performed, and a pattern has been identified that the NRPCT considers important to future researchers. Specifically, the NRPCT observed from Welch's summary that either cast or out-gassed (prior to irradiation) LiH samples were unlikely to grow (swell) during irradiation. Welch used the term "good" to describe the post-irradiation test results. The NRPCT believes that casting completely converts the LiOH impurity to Li_2O and H_2 , and out-gassing converts a large fraction of it (depending on time at temperature, etc.). Should Bowman's assertion be correct, the LiH may be retaining some of this hydrogen, especially at lower temperatures which could play a role in bubble formation. This needs to be studied as a priority by future researchers. For samples that were not out-gassed or cast, "gas evolution" during irradiation was usually noted in Welch's summary. Bowman further reports that gas evolution during his experiments was likely due to bubble rupture. The NRPCT suspects that conversion of LiOH to Li_2O and H_2 was contributing to this gas evolution observation.

LiH swelling is believed to be driven by the presence of H_2 gas formed during radiation damage, most likely in bubbles within the LiH grains, but potentially also forming near LiOH/LiH phase boundaries if LiOH is present. As discussed above, gamma irradiation forms H_2 bubbles, which can drive swelling. However, the SNAP and ANP literature includes many mixed neutron and gamma irradiation tests that did not show "growth" (swelling), some at lower temperatures where the thermally driven recombination of Li and H_2 would not be expected to be significant (this excludes cascade effects or

other high energy local temperature excursions). The NRPCT did not find indications in the literature of the relative gamma-to-neutron dose in the tests with the exception of SP-100 ARMF testing (Reference (x)), which may be a subject for future researchers to consider; however, as mentioned above, the NRPCT literature review was not exhaustive due to project restructuring.

As discussed in the SNAP/ANP review section of this report, including the meta analysis, (Section 4), one of the correlations with swelling was whether the specimens were cast or out-gassed before irradiation. If the specimens were either cast, or out-gassed before irradiation, they did not swell—exceptions were potentially due to failed tests (leaks) or deliberate inclusion of LiOH in the specimens (STIR 2, Reference (e)). This was a striking correlation, which the NRPCT was surprised not to find commonly discussed/explored in the literature. In the SP-100 close out report on LiH irradiations (Reference (kk)), notes and presentation material suggest vaguely that (among other things) out-gassing might have contributed to the swelling. The NRPCT performed thermodynamic analyses to validate previous theories (References (e) and (aa)) that LiOH impurity will combine with LiH to form Li_2O and H_2 gas at elevated temperatures. The thermodynamic analysis indicated that this reaction is favorable at all temperatures considered, shown in Figure 13 (also discussed in Reference (z)); however, kinetics would limit the extent of reaction at lower temperatures. Figure 13 in particular shows that 0.25 moles of LiOH in excess LiH will go completely to 0.25 moles of H_2 and Li_2O over the entire temperature range.

Figure 13: Thermodynamics of $\text{LiH} + \text{LiOH} \rightarrow \text{Li}_2\text{O} + \text{H}_2$ (gas)

To better assess how favorable the reaction between LiOH and LiH to form Li_2O and H_2 is, Figure 14 shows the predicted free energies of reaction and equilibrium constants (K). The vertical dashed lines indicate phase changes of either of the reactants. The predicted free energies of reaction are very negative, and become increasingly negative with increasing temperature, indicating the strong thermodynamic driving force for reaction. The corresponding equilibrium constants, K_{eq} , defined by the product of the activities (a) of the reaction products (raised to the appropriate power based on the balanced reaction formula) divided by the product of the reactant activities (also raised to the

appropriate power based on the balanced reaction formula, which are all first power in this case),

$$(K_{eq} = \frac{a_{Li_2O(s)} a_{H_2(g)}}{a_{LiH(s)} a_{LiOH(s)}})$$

investigated confirming that the reaction strongly favors “completion”.

Figure 14: Predicted Free Energies and Equilibrium Constants for Reaction of $LiH + LiOH \rightarrow Li_2O + H_2(g)$

Figure 15 displays the expected equilibrium products for the reaction between lithium hydride and increasing quantities of water. The graph indicates that thermodynamically complete reaction is expected to occur between the LiH and H_2O (up to 25 mole% H_2O was examined) to form Li_2O and $H_{2(g)}$. The literature (References (aa), (ee), (e)) indicates that $LiOH$ is the primary product formed at room temperature for reaction of LiH with H_2O impurities. Presumably kinetics inhibit complete reaction of the LiH at these reduced temperatures, forming $LiOH$ as an intermediate product. Figure 16 displays the expected equilibrium products for the reaction between lithium hydride and increasing quantities of water, but the formation of Li_2O is intentionally hindered to investigate the intermediate step of the $LiOH$ formation. $LiOH$ is found to be the dominant product, in agreement with experiment, when the formation of Li_2O is hindered.

Figure 15: Predicted Reaction Products for Reaction of LiH with <A> moles of H₂O

Figure 16: Predicted Reaction Products for Reaction of LiH with <A> moles of H₂O (Ceasing Formation of Li₂O)

Figure 17 demonstrates that excess hydrogen cannot readily react with the Li_2O impurity to reverse the lithium hydride→lithium hydroxide→lithium dioxide reactions, which indicates that the hydrogen evolved from the reaction must escape the matrix or form bubbles because a significant excess of H_2 (100 moles H_2 to 1 mole Li_2O in this case) and elevated temperatures are required before the reactions are forced in the reverse direction to any measurable extent. This contradicts the previous premise that the reversibility of these reactions limits the H_2 evolved at elevated temperatures (Reference (aa)).

Figure 17: $\text{LiH} + \text{LiOH} \rightarrow \text{Li}_2\text{O} + \text{H}_2$ (gas) Unlikely To Reverse with Excess Hydrogen

Thus, if LiOH is in the sample upon heat up, it will react to generate H_2 gas. Proximity to a LiH phase is required for this reaction, which can affect kinetics and extent. Depending on the test vessel volume available for the gas to expand into, the temperature of the gas, and the starting moles of LiOH , a closed test vessel could become pressurized due to this reaction—which may in part explain some of the SP-100 B-2A failures (Reference (x)). However, the role that LiOH plays in direct swelling of the LiH under irradiation remains unresolved, and some skepticism exists within the NRPCT that it is a significant contributor. One possibility is that the LiOH reaction with LiH to form Li_2O and H_2 introduces H_2 into the LiH (most likely at phase boundaries), which diffuses throughout the LiH (as suggested by Bowman), filling vacancies, residing as interstitials, or accelerating the formation of bubbles. This may overwhelm the normal process of Li recombining with available H_2 , accelerating bubble-driven swelling, similar to the gamma irradiation mechanism discussed above.

The reaction of LiH and LiOH would typically occur at a phase boundary, especially if the LiOH formed on the LiH due to reaction with water, perhaps as humidity near a pure starting powder. At the phase boundary, Li_2O would build up as well as H_2 . The Li_2O would be expected to impede the reaction, by acting as a diffusion boundary between the reactants. At higher temperatures, e.g., casting or out-gassing temperatures, the reaction would be expected to proceed, potentially to completion.

Another consideration is the local cascade following neutron absorption in the ^6Li , or neutron scattering, typically of hydrogen. In the ^6Li absorption case, high energy He and tritium are ejected, creating a cascade, or local, brief melting of the LiH prior to dissipating their energy. The effects of these interactions need to be studied. Of particular interest is the state of the LiH and any local bubbles after the cascade, and as a function of average temperature.

Unfortunately, the NRPCT could not find any micrographs in the literature which might help explore what was changing when the samples were either cast or out-gassed after pressing. There is reference in SP-100 literature to micrographs created by Brasier (Reference (ff), INEL), but these were not obtained in time to support this report. Section 8 discusses testing that should provide this information and resolve these issues.

10.3. Tritium-Doped LiH Irradiation Swelling Experiment

Although not directly applicable to the Prometheus Project, or the use of LiH in a space shield application, Pretzel (Reference (z)) performed studies of the swelling and gas evolution of LiH doped with varying amounts of tritium (LiT) at varying temperatures. Of particular interest was an experiment with 70 mole % LiT monitored at room temperature for ~800 days. The sample initially swelled without releasing gas, (consistent with the observation by Bowman) and then at 200 days began to release He and H_2 (in various isotopic combinations). At this point, the swelling rate stabilized—presumably because the addition of gas to the LiH sample was lower due to escape. The swelling rate was roughly constant for the next 200 days, when the increased loss of He caused the swelling rate to lower again. At about 654 days, after roughly 25% expansion, the sample crumbled and the release of helium increased significantly. After about 400 days, the H_2 release was constant. Pretzel believed that the LiOH reacted with the LiH to release H_2 initially, but then the rate of H_2 introduction to the LiH crystal was due to radiation damage, and balanced somewhat by the recombination of Li and H. Pretzel also noted that the final rupture of the LiH crystals often shot fragments around the container. Further, Pretzel performed a relatively detailed analysis of the radiation damage mechanisms that should be repeated under space shield conditions.

The NRPCT recommends that future researchers consider this work, as well as Bowman's, when studying LiH.

11. Conclusions

1. SNAP and ANP provided more useful information for understanding LiH in a space shield application than was portrayed in SP-100 summaries. The Welch summaries, in particular, were very valuable.
2. The meta analysis of the Welch irradiation experiment summary (Table 1) helped identify correlations that are likely important to understanding LiH swelling performance, and guide future research. Chief among them is the correlation that cast or cold-pressed and out-gassed LiH was unlikely to swell under mixed neutron and gamma irradiation at any test temperature and any test fluence, whereas, cold-pressed LiH without out-gassing was much more likely to swell.
3. LiH material properties, compiled for preconceptual design, are provided in Attachment 1. However, swelling under irradiation is not provided, except for certain gamma-induced swelling data. Designers should not use the values provided, since mixed neutron and gamma irradiation data does not appear to follow the gamma-only data. This document does not

recommend LiH swelling correlations for space shield application, because many tests showed zero swelling, whereas others showed up to 20% swelling. Future researchers must resolve this, however, the fact that many LiH samples did not swell is encouraging and suggests a positive outcome is possible.

4. A hypothesis is presented herein that LiOH may be a key contributor to mixed neutron and gamma irradiated swelling. Alternatively, microstructural changes associated with casting or pre-irradiation out-gassing may play a key role in swelling. Further, if the sample is simply cold pressed, other dissolved impurities (gasses, water, etc.) may also be playing a role in the swelling.
5. LiH is commonly believed to swell under mixed neutron and gamma irradiation due to hydrogen gas build up, likely forming bubbles, which drive swelling. Several useful papers on gamma irradiation and tritium self-irradiation help explain this, as discussed in Sections 9 and 10.
6. Stoichiometric LiH is likely preferable to LiH + 2% free Li due to thermal migration issues and canning corrosion. Although not explored extensively, processing may also be easier with the stoichiometric material, since there may be difficulties in obtaining and maintaining homogenous distribution of the free Li if out-gassing or casting is used (to minimize swelling).
7. A parallel approach to resolving the swelling mechanism uncertainties and qualifying LiH is proposed in Section 8. Essentially, out-of-pile testing, X-ray testing and modeling should be done in parallel to mixed neutron and gamma irradiations. Due to the large amount of tritium created during these irradiations, a dedicated laboratory was envisioned.
8. Future researchers are cautioned not to fabricate LiH samples prior to understanding the literature, since key errors and rework are likely if the wrong chemistry controls and processing are used. An out-of-pile testing program (Section 8) is recommended prior to fabricating specimens for irradiations.

12. Recommended Future Work

1. Section 8 provides a phased approach to testing and qualifying LiH.
2. Atomistic modeling should continue to help fully understand the mechanisms of LiH swelling and recovery.
3. Ideally, stoichiometric, natural enrichment LiH would be used in the shield. Should that not be possible, some alternative engineered material ideas are presented below for future consideration:
 - a) Provide storage sites in the material for the irradiation-produced gas by building a LiH foam or similar cellular structure consisting of nano-scale cells or voids (i.e., developing an engineered material to facilitate gas storage). A disadvantage of this approach would be the reduction in density. Should the density reduction be small, this might be advantageous.
 - b) Provide for the release of irradiation produced gas by fabricating nano-scale channels into the material, allowing internal gas to readily migrate to the surface (i.e., developing an engineered material to facilitate gas transport).

- c) Create cast lithium hydride material using directional solidification to preferentially create gas transport channels. Machine off impurities and the equiaxed grains located in the chill zone in a post-casting machining operation. The resulting material would be of high purity and may contain gas transport channels (grain boundaries) directionally connected to the surface of the part.
- d) Produce a composite lithium hydride material, where the reinforcing material both reinforces the matrix (as in typical ceramic matrix composites) while also providing a channel for internal gas to escape to the surface. A composite material could also synergistically result in improved thermal conductivity (reducing material temperature gradients) by selecting a reinforcement material having a high thermal conductivity.

Each of these ideas would need verification, and likely extensive testing.

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Attachment 1 to Enclosure 2 to MDO-723-0048:
LiH Material Properties for Project Prometheus

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All data was plotted with Microsoft Excel and JMP, statistical analysis software (SAS Institute). JMP was used to fit data using the least squares method. Residual plots were examined to determine the quality of the regression data fit. In some analyses Cook's D statistics were used to examine the influence of individual data points on the least squares model (Reference (a)). Where applicable, 95% prediction intervals were determined which specify the confidence on a single future value. However, these confidence intervals do not account for uncertainty associated with the individual measurements. Results from future test programs will be necessary to quantify the measurement uncertainty.

The following properties are for natural lithium hydride (~7.6% Li^6 , 92.4% Li^7) (Reference (b)).

1. Composition

Table 1 gives the typical composition of LiH as described in Reference (c). It is recognized that the typical composition adds up to greater than 100%. However, these are the values reported for as procured material from the Union Carbide Nuclear Company, Y-12 Plant, Oak Ridge, Tennessee.

Table 1: Composition of LiH as Given by Welch

Element	Typical	Minimum	Maximum
	wt%		
Li	86.6	85.5	-
H	12.4	12.0	-
OH	1.0	-	2.5
CO_3	0.75	-	1.5
Cl	0.05	-	0.1
Na (ppm)	100	-	300
Ba (ppm)	30	-	80
Ca (ppm)	40	-	200
Cr (ppm)	6	-	25
Co (ppm)	40	-	60
Fe (ppm)	500	-	1500
K (ppm)	100	-	400

2. Melting Temperature and Maximum Use Temperature

The melting temperature of lithium hydride is 961K, given by the phase diagram from References (c) and (d).

$$T_{\text{melt}} = 961 \text{ K}$$

For a high dose region, the SP-100 project limited the use of LiH to a temperature range of 600-800K to prevent unacceptable swelling (Reference (e)).

The operating temperature range for LiH is bounded at the upper end by $T_{\text{melt}} - \text{offset}$, shown on the phase diagram (Figure 1). SP-100 set the upper temperature limit at 800K (Reference (e)), but the basis for this limit has not been verified by the NRPCT. The lower temperature limit is a function of the environment and design. For the Prometheus gas reactor with 900K reactor vessel and piping temperature constraints, an 800K upper temperature limit is expected to be easily met. At this time the lower temperature limit has not been set, and in fact, having no minimum temperature is the most desirable case. In SP-100, 600K was set as the lower temperature limit because recombination of radiolytically decomposed LiH is very fast, resulting in near zero swelling at far higher gamma dose rates than those under consideration for Prometheus shields. However, the SP-100 lower temperature limit of 600K would possibly require incorporation of heaters in the Prometheus shield, which introduces cost, complexity and reliability concerns. A lower temperature limit for the Prometheus shield LiH will be a trade off between the amount of swelling that is allowable in the design, and the swelling characteristics of the LiH due to environmental conditions (temperature, dose and dose rates). The composition of the LiH is also believed to be a factor. The design space for LiH use has yet to be defined.

Figure 1: Phase Diagram for LiH

3. Density

The density correlation for LiH given below is generated using linear regression of data from References (d) and (f). A sharp decrease in density, related to the change in slope is observed at the melting temperature of LiH (961K). Individual confidence bands (95%) are also shown in Figure 2. The raw data points are given in Table 2. The equations are valid for 298 -1233K.

For $T \leq 961\text{K}$

$$\rho = -1.3 \times 10^{-4} \cdot T + 0.82$$

$T > 961\text{K}$

$$\rho = -2.6 \times 10^{-4} \cdot T + 0.815$$

where

ρ = density, g/cm³

T = temperature, K

$R^2 = 0.995$

Figure 2: Density of LiH

Table 2: Data for Density of LiH

T (K)	Density	Source
298	0.78	NASA
473	0.76	NASA
673	0.73	NASA
798	0.72	NASA
873	0.71	NASA
961	0.69	NASA
961	0.58	NASA
973	0.55	NASA
1023	0.55	NASA
1073	0.54	NASA
1123	0.53	NASA
1173	0.52	NASA
1223	0.49	NASA
298	0.78	Mueller
473	0.76	Mueller
673	0.73	Mueller
798	0.72	Mueller
873	0.71	Mueller
961	0.69	Mueller
973	0.55	Mueller
1223	0.49	Mueller

4. Thermal Conductivity

LiH has a high specific heat but low thermal conductivity. Therefore, the regions at elevated temperatures tend to sustain the temperature. The following correlation is given by a power fit of thermal conductivity data (Figure 3) and correlations given by References (f) and (g) for LiH. The equation is valid for 200-961K.

$$k = 456.31 \cdot T^{-0.71}$$

where

k = thermal conductivity, W/m-K

T = temperature, K

$R^2 = 0.993$

T (K)	Thermal Conductivity (W/m-K)	Source
335	7.31	NASA
374	6.50	NASA
445	5.92	NASA
509	5.56	NASA
539	5.37	NASA
577	5.07	NASA
625	4.73	NASA
681	4.50	NASA
722	4.36	NASA
786	4.09	NASA
200	11.06	NRL
300	7.88	NRL
400	6.29	NRL
500	5.33	NRL
600	4.69	NRL
700	4.24	NRL
800	3.90	NRL
900	3.63	NRL
961	3.50	NRL
350	10.87	ORNL
375	9.94	ORNL
400	8.99	ORNL
438	7.79	ORNL
450	7.28	ORNL
475	7.01	ORNL
500	6.60	ORNL
550	5.93	ORNL
600	5.57	ORNL

Figure 3: Thermal Conductivity of LiH with Tabular Data Included

Figure 3 displays thermal conductivity data for LiH + 2% Li (Reference (h)). The additional Li increases the thermal conductivity by adding additional free electrons. Since at elevated temperatures conducting electrons are the dominant method of energy transport, the difference between LiH and LiH + 2% Li decreases as temperature increases.

5. Specific Heat

NASA (Reference (f)) uses Lang's data obtained using a drop calorimeter to measure enthalpy to fit a specific heat curve. The specific heat curve, adjusted to metric units, valid for 298-838 K is given in Figure 4.

$$C_p = 6.01 \cdot T + 2013.7$$

where

C_p = specific heat, J/kg-K

T = temperature, K

Terry (Reference (g)) of the Naval Research Laboratory used the superposition of the acoustic and optical lattice vibrations to determine the heat capacity of LiH, which is valid above 298 K.

$$C_p = b_0 + \sum_{m=1}^5 b_m (T - 280)^m$$

m	b_m
0	27.08
1	0.109
2	-2.80×10^{-4}
3	4.75×10^{-7}
4	-2.94×10^{-10}
5	5.60×10^{-14}

where

C_p = molar specific heat, J/mol-K

m = index

b_m = coefficients for molar specific heat

T = temperature, K

T (K)	C_p (J/kg-K)	Source
311	3882	NASA
422	4550	NASA
533	5218	NASA
644	5886	NASA
755	6554	NASA
839	7055	NASA
298	3643	Terry
300	3668	Terry
400	4643	Terry
500	5276	Terry
600	5789	Terry
700	6333	Terry
800	6996	Terry
900	7815	Terry

Figure 4: Specific Heat of LiH with Tabular Data Included

Since the primary mode of energy transport in LiH is through lattice vibration and Terry's fundamental specific heat curve exhibits similar trend and values as the 1958 drop calorimeter measurements made by Lang, the equation presented by Terry, which has a greater range of applicability is the preferred specific heat curve.

For the specific heat of LiH, the curve given by Terry (Reference (g)) is recommended.

6. Thermal Expansion

Mel'nikova (Reference (i)) calculated the coefficient of thermal expansion and lattice constant of natural lithium hydride (as well as isotopic compositions) using a quasi-harmonic approximation. This equation assumes that the Grüneisen constant is independent of temperature, volume, and isotopic composition, which lithium hydride satisfies fairly well (Reference (i)).

$$\alpha(T) = 1.1837 \cdot 10^{-6} \cdot c_p(T)$$

where

$\alpha(T)$ = coefficient of linear expansion of crystalline lithium hydride

c_p = molar specific heat (J/mol-K)

The calculation is accurate to within 2% of the experimental data used to verify the equation (Zalkin Reference (j)), which is single crystal x-ray diffraction data.

Mel'nikova presents the results of his equation using the Zalkin data, which is presented in Figure 5. The fundamentally derived thermal expansion is valid from 0K to the melting point; however, it was validated for temperatures 298-798K. For comparison, the Mel'nikova equation is evaluated using both the Terry (Reference (g)) and NASA (Reference (f)) specific heat equations presented in section 5. The uncertainty associated with the Mel'nikova equation increases based on the uncertainty associated with the specific heat used to evaluate the equation.

Using the Terry equation for specific heat (Section 5) with the Mel'nikova equation above, is the preferred equation for the thermal expansion coefficient of LiH. The Mel'nikova derivation can be used for all temperatures with increasing uncertainty at temperatures greater than 798K.

	Mel'nikova	Equation (Terry)	Equation (Nasa)
Temp	α	α	α
K	$\times 10^{-6} \text{ 1/K}$	$\times 10^{-6} \text{ 1/K}$	$\times 10^{-6} \text{ 1/K}$
100	7.5	-5.56	
150	16	8.34	
200	22.5	19.3	
250	28.4	27.9	
298.15	34.3	34.3	
300	34.6	34.5	35.9
350	39.7	39.7	38.7
400	43.7	43.7	41.6
450	46.9	46.9	44.4
500	49.6	49.6	47.2
550	52.1	52.1	50.0
600	54.5	54.5	52.9
650	56.9	56.9	55.7
700	59.5	59.6	58.5
750	62.5	62.5	61.4
800	65.8	65.8	64.2
850	69.4	69.5	
900	73.5	73.5	
950	77.8	77.9	
965	79.2	79.3

Figure 5: Thermal Expansion Coefficient of LiH with Tabular Data Included

7. Modulus of Elasticity

Lundberg (Reference (k)) published data for the Young's Modulus of LiH in flowing helium. The moduli were calculated from a rough stress-strain plot obtained by plotting the crosshead motion versus the load on the sample. Due to the systematic error associated with the strain measurement techniques, according to Lundberg, "the absolute values are probably not too accurate (Reference (k))." A power law equation can be fit using least squares fitting techniques, given in Figure 6. The equation is valid for 339 – 689K.

$$E = 6.516 \times 10^{16} \cdot T^{-5.191}$$

where

E = Young's Modulus, MPa

T = temperature, K

Temperature	Young's Modulus
K	MPa
339	3654
339	6826
339	6205
339	5792
539	285.4
539	---
539	298.5
539	---
555	167.5
689	87.56
689	208.2
689	206.2
689	165.5

Figure 6: Elastic Modulus of LiH with Tabular Data Included

Welch states that the average Young's modulus for cold-pressed and sintered LiH at room temperature is 7.24×10^4 MPa (10.5×10^6 psi) (Reference (c)). Young's modulus decreases by an order of magnitude over the temperature range of the data. The large decrease in elasticity occurs at approximately 435 K. At approximately 435 K a liquid alpha phase appears in the solid lithium hydride. The presence of the liquid phase causes the material to become weaker and less resistant to deformation when under stress. The NRPCT has not verified this.

Since the modulus is strongly dependent on the strain rate at elevated temperatures, LiH does not behave elastically (Reference (c)). Stress-strain rate curves are given in Section 9 that demonstrate the non-linearity of the stress-strain rate relationship.

Therefore, the recommended equation for the Young's Modulus of LiH is the power law equation given above.

8. Yield Strength

Data for the yield strength of LiH has not been located.

9. Ultimate Tensile Strength

Welch (Reference (c)) demonstrated the ultimate tensile strength of cold-pressed and sintered LiH is a function of strain rate (Figure 7). The tests were ultimately tested in static helium atmosphere. Originally, the tests at elevated temperature were attempted in a vacuum, but the extensometer consistently slipped off the samples. The stress-strain rate plot (below) shows that the LiH does not obey Hooke's law to the fracture point. Therefore, LiH is not truly a brittle material.

Figure 7: Ultimate Tensile Strength Curves of LiH from Welch

The ultimate tensile strength as a function of temperature and strain rate for LiH is given in Table 3. From the data it is observed that LiH is not that strain rate sensitive.

Table 3: Ultimate Tensile Strength Data for LiH

T (K)	UTS (MPa)	strain rate in/in/min
533	13.72	0.00057
533	13.21	0.00057
644	5.72	0.00057
644	6	0.00057
728	2.43	0.00057
728	1.71	0.00057
728	1.63	0.00057
728	2.73	0.00057
533	15.31	0.0057
533	15.38	0.0057
644	8	0.0057
644	8.2	0.0057
728	3.35	0.0057
533	14.07	0.00143
533	14	0.00143
533	17.79	0.0143
533	17.37	0.0143
298	17.17	0.001
298	19.55	0.001

The NRPCT cannot recommend an equation for ultimate tensile strength of LiH, more data is necessary to reach a conclusion.

10. Poisson's Ratio

Data for the Poisson's ratio of LiH has not been located.

11. Irradiation Swelling

The information included herein is a summary of gamma and mixed neutron and gamma irradiation testing results found through literature research. More detail on the available irradiation data is discussed in Attachments 2, 3, and 4. The gamma irradiation test data is consistent but LiH may not behave as predicted by the gamma data in a mixed neutron/gamma environment. The mixed neutron/gamma data is inconsistent, with some specimens swelling extensively and others not at all. Until the reasons for the differences in LiH swelling are determined with supplemental testing and modeling, this data should not be used by shield designers.

11.1. Gamma Irradiation

Souers in Reference (I) documents test results from exposure of LiH to ^{60}Co gamma radiation. Brookhaven National Laboratory (BNL) performed the gamma testing of LiH. Table 4 displays dose, dose rate temperature and swelling results.

Table 4: ^{60}Co BNL Gamma Test 1969 (Reference (I))¹

Sample # ²	Total Dose (Grads) ³	Temperature (K)	Dose Rate (Mrads/hr)	Average Swelling % ⁴
1 0.2	0.2	360	15	0.17
2 0.2	0.2	415	15	0.34
3 0.2	0.2	428	15	0.23
4 0.2	0.2	449	15	0.41
1 0.5	0.5	361	15	0.80
2 0.5	0.5	392	15	1.07
3 0.5	0.5	433	15	1.48
4 0.5	0.5	454	15	1.82
5 0.5	0.5	488	15	1.86
1 1.3	1.3	362	15	1.90
2 1.3	1.3	393	15	5.08
3 1.3	1.3	444	15	6.25
4 1.3	1.3	464	15	6.75
5 1.3	1.3	494	15	8.58
6 1.3	1.3	535	15	10.56
7 1.3	1.3	542	15	5.14
8 1.3	1.3	626	15	0.13
1 3.5	3.5	394	15	6.98
2 3.5	3.5	487	15	11.40
3 3.5	3.5	492	15	12.44
4 3.5	3.5	536	15	11.40
5 3.5	3.5	543	15	10.56
1 14.0	14	316	15	10.45
2 14.0	14	339	15	15.64
3 14.0	14	359	15	16.34
4 14.0	14	373	15	18.22
5 14.0	14	423	15	21.70
1 28.0	28	473	15	24.47

Sample # ²	Total Dose (Grads) ³	Temperature (K)	Dose Rate (Mrads/hr)	Average Swelling % ⁴
2_28.0	28	602	15	0.12
3_28.0	28	630	15	0.11
4_28.0	28	666	15	0.13
5_28.0	28	718	15	0.10
1_47.0	47	323	15	8.97
2_47.0	47	373	15	12.30
3_47.0	47	394	15	15.81
4_47.0	47	433	15	21.23
5_47.0	47	467	15	21.23
¹ Used image pro script to get data points off original data plot.				
² LiH made from lithium metal and hydrogen gas, contained 60-150ppm Na; 3-90ppm Al, Ca and Cu; few ppm Fe; 1000-5000 ppm O ₂ ; 250 ppm C. LiH crystals were welded into cans under He; placed in a cylinder with electrical resistance tape heater.				
³ The lowest temperature point in each set is 25% lower in dose than the value given.				
⁴ Measured volume displacement with a gas comparison pycnometer. Micrometer measurement not possible because all samples fragmented under irradiation. Accuracy reported +/- 0.03 cm ³ . Values listed not from original measurement but taken using an image pro script from the 1969 Souers Figure 8. Accuracy of each value varies due to data plotted on a log scale and was not calculated.				

Figure 8 depicts this data. Higher total dose results in higher volumetric swelling and swelling drops off to less than 1% above 600K. The exact mechanism causing this swelling was discussed in great detail in Reference (I).

Figure 8: BNL Gamma Data on LiH Crystals (Reference (I))

Reference (l) reported gamma irradiation swelling of 25% at 500K for a dose of 14.7 Grad. This dose was ~ 5X what was expected on Prometheus LiH (maximum ~3 Grad), and the dose rate was ~750X of expected (15×10^6 Rad/hr versus 2×10^4 Rad/hr). In the 400 to 500K temperature range, lower doses produced lower swelling, e.g., ~2% at 0.5 Grad at ~500K, or ~8% at 1 Grad at ~500K. Although 3 Grad is currently the predicted maximum gamma dose for the LiH in a Prometheus shield, the Reference (l) dose rate was still far in excess of prototypical, as shown in Figure 9. Given that the gamma-induced swelling is expected to be a rate balance between ionization and thermal recombination, dose rate is a key variable to understand. Reference (n) showed that decreasing dose rate resulted in reduced swelling. Figure 9 compares data from Reference (l) and (n) which indicates dose rate may have an effect on swelling, however, the lowest dose rate tested ($\sim 1 \times 10^6$ Rad/hr) was still far above that expected for Prometheus. At SP-100 proposed temperature range of >600K, prior gamma testing reported <0.2% swelling regardless of dose and dose rate (up to 717K) (Reference (m)).

Figure 10 depicts both Souers and Disney gamma test data. The more recent 1992 Disney GTRR data closely mimics the performance seen in Souers BNL tests. When comparing similar total doses between the two tests (Figure 11 – subset of the combined data), the tests confirm the same trend that higher total dose results in higher volumetric swelling and swelling drops off to less than 1% above 600K. A discussion of swelling mechanisms for neutron and gamma is presented in Section 10 of Enclosure 2.

Figure 9: LiH Swelling Due to Gamma Irradiation

Figure 10: BNL and GTTR Gamma Test Results on LiH

Figure 11: Subset of BNL/GTTR Gamma Test Results on LiH Comparing Similar Total Gamma Dose Data

11.2. Mixed Neutron and Gamma Irradiation

This section does not provide designers with correlations to predict LiH swelling in a mixed neutron and gamma environment. Designers should not use gamma-only data to predict swelling. Unfortunately, the compilation of mixed neutron and gamma data from SNAP/ANP and SP-100 tests is inconsistent. The Aircraft Nuclear Propulsion Program produced 23 data points that seem to present no clear pattern, as shown in Figure 12. An additional description of the data can be found in Attachments 2, 3, and 4. However, many of the historic tests produced no swelling. This data suggests that given further research, LiH may be qualified as a standard, high performance, space neutron shield material.

Figure 12: Summary of XMA-1A Test Data

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Attachment 2 to Enclosure 2 to MDO-723-0048:

Early (Pre- SP-100) Irradiation Experiments

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1. Earlier than SP-100 LiH Irradiation Testing

1.1. XMA-1A Shield Materials Testing

In the 1950s, tests were conducted [as part of the Aircraft Nuclear Propulsion (ANP) Program] to simulate 100 hour operation of the XMA-1A power plant that was designed to power a subsonic nuclear powered aircraft, shown in Figure 1, which used a LiH shield. The tests were conducted between 366 and 811 K, with a thermal neutron dose between 10^{16} and 10^{18} n/cm².

Twenty three samples were tested during this program. The test results are summarized in Figure 2.

Figure 1: Schematic of Nuclear Powered Aircraft (Reference (a))

Figure 2: Summary of XMA-1A Test Data

Only two of the 23 test specimens exhibited any powdering or swelling (represented in Figure 2 by a value ≤ 0.4). In one case, a leak of the capsule occurred and was identified. In the second case, the test equipment indicated a leak, but the leak was not found. All of the recovered LiH was solid, crystalline material either whole or in large chunks. Several of these samples were tested at a thermal fluence greater than 10^{18} n/cm². These samples received this large dose in a short period of time; thus, the flux was high, yet the samples survived with minimal damage (Reference (b)).

1.2. Minushkin Lithium Hydride Radiation Stability Study

To evaluate LiH as a potential neutron shield material for the aircraft reactor shield, in 1956, Minushkin performed a series of irradiations to determine the stability of LiH in a radiation

environment. Several cold-pressed LiH cylinders and one run with crystals were irradiated at the Brookhaven National Laboratory (BNL) reactor. A summary of the specimens, test conditions, and results are given in Table 1.

Table 1: Test Conditions and Results for Minushkin's LiH Radiation Stability Study (Reference (c))

RUN	SAMPLE FORM	INTEGRATED DOSAGE, nvt	TEMPERATURE, °F IRRADIATION	MAXIMUM PRESSURE, psia	NOTES
1	Compacted powder	$\sim 2 \times 10^{16} *$	400	10	Sample blackened and expanded to fill capsule.
2	Compacted powder	$\sim 2 \times 10^{16} *$	400	7.8	Sample blackened and expanded to fill capsule.
3	Compacted powder	$1.05 \times 10^{18} **$	400-610	11.9	Sample blackened, outside surfaces appear to have flaked off, leaving coarse powder and cylinder of smaller diameter than original.
4	Compacted powder	$1.12 \times 10^{18} **$	400-610	15	Sample blackened and completely disintegrated to a coarse crystalline powder.
5	Compacted powder	$1.55 \times 10^{15} **$	100	10	Capsule contained 6 psia He overpressure. Sample slightly blackened but no evidence of growth or disintegration.
6	Crystals	$\sim 10^{18} *$	400-600	25	Sample not yet examined after irradiation.
7	Compacted powder	0	400-600	25	After 2 days, no sign of blackening or growth
8	Compacted powder	0	400-600	25	After 7 days, no sign of blackening or growth
* Based on unperturbed thermal neutron flux as reported by BNL for sample location, with allowance for flux depression by sample. ** Based on count of cobalt monitor wires wrapped around samples.					

The cold-pressed LiH compacts were unconstrained during irradiation in a stainless steel type 347 capsule (Figure 3). The initial density of the specimens was 97.5% of theoretical density. The specimens were handled in either dry-nitrogen or dry-helium atmospheres until the capsules were vented and pumped down to 0.2 mm Hg prior to reactor insertion. The chemical analysis of the powder used to press the specimens shows a maximum hydroxide content of 1.2 wt. %, shown in Table 2.

Table 2: Chemical Analysis for LiH Powder Before Pressing of Minushkin's Specimens (Reference (c))

	Weight per cent
Lithium	87.00
Hydrogen	12.54
Hydroxide	1.20
Carbonate	0.18
Chloride	0.12
Carbon	0.04

Figure 3: Schematic for Irradiation Capsule for Minushkin Experiments (Reference (c))

- a. No irradiation.
- b. Integrated thermal dosage of 1.55×10^{15} n/cm².
Sample broken during PIE.
- c. Integrated thermal dosage of 1.05×10^{18} n/cm².
- d. Integrated thermal dosage of 1.12×10^{18} n/cm².

Figure 4: Visual Results from Minushkin Experiments (Reference (c))

Minushkin attributes the increase in pressure to gas evolution from the reaction of LiH with the impurity LiOH. Minushkin believes that the reaction is irreversible, but did not continue to completion. He speculates that the hydrogen might recombine with the lithium oxide (Li₂O), products of the reaction. Therefore, if the hydrogen gas is removed it is theorized that the reaction will go to completion at 478K.

The radial growth of specimens 1 and 2 corresponds to ~30% area change. The two specimens tested out-of-pile did not exhibit signs of growth or discoloration, as seen in Figure 4. The x-ray diffraction measurements showed no increase in unit cell lattice size; the lattice parameter was 4.082 ± 0.001 Å for all samples before and after irradiation. The peaks measured for runs 5 and 7 indicated the presence of LiOH. However, runs 3 and 4 showed definite broadening of the peaks, which Minushkin attributes to the presence of Li₂O and possibly Li metal. The absence of the LiOH peak in runs 3 and 4 suggest that the gas production is mostly due to the reaction of LiOH with LiH.

Minushkin concludes that the growth and disintegration of the specimens is caused by radiation, while the gas evolution is caused by the reaction of impurities (e.g. LiOH) with LiH at elevated temperatures (Reference (c)).

1.3. Aitken and Henry Radiation Damage to Lithium Hydride Study

Aitken and Henry ran three experiments in the C-42 hole of the Low-Intensity Test Reactor (LITR)¹ at the Oak Ridge National Laboratory (ORNL) to ascertain the applicability Minushkin’s results have on the higher temperature, high flux environment expected in the GE-ANPD reactor-shield assembly.

The three experiments were tested in identical conditions, except for their fabrication technique. The first specimen was cast into the capsule shown in Figure 5. The second specimen was powder-pressed and machined to fit tightly into the capsule. The third was the same specimen as the second, except the cylinder was machined to provide a gap between the specimen and the capsule wall of 1/16 inch.

The chemical analysis of the cold-pressed and cast specimens indicated 2.4 wt. % and 0.6 wt. % hydroxide (OH) content, respectively. All of the samples were out-gassed to remove LiOH from the specimens. Prior to irradiation, the cast and confined cold-pressed specimen capsules were evacuated to ~20 mm Hg (which is greater than the anticipated dissociation pressure at the irradiation temperatures). The unconfined cold-pressed capsule was evacuated to ~75 mm Hg to facilitate heat transfer across the gap.

The conditions and results of the three experiments are given in Table 3. The pressure within the capsules remained constant throughout the experiment; thus, the gas evolved was not greater than expected due to dissociation.

Figure 5: Schematic for Irradiation Capsule for Aitken and Henry Experiments (Reference (d))

Table 3: Results for Aitken and Henry Radiation Experiments (Reference (d))

Time	Flux		Dosage (nvt)
100 hours	1.25e13 thermal 0.3e13 fast		4e18 thermal 1e18 fast
	Cast	Confined Powder-pressed	Unconfined Powder-pressed
Avg temperature at center (°F)	970	972	1000
Avg temperature at periphery (°F)	818	738	602
Avg temperature difference (°F)	152	234	398
Avg He flow rate, scfm	3.5	3.8	8
Pressure change above LiH, mm	<10	<10	<10
Change in dimensions of container	none	none	none

¹ The LITR was first built as a hydraulic and mechanical mockup for the Materials Testing Reactor (MTR). In 1951 it was converted to a 3 MW reactor that operated until October 10, 1968.

Aitken and Henry speculate that the helium (~0.5 millimoles) and tritium produced by the ^6Li neutron capture were retained within the matrix. Furthermore, the specimens did not exhibit any measurable growth, including no change in lattice spacing. The specimens did show evidence of microcrystalline fracturing (Reference (d)).

1.4. LTH_x – 5 and –4/– 6

In 1957, lithium hydride specimens in separate capsules were irradiated in Hole C-48 of the LITR at ORNL. Specimen A (LTH_x-5) was irradiated at 588 K, while specimen B (LTH_x-6) was irradiated at ~344 K for 583 hours.

The LiH, which was cold-pressed at Y-12, initially contained 1.34 wt. % of OH. Each specimen was a right cylinder with a diameter of 0.765 inches and a height of 4 inches. The specimen contained a central thermocouple well of 0.129 inches in diameter and 3.25 inches deep.

Each specimen was monitored by 10 thermocouples (both in the well and on the exterior of the specimen). The specimens were placed in stainless steel He-cooled jackets, which were then placed in stainless steel canisters. Cooling air flowed from the bottom of the capsule over the He jacket. The He pressure was maintained between 25 and 35 psig. The capsules shared a vacuum pump system. A schematic of the test assembly is shown in Figure 6.

The test assembly was inserted in the reactor on November 12, 1957. The reactor was cycled several times at the beginning of the test to adjust the position of the samples, which was altered to control the temperature of the samples. It

Figure 6: Schematic of Irradiation Capsule for LTHx-5 and -6 Test (Reference (e))

was determined that capsule B (LTH_x-6) could not be maintained at 477 K while capsule A (LTH_x-5) was maintained at 588 K. Hence, the significantly lower temperature (344 ± 8 K), than originally designed, for the LTH_x-6 sample.

The samples were removed from the reactor on November 19, 1957 to make way for other tests. The samples were evacuated and then filled with He to protect them until they were reinserted into the reactor on December 3, 1957. The test was operated for a total of 583 hours. The samples were removed from the reactor on December 31, 1957.

Both capsules A and B were disassembled in a hot cell and then transferred to a dry box after the samples were removed from the capsule.

Sample A received a total thermal dose of 3.0×10^{17} n/cm² at a thermal flux of 1.5×10^{11} n/cm²/sec at 588 K. Sample A fit snug in the capsule. It was black and soft; some powder was found in the capsule. Since the sample was snug, some effort was required to remove it from the capsule. During the process, $\sim \frac{1}{2}$ " of the specimen was inadvertently cut off and ignited by contact with the cutting tool.

Sample B received a total thermal dose of 1.1×10^{16} n/cm² at a thermal flux of 5.4×10^9 n/cm²/sec at ~ 344 K. Upon inspection, specimen B was gray with white specks. No powder was found and the specimen was hard.

X-ray diffraction analysis was performed on each specimen to determine the species present post-irradiation. LiOH was present in the LTH_x-5 (specimen A) sample, which unfortunately was the sample that temperature was controlled on. Reagan notes that a faint line could be that of LiOH·H₂O. Reagan did note the presence of LiOH on LTH_x-6 (specimen B) (Reference (e)).

1.5. Souers Data

Reference (f) documents test results from exposing LiH to ⁶⁰Co gamma radiation. Brookhaven National Laboratory (BNL) performed the gamma testing of LiH. Table 4 displays dose, temperature and swelling results.

Table 4: ⁶⁰Co BNL Gamma Test 1969 (Reference (f))¹

Sample # ²	Total Dose (Grads) ³	Temperature (K)	Dose Rate (Mrads/hr)	Average Swelling % ⁴
1_0.2	0.2	360	15	0.17
2_0.2	0.2	415	15	0.34
3_0.2	0.2	428	15	0.23
4_0.2	0.2	449	15	0.41
1_0.5	0.5	361	15	0.80
2_0.5	0.5	392	15	1.07
3_0.5	0.5	433	15	1.48
4_0.5	0.5	454	15	1.82
5_0.5	0.5	488	15	1.86
1_1.3	1.3	362	15	1.90
2_1.3	1.3	393	15	5.08
3_1.3	1.3	444	15	6.25
4_1.3	1.3	464	15	6.75

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Sample # ²	Total Dose (Grads) ³	Temperature (K)	Dose Rate (Mrads/hr)	Average Swelling % ⁴
5_ 1.3	1.3	494	15	8.58
6_ 1.3	1.3	535	15	10.56
7_ 1.3	1.3	542	15	5.14
8_ 1.3	1.3	626	15	0.13
1_ 3.5	3.5	394	15	6.98
2_ 3.5	3.5	487	15	11.40
3_ 3.5	3.5	492	15	12.44
4_ 3.5	3.5	536	15	11.40
5_ 3.5	3.5	543	15	10.56
1_ 14.0	14	316	15	10.45
2_ 14.0	14	339	15	15.64
3_ 14.0	14	359	15	16.34
4_ 14.0	14	373	15	18.22
5_ 14.0	14	423	15	21.70
1_ 28.0	28	473	15	24.47
2_ 28.0	28	602	15	0.12
3_ 28.0	28	630	15	0.11
4_ 28.0	28	666	15	0.13
5_ 28.0	28	718	15	0.10
1_ 47.0	47	323	15	8.97
2_ 47.0	47	373	15	12.30
3_ 47.0	47	394	15	15.81
4_ 47.0	47	433	15	21.23
5_ 47.0	47	467	15	21.23
¹ Used image pro script to get data points off original data plot.				
² LiH made from lithium metal and hydrogen gas, contained 60-150ppm Na; 3-90ppm Al, Ca and Cu; few ppm Fe; 1000-5000 ppm O ₂ ; 250 ppm C. LiH crystals were welded into cans under He; placed in a cylinder with electrical resistance tape heater.				
³ The lowest temperature point in each set is 25% lower in dose than the value given.				
⁴ Measured volume displacement with a gas comparison pycnometer. Micrometer measurement not possible because all sample fragmented under irradiation. Accuracy reported +/- 0.03 cm ³ . Values listed not from original measurement but taken using an image pro script from the 1969 Souers Figure 7. Accuracy of each value varies due to data plotted on a log scale and was not calculated.				

Figure 7 depicts this data. The data shows temperature and total dose have large effects on volumetric swelling. Higher total dose results in higher volumetric swelling, and swelling drops off to less than 1% above 600K. The exact mechanism causing this swelling was discussed in great detail in Reference (f). Additional discussion of this data in comparison with SP-100 GTTR gamma test data is presented in Attachment 1 to Enclosure 2.

Figure 7: BNL Gamma Data on LiH crystals (Reference (f))

1.6. NARF Experiment

In 1962, LiH canned (absent of the stainless steel honeycomb structure) in aluminum was used to mockup the SNAP 10A shield during an irradiation of electronic components. During this test, the LiH swelled and ruptured the container. The containers were redesigned to accommodate swelling, but, in a subsequent irradiation, ruptured again. The maximum fluence on the shield was estimated to be 10^{17} - 10^{18} n/cm² ($E > 0.1$ Mev) at a maximum temperature of 783 K. The investigation into the incident concluded that the original container rupture was due to differential thermal expansion between the aluminum and the LiH (coefficient of thermal expansion of Al $\sim 12 \times 10^{-6}/^{\circ}\text{F}$ versus $\sim 28 \times 10^{-6}/^{\circ}\text{F}$ for LiH). Reusing the original LiH bricks in the subsequent testing ultimately caused the second rupture. The initial rupture allowed for the water vapor present in air to react with the LiH to form lithium hydroxide (LiOH). The LiOH, at elevated temperatures, reacts with LiH to produce hydrogen (H₂) gas:

It is suspected that the gas at these temperatures, combined with the reduced available volume due to the coefficient of thermal expansion differences, drastically increases the pressure within the container, potentially causing rupture.

The unexpected behavior of the LiH occurred close to the scheduled launch of SNAP 10A. In an attempt to clarify the results of the investigation, Hammil and Waldrop began irradiation testing at the General Dynamics/Fort Worth Nuclear Aircraft Research Facility (NARF) reactor (Reference (g)). Hamill and Waldrop (Reference (h)) used a 304 stainless steel can to contain isostatically pressed LiH specimens, which were 6 in. diameter and 6 in. long cylinders with an initial perforated stainless steel honeycomb structure manufactured in a dry (< 35 ppm water vapor) atmosphere. The out-gassed assembly received a neutron dose of 1.6×10^{17} n/cm² ($E > 0.1$ Mev) at 423 K to 441 K (center of the cylinder) for 44.6 hours. The cooling air flow was varied to maintain temperature. The test was terminated when the can seal was believed to have been compromised.

The post-irradiation exam (PIE) occurred at Oak Ridge National Laboratory (ORNL) in a hot cell without moisture controls. The gas in the can was determined to be air. A chemical analysis determined that the remaining LiH equivalent was 89.9% (the balance being ~11% LiOH) compared to the original purity level of 97.8%. Since the marks made on the LiH during the pre-irradiation exam were in tact, dimensional changes were able to be obtained, given in Table 5.

Table 5: Dimensional Measurements On Lithium Hydride Specimen Before and After NARF Irradiation (Reference (g))

Point	Length (in.)			Diameter (in.)		
	Preirradiation	Postirradiation	% Change	Preirradiation*	Postirradiation	% Change
1	6.0028	6.0820	1.34	6.0060	6.0775	1.19
2	6.0013	6.0878	1.44	6.0055	6.0910	1.42
3	6.0023	6.0849	1.37	6.0060	6.1248	1.98
4	6.0017	6.0784	1.28	6.0060	6.1493	2.39
	Average		1.38			

*Diameter measurements taken at 2-in. intervals along the specimen. Point 4 was the reactor end.

In addition to the dimensional changes, x-ray diffraction measurements were made on both unirradiated and irradiated LiH yielding a volume increase of 0.03% in the crystal lattice structure.

Hamill and Waldrop concluded that the only significant radiation-induced damage in their experiment was the 2.4% expansion noted by the dimensional analysis. The initial NARF failure was caused by a test design flaw, and the second NARF failure was caused by improper environmental controls while handling LiH (Reference (h)). They concluded that proper handling of LiH in a dry atmosphere would prevent the formation of LiOH and prevent significant gas evolution.

1.7. STIR Experiment

The Shield Test Irradiation Reactor (STIR) Experiment was designed to validate the Shultz proposed theory of radiation-induced expansion in LiH. The theory, which was in disagreement with both the Hamill-Waldrop and STIR experiments, proposed that the expansion in LiH was due to the formation of lithium oxide (Li₂O) and the agglomeration of lithium metal causing ~28% volume expansion due to the transformation from FCC LiH to BCC lithium.

Generally, the NRPCT agrees with the goals of this set of experiments, but finds the results indecipherable due to too many variables in play at once. Future researchers may learn more from STIR with deeper analysis.

The STIR experiment irradiated four lithium hydride specimens: two cast and two cold pressed.

- Cast LiH, high purity, minimum LiOH contamination.
- Cast LiH exposed to atmospheric moisture to form a layer of LiOH (about 1.2 wt % LiOH contamination).
- Cold-pressed LiH, high purity, minimum LiOH contamination, out-gassed at 810K for two hr.
- Cold-pressed LiH, plus about 11 wt % LiOH, out-gassed at 810K for two hr.

The control specimens (high purity) were handled in a dry box (10 ppm water vapor, < 3% O₂). The test specimens were irradiated for 16 hours at 387 ± 8 K for a fast-neutron dose of $1.4\text{--}3.1 \times 10^{17}$ n/cm² ($E > 0.1$ Mev), dependent upon the location in the test capsule (shown in Figure 8).

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Figure 8: Schematic of Irradiation Capsule for STIR Experiment (Reference (g))

The capsule was opened in a nitrogen filled box to prevent contamination due to atmospheric moisture. The visual observations and dimensional measurements were made at this time.

Table 6 displays the information captured.

The cast LiH control specimen partially disintegrated. Therefore, post-irradiation dimensional changes were not measured. It is also curious as to why the size of the cold-pressed LiH with 11 wt% LiOH specimen had different dimensions than the other three specimens.

The lattice parameter determined by x-ray diffraction was 4.085 Å, compared to the unirradiated control of 4.084 Å. The measured volume expansion measured for samples b and c was 3-4%. The lattice constant expanded 0.01–0.02 %.

Table 7 contains photographs that were taken during pre- and post-irradiation examinations.

Table 6: Summary STIR Test: Visual and Dimensional Results (Reference (g))

Sample	Visual	Dimensional			
		Position	Preirradiation	Postirradiation	% Change
a. Cast LiH, high purity, minimum contamination	Sample partially disintegrated into small crystals. The cylinder was very fragile and easily broken. The LiH was a shiny black.	Diameter	1.500 1.497 1.441 1.442	Sample crumbled and original measurement points lost.	
		Length	1.462 1.466		
b. Cast LiH, surface layer of LiOH contamination	The specimen was intact and gray-white in color. The sample was hard to break (similar to an ordinary cast LiH rod). Upon fracturing, the LiH also was found to be shiny black.	Diameter	1.473 1.455 1.471 1.466	1.486 1.473 1.487 1.484	0.88 1.24 1.09 1.23
		Length	1.596 1.584	1.606 1.592	0.63 0.50
c. Cold-pressed LiH, high purity, minimum contamination	The sample was intact, and shiny black. Small fragments readily broke off the rough end and edges.	Diameter	1.0025 1.0025 1.0025 1.003	1.015 1.014 1.015 1.014	1.24 1.14 1.24 1.09
		Length	1.442 1.445	1.461 1.465	1.32 1.38
d. Cold-pressed LiH + 11 wt % LiOH	The specimen was intact and apparently unchanged when first examined. Several days later when photographed and sampled, one end was significantly swollen and fragmented upon contact.	Diameter	0.502 0.501 0.5015 0.5015	0.502 0.502 0.502 0.502	0.0 0.2 0.1 0.1
		Length	Not taken, as end was broken on fabrication.		

Table 7: Visual Results from STIR Test (Reference (g))

	Unirradiated Specimen	Irradiation Specimen
a)Cast LiH, high purity, minimum contamination	A black and white photograph of a dark, rectangular, solid specimen of Cast LiH. It is placed on a light-colored surface next to a metric ruler for scale. The ruler shows markings from 2 to 5 cm.	A black and white photograph of the same Cast LiH specimen after irradiation. The specimen is now dark, irregular, and appears to be crumbling or fragmented. It is shown next to a pair of tweezers and a ruler for scale. The ruler shows markings from 3 to 5 cm. The text "3-16-67 UNC" is visible at the bottom of the image.

	Unirradiated Specimen	Irradiation Specimen
b) Cast LiH, surface layer of LiOH contamination
c) Cold-pressed LiH, high purity, minimum contamination
d) Cold-pressed LiH + 11 wt% LiOH

The control samples were accidentally contaminated with water vapor during the preparation for the PIE. Table 8 displays the results of the chemical analysis. Both cast specimens contained the same amount of hydroxide post-irradiation. Furthermore, the cold-pressed LiH control specimen contained a significant amount of hydroxide.

Table 8: Summary STIR Test: Chemical Analysis (Reference (g))

Sample	Weight Percent of Constituent							
	Hydroxide*		Carbonate		Lithium		Hydrogen	
	Control	Irradiated	Control	Irradiated	Control	Irradiated	Control	Irradiated
No. 1 Cast LiH, high purity, minimum contamination	1.4	2.4	ND	<0.002	85.4	85.4	12.36	12.18
No. 2 Cast LiH, surface layer of contamination††	ND§ ND	2.4** 27.5††	ND ND	<0.002** 3.05††	84.1 ND	84.8** 21.4††	11.54**,††	12.19** 11.03††
No. 3 Cold-pressed LiH, high purity, minimum contamination	ND	6.2	ND	0.14	85.8	80.9	12.30	11.67
No. 4 Cold-pressed LiH plus about 11 wt % LiOH contamination††	ND	11.2	ND	0.25	77.1	76.1	10.11	9.82

*Chemical analysis methods cannot differentiate between lithium oxide and lithium hydroxide.

†A portion of the lithium hydroxide probably was the hydrate LiOH · H₂O. No analysis was made for the weight percent of H₂O.

§ND = Not determined.

†† Surface

Despite the specimen contamination, the STIR experiments concluded, similarly to Hamill and Waldrop, that the volumetric expansion cannot be attributed to a lattice expansion (Reference (g)). The LiOH content of the control and irradiated samples should receive further study prior to drawing conclusions. The out-gassing step on the pressed samples could have converted the existing LiOH into Li₂O, essentially “purifying” these samples—assuming LiOH (and not Li₂O) is the dominant impurity driving swelling during these tests. Further, Table 8 indicates that the chemical analysis could not distinguish between LiOH and Li₂O. It may be that the characterization of “pure” and “impure” is misleading in this entire set of experiments. The NRPCT notes that none of these samples swelled to the extent that might be predicted if relatively high concentrations of LiOH was present during the testing.

1.8. SNAP10AFS3 Shield Irradiation Test

The SNAP10AFS3 Shield (Figure 9) Irradiation Test started on January 22, 1965. The test ran for 10,000 hours, accumulating a fast neutron dose $\sim 3 \times 10^{18}$ n/cm². The total calculated dose and dose rate is given in Table 9. The 97.8% pure LiH was cold-pressed in a dry atmosphere (< 35 ppm

of water vapor), then canned in a 316 stainless steel vessel with a helium (He) gas pressure of 760 torr.

The maximum measured temperature in the shield was 685 K, which occurred 4 inches below the top surface of the LiH block. The surface of the shield was 652 K. The bottom surface of the shield was not instrumented, but estimated to be 533 ± 28 K.

Figure 9: SNAP 10AFS3 Shield Assembly (Reference (g))

Table 9: Activation Analysis of The SNAP 10AFS3 Shield Vessel (Reference (g))

Position	Fast Neutron ($E > 1.0$ Mev)		Thermal Neutron	
	Flux ($n/cm^2/sec$)	Dose (n/cm^2)*	Flux ($n/cm^2/sec$)	Dose (n/cm^2)*
Top	7.16×10^{10}	2.58×10^{18}	1.36×10^{10}	4.9×10^{17}
Bottom	2.47×10^8	8.9×10^{15}	1.04×10^9	3.75×10^{16}
* 10,000 hr or 3.6×10^7 sec.

Figure 10: SNAP 10AFS3 Shield – LiH Block (Reference (g))

The PIE was performed several months after the conclusion of the 10,000 hour experiment. The internal pressure was measured to be ~430 torr. The pressure loss was attributed to diffusion of He or a slow leak over the long-term test.

The LiH block was hard and solid, similar to an unirradiated block, after the irradiation (depicted in Figure 10). The dimensions of the LiH block did not change within the accuracy of the measurement technique ($\pm 1.2\%$). The dimensional measurements of the SNAP 10AFSA shield are given in Table 10.

Table 10: Dimensional Measurements of The SNAP 10AFS3 Shield (Reference (g))

Position	As-Made (in.)	Postirra- diation (in.)	Difference (in.)	Percent Change
Length	27.47	27.42	-0.05	-0.2
Diameter A-1	17.56	17.39	-0.17	-1.0
A-2	18.80	18.67	-0.13	-0.7
A-3	19.54	19.65	+0.11	+0.6
A-4	20.92	20.54	-0.38	-1.8
90° to Diameter A-1	17.56	17.14	-0.42	-2.4
A-2	18.40	18.39	-0.01	-<0.1
A-3	19.32	19.68	+0.36	+1.8
A-4	20.54	20.78	+0.24	+1.1

Samples were removed from various locations for chemical analysis. However, a heavy layer of whitish hydroxide contamination was observed prior to analysis, which was not present during the original sampling. The contamination was partially scraped off the surface. This process was performed twice, noted by the two hydroxide measurements given in Table 11. The uncontaminated LiH was estimated to contain no more than 2-3% hydroxide.

The lattice parameter was measured to be 4.084 Å, which agrees fairly well with the STIR experiment measurement (4.085 Å) (Reference (g)).

1.9. Summary

In Reference (g), Welch compiles a summary of almost 50 lithium hydride specimens tested at a variety of facilities under an assortment of conditions (reproduced [minus a few columns] as Table 12 for the reader's convenience), which includes all of the data points discussed within this Attachment. Table 12 includes several potential performance indicators: growth, blackening, and results of the experiment (this appears to be a judgment by Welch "good" or "bad" depending on whether or not swelling, spallation, or other gross deterioration occurred).

Table 11: Chemical Analysis of the Irradiated LiH From the SNAP 10AFS3 Shield (Reference (g))

CHEMICAL ANALYSIS OF THE IRRADIATED LiH FROM THE SNAP 10AFS3 SHIELD

Constituent	Weight Percent	
	Location of Sample	
	Top	Bottom
Hydrogen	11.65*	11.90†
Lithium	82.10	82.55
Hydroxide	4.65 (4.99)‡	3.38 (4.08)‡
Carbonate	0.04	0.03

*Equivalent to 92.0 wt % LiH.

†Equivalent to 93.8 wt % LiH.

‡Original analysis values.

Table 12: Summary of LiH Irradiation Data (Reference (g))

	Identification	Temperature (oF)	Material Form	Constrained	nvt, Thermal	nvt, Fast	Out-gassed	Facility	Growth	Blackened	f/t Ratio	Gas Evolved	Duration (hr)	Results
1	Welch LTHxV2-3	200	P*	Uc*	4.4E+16	1.1E+16	Yes	LITR	No*	U*	<1	No	157	Good.
2	Welch STIR 2	237±14	Ct*	C*	1.3E+16	3.1E+17	No	STIR	-1%	Yes	>1	NM*	16	Bad. About 1% linear expansion.
3	Welch LTHx-6	160±15	P	Uc	1.1E+16	2.5E+16	Yes	LITR	U	In center	<1	Maybe	583	Bad. Soft under hard crust 1/16 in. Interconnected to LTHx-5.
4	Hamill-Waldrop	302-335	P	Uc	4.0E+15	1.6E+17	Yes	NARF	Yes	Yes	>1	Maybe	45	Bad. ~2.4% maximum expansion. Capsule leaked.
5	Minushkin No.5	100	P	Uc	1.6E+15	U	No	BNL	No	Slightly	<1	Yes	335	Good.
6	Welch Hx3-4	400	P	Uc	1.4E+18	U	Yes	X-pile	No	U	<1	No	444	Good.
7	Aitken and Henry	972	P	C	4.0E+18	1E+18	Yes	LITR	No	Slightly	<1	No	100	Good.
8	Welch LTHxV2-2	400	P	Uc	3.7E+15	9E+14	Yes	LITR	No	U	<1	No	130	Good.
9	Welch LTHxV2-1	560	P	Uc	2.5E+16	6E+15	Yes	LITR	No	U	<1	No	149	Good.
10	Welch LTHx-5	550±50	P	Uc	3.1E+18	3E+17	Yes	LITR	Yes	Yes	<1	Maybe	583	Bad. Leak Suspected. Powdered.
11	Aitken and Henry	1000	P	Uc	4.0E+18	1E+18	Yes	LITR	No	Slightly	<1	No	100	Good.
12	Minushkin No. 2	400	P	Uc	2.0E+16	U	No	BNL	Yes	Yes	<1	Yes	10-14 day	Bad.
13	Welch LTHxV2-4	800	P	Uc	4.1E+16	1E+16	Yes	LITR	No	U	<1	No	146	Good.
14	Welch Hx1-1	235-260	Ct	C	5.0E+17	U	Yes	X-pile	No	U	<1	No	155	Good.
15	Welch Hx1-2	235-260	Ct	C	5.0E+17	U	Yes	X-pile	No	U	<1	No	155	Good.
16	Welch Hx1-3	235-260	Ct	C	5.0E+18	U	Yes	X-pile	No	U	<1	No	155	Good.
17	Aitken and Henry	970	Ct	C	4.0E+18	1E+18	Yes	LITR	No	Slightly	<1	No	100	Good.
18	Welch LTHxV2-5	1000	P	Uc	3.3E+16	8E+15	Yes	LITR	No	U	<1	No	117	Good.
19	Welch LTHx-9B	790±10	P	Uc	8.5E+17	2E+17	Yes	LITR	No	U	<1	No	118	Good.
20	Welch Hx2-6	1000	Ct	C	5.9E+17	U	Yes	X-pile	No	U	<1	No	181	Good.
21	Welch LTHx-11	810	Ct	C	1.6E+18	4E+17	Yes	LITR	No	U	<1	No	149	Good.
22	Minushkin No.4	400-610	P	Uc	1.1E+18	U	No	BNL	Yes	Yes	<1	Yes	10-14 day	Bad.
23	Welch Hx2-2	800	Ct	C	5.9E+17	U	Yes	X-pile	No	U	<1	No	181	Good.
24	Minushkin No. 3	400-610	P	Uc	1.1E+18	U	No	BNL	Yes	Yes	<1	Yes	10-14 day	Bad.
25	Welch MTR	790±10	P	C	1.7E+18	4E+17	Yes	MTR	No	No	<1	No	100	Good.
26	Welch Hx3-1	250	Ct	C	1.4E+18	U	Yes	X-pile	No	U	<1	No	444	Good.
27	Welch STIR 3	237±14	P	Uc	1.3E+16	2.7E+17	Yes	STIR	-1%	Yes	>1	NM	16	Bad. About 1% linear expansion.
28	Welch LTHx-10	580±30	Ct	C	6.9E+17	1.7E+17	Yes	LITR	No	U	<1	No	148	Good.
29	Welch Hx3-2	250	P	Uc	1.4E+18	U	Yes	X-pile	No	U	<1	No	444	Good.
30	Welch LTHx-8	580±30	P	Uc	9.9E+17	2.5E+17	Yes	LITR	No	U	<1	No	118	Good.
31	Welch LTHx-4	400	P	Uc	2.1E+19	5E+18	Yes	LITR	Yes	U	<1	Maybe	744	Bad. Leaked.
32	Welch Hx1-2	300	Ct	C	5.0E+17	U	Yes	X-pile	No	U	<1	No	155	Good.
33	Welch LTHx-9	770±45	P	Uc	7.2E+16	1.8E+16	Yes	LITR	No	U	<1	No	150	Good.
34	Welch LTHx-12	1000	P	Uc	1.3E+19	4E+18	Yes	LITR	No	U	<1	No	155	Good.
35	Minushkin No.1	400	P	Uc	2.0E+16	U	No	BNL	Yes	Yes	<1	Yes	10-14 day	Bad.
36	Welch Hx2-5	400	Ct	C	5.9E+17	U	Yes	X-pile	No	U	<1	No	181	Good.
37	Welch STIR 1	237±14	Ct	Uc	1.3E+16	3.1E+17	Yes	STIR	Yes	Yes	>1	NM	16	Bad. Specimen spalled.
38	Welch Hx3-3	400	Ct	C	1.4E+18	U	Yes	X-pile	No	U	<1	No	444	Good.
39	ANL 4010	U	Crystals	No	U	U	No	CP-3	U	Yes	<1	Yes	240	Good. No change in appearance.
40	S10AFS3	775	P	C/Uc	1.0E+17	2.58E+18	Yes	S10A	ND	No	>1	No	10000	Good.
41	ANL 4208	U	Ct	C/Uc	8.0E+17	U	Yes	CP-3	U	Yes	<1	No	2160	Good.
42	NARF 8-10	ca 950	P	Uc	2e15 - 2e16	1E17 - 1E18	No	NARF	Yes	Yes	>1	Yes	350	Bad.
43	NARF No. 7	ca 951	P	C	1.3E+15	5.5E+16	No	NARF	Yes	Yes	>1	Yes	110	Bad.
44	NARF brick	ca 952	P	Uc	3.0E+15	1.4E+17	No	NARF	Yes	Yes	>1	Yes	220	Bad.
45	Welch STIR 4	237±14	P	Uc	1.3E+16	2.4E+17	Yes	STIR	No	No	>1	NM	16	Good.
46	Minushkin No.6	400-600	Crystals	Uc	1.0E+18	U	No	BNL	U	U	<1	Yes	10-14 day	U.
47	HW 10090	U	Ct	U	U	U	Yes	H-F pile	U	U	U	U	U	Good.

*Definition of abbreviations:

P = Cold-pressed

Ct = Cast

Uc = Unconstrained

C = Constrained

U = Unknown

No = No visible change observed

ND = Not detected

NM = Not measured

1.10. References

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Attachment 3 to Enclosure 2 to MDO-723-0048:

Meta Analysis of Early Irradiation Experiments

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1. Meta Analysis

1.1. Background

The need for meta analysis has arisen from the flood of information available in the published literature. The approach was originally developed by Gene Glass in 1976, who proposed a method of integrating the findings from a body of research (Reference (a)). In 1967, Frank H. Welch compiled data from 47 lithium hydride mixed neutron/gamma radiation tests. Meta analysis provides an opportunity to statistically analyze the data compiled by Welch for useful information. Table 1 is a reproduction of the Welch table, with some minor changes for ease of reproduction (Reference (b)).

Table 1: Summary of LiH Irradiation Data (Reference (b))

	Identification	Temperature (oF)	Material Form	Constrained	nvt, Thermal	nvt, Fast	Out-gassed	Facility	Growth	Blackened	f/t Ratio	Gas Evolved	Duration (hr)	Results
1	Welch LTHxV2-3	200	P*	Uc*	4.4E+16	1.1E+16	Yes	LITR	No*	U*	<1	No	157	Good.
2	Welch STIR 2	237±14	Ct*	C*	1.3E+16	3.1E+17	No	STIR	-1%	Yes	>1	NM*	16	Bad. About 1% linear expansion.
3	Welch LTHx-6	160±15	P	Uc	1.1E+16	2.5E+16	Yes	LITR	U	In center	<1	Maybe	583	Bad. Soft under hard crust 1/16 in. Interconnected to LTHx-5.
4	Hamill-Waldrop	302-335	P	Uc	4.0E+15	1.6E+17	Yes	NARF	Yes	Yes	>1	Maybe	45	Bad. ~2.4% maximum expansion. Capsule leaked.
5	Minushkin No.5	100	P	Uc	1.6E+15	U	No	BNL	No	Slightly	<1	Yes	335	Good.
6	Welch Hx3-4	400	P	Uc	1.4E+18	U	Yes	X-pile	No	U	<1	No	444	Good.
7	Aitken and Henry	972	P	C	4.0E+18	1E+18	Yes	LITR	No	Slightly	<1	No	100	Good.
8	Welch LTHxV2-2	400	P	Uc	3.7E+15	9E+14	Yes	LITR	No	U	<1	No	130	Good.
9	Welch LTHxV2-1	560	P	Uc	2.5E+16	6E+15	Yes	LITR	No	U	<1	No	149	Good.
10	Welch LTHx-5	550±50	P	Uc	3.1E+18	3E+17	Yes	LITR	Yes	Yes	<1	Maybe	583	Bad. Leak Suspected. Powdered.
11	Aitken and Henry	1000	P	Uc	4.0E+18	1E+18	Yes	LITR	No	Slightly	<1	No	100	Good.
12	Minushkin No. 2	400	P	Uc	2.0E+16	U	No	BNL	Yes	Yes	<1	Yes	10-14 day	Bad.
13	Welch LTHxV2-4	800	P	Uc	4.1E+16	1E+16	Yes	LITR	No	U	<1	No	146	Good.
14	Welch Hx1-1	235-260	Ct	C	5.0E+17	U	Yes	X-pile	No	U	<1	No	155	Good.
15	Welch Hx1-2	235-260	Ct	C	5.0E+17	U	Yes	X-pile	No	U	<1	No	155	Good.
16	Welch Hx1-3	235-260	Ct	C	5.0E+18	U	Yes	X-pile	No	U	<1	No	155	Good.
17	Aitken and Henry	970	Ct	C	4.0E+18	1E+18	Yes	LITR	No	Slightly	<1	No	100	Good.
18	Welch LTHxV2-5	1000	P	Uc	3.3E+16	8E+15	Yes	LITR	No	U	<1	No	117	Good.
19	Welch LTHx-9B	790±10	P	Uc	8.5E+17	2E+17	Yes	LITR	No	U	<1	No	118	Good.
20	Welch Hx2-6	1000	Ct	C	5.9E+17	U	Yes	X-pile	No	U	<1	No	181	Good.
21	Welch LTHx-11	810	Ct	C	1.6E+18	4E+17	Yes	LITR	No	U	<1	No	149	Good.
22	Minushkin No.4	400-610	P	Uc	1.1E+18	U	No	BNL	Yes	Yes	<1	Yes	10-14 day	Bad.
23	Welch Hx2-2	800	Ct	C	5.9E+17	U	Yes	X-pile	No	U	<1	No	181	Good.
24	Minushkin No. 3	400-610	P	Uc	1.1E+18	U	No	BNL	Yes	Yes	<1	Yes	10-14 day	Bad.
25	Welch MTR	790±10	P	C	1.7E+18	4E+17	Yes	MTR	No	No	<1	No	100	Good.
26	Welch Hx3-1	250	Ct	C	1.4E+18	U	Yes	X-pile	No	U	<1	No	444	Good.
27	Welch STIR 3	237±14	P	Uc	1.3E+16	2.7E+17	Yes	STIR	-1%	Yes	>1	NM	16	Bad. About 1% linear expansion.
28	Welch LTHx-10	580±30	Ct	C	6.9E+17	1.7E+17	Yes	LITR	No	U	<1	No	148	Good.
29	Welch Hx3-2	250	P	Uc	1.4E+18	U	Yes	X-pile	No	U	<1	No	444	Good.
30	Welch LTHx-8	580±30	P	Uc	9.9E+17	2.5E+17	Yes	LITR	No	U	<1	No	118	Good.
31	Welch LTHx-4	400	P	Uc	2.1E+19	5E+18	Yes	LITR	Yes	U	<1	Maybe	744	Bad. Leaked.
32	Welch Hx1-2	300	Ct	C	5.0E+17	U	Yes	X-pile	No	U	<1	No	155	Good.
33	Welch LTHx-9	770±45	P	Uc	7.2E+16	1.8E+16	Yes	LITR	No	U	<1	No	150	Good.
34	Welch LTHx-12	1000	P	Uc	1.3E+19	4E+18	Yes	LITR	No	U	<1	No	155	Good.
35	Minushkin No.1	400	P	Uc	2.0E+16	U	No	BNL	Yes	Yes	<1	Yes	10-14 day	Bad.
36	Welch Hx2-5	400	Ct	C	5.9E+17	U	Yes	X-pile	No	U	<1	No	181	Good.
37	Welch STIR 1	237±14	Ct	Uc	1.3E+16	3.1E+17	Yes	STIR	Yes	Yes	>1	NM	16	Bad. Specimen spalled.
38	Welch Hx3-3	400	Ct	C	1.4E+18	U	Yes	X-pile	No	U	<1	No	444	Good.
39	ANL 4010	U	Crystals	No	U	U	No	CP-3	U	Yes	<1	Yes	240	Good. No change in appearance.
40	S10AFS3	775	P	C/Uc	1.0E+17	2.58E+18	Yes	S10A	ND	No	>1	No	10000	Good.
41	ANL 4208	U	Ct	C/Uc	8.0E+17	U	Yes	CP-3	U	Yes	<1	No	2160	Good.
42	NARF 8-10	ca 950	P	Uc	2e15 - 2e16	1E17 - 1E18	No	NARF	Yes	Yes	>1	Yes	350	Bad.
43	NARF No. 7	ca 951	P	C	1.3E+15	5.5E+16	No	NARF	Yes	Yes	>1	Yes	110	Bad.
44	NARF brick	ca 952	P	Uc	3.0E+15	1.4E+17	No	NARF	Yes	Yes	>1	Yes	220	Bad.
45	Welch STIR 4	237±14	P	Uc	1.3E+16	2.4E+17	Yes	STIR	No	No	>1	NM	16	Good.
46	Minushkin No.6	400-600	Crystals	Uc	1.0E+18	U	No	BNL	U	U	<1	Yes	10-14 day	U.
47	HW 10090	U	Ct	U	U	U	Yes	H-F pile	U	U	U	U	U	Good.

*Definition of abbreviations:

P = Cold-pressed
Ct = Cast
Uc = Unconstrained

C = Constrained
U = Unknown
No = No visible change observed

ND = Not detected
NM = Not measured

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In Reference (b) Welch states:

“Reviewing all of the available information on the reactor irradiations of LiH, including the detailed information presented in the previous sections, it is concluded that no simple process explains the observed phenomena.

Nearly 50 specimens were irradiated, as shown in Table 1, under many different conditions of temperature, fast- and thermal-neutron dose, time, form, etc. These irradiations have been categorized as bad or good depending on whether or not swelling, spalling, or other gross deterioration was noted. Fourteen irradiations are noted as bad.

A temperature-thermal neutron dose plot of the irradiations (Figure 75) reveals that close to nearly every case noted as "bad" are found "good" tests. The obvious exceptions are No.'s 31, 42, 43, and 44, and it is interesting to note that the last three are the more hastily conducted NARF tests. Thermal neutron dosage per se may reasonably well be ruled out as a factor causing damage.”

This table, being a collection of data from multiple sources, is clearly difficult to interpret. At the time of his report (1967) the notion of “meta-analysis” did not exist, and only subjective conclusions were drawn. Subsequently, meta analysis has been developed and applied principally in the medical field, to aggregate findings from data compilations such as the one created by Welch.

1.2. Description of Meta Analysis

Meta analysis provides an opportunity to statistically analyze the data compiled in Table 1 for useful information. Meta analysis is the statistical analysis of a large collection of results from individual studies for the purpose of integrating the findings. This methodology overcomes the human mind's limitation in identifying relationships among a large number of factors, commonly encountered by a researcher attempting to synthesize information to find global relationships from a large number of publications or experimental results.

By combining multiple experiments and their findings, meta analysis can identify statistically significant differences in treatments unsolvable in the root experiments, and can test hypotheses not considered by the original investigator. Furthermore, this method can provide aggregated estimates of response performance. A single experiment with a small population frequently cannot yield results of statistical significance. Larger sample sizes, while desirable, are often prohibitively expensive, experimentally difficult, or unethical in cases involving human subjects. Additionally, meta analysis can help identify new questions, supported by the aggregation of previous data, for future research. Thus meta analysis effectively complements traditional research methods.

The steps for performing a meta analysis are:

- Formulate the problem
- Perform a literature search
- Evaluate and code the literature
- Statistical analysis
- Interpretation of results
- Graphical presentation of results

The statistical analysis typically employs logistic regression or paired comparisons. However, other methods can be applied as appropriate, i.e., neural networks, regression trees, etc.

1.3. Potential Sources of Error in a Meta Analysis

There are multiple possible sources of error that must be considered when performing a meta analysis. These are:

Selection bias: Positive results are more likely to be published than negative

Publication bias: A study, once published, can influence future studies

Experimental design: An incomplete experiment could have been performed, e.g., not evaluating the entire experimental volume

Experimental procedure/method: poorly designed experiment, failed experiment, mistakes, damaged samples, confounded results, or missing data

Misprints: Missing or incorrect data due to publication, review, transcription, or duplication errors

Selection bias and publication bias were not considered significant error sources due to the source of the Table 1 data being laboratory reports, not peer reviewed journal articles. A potentially more significant source of error is the lack of independence of the table's creator (Welch) who authored 30 out of the 47 reports. He may have been further biased in that he compiled the table as part of the qualification of lithium hydride for the SNAP program in which he was believed to be a stakeholder. Errors due to the experimental design and procedure were documented in the various reports and are discussed in Attachment 2. A copying error resulted in some missing values, which are identified in Table 1 as "U" (unknown).

1.4. Results

Table 2 summarizes the variables presented in Table 1 showing the frequency of occurrence by material.

Table 2: Summary of experimental material forms.

Experimental Factor – material form	Percent of samples	Number of samples
Crystal	4	2
Cast	35	17
Pressed	61	30

The results of the significant pairwise comparisons of the experimental variables are shown below. All relationships are significant at 5% or less.

Some specimens were out-gassed prior to irradiation. The pairwise analysis demonstrated that out-gassing and growth were correlated, but not perfectly. As shown in Figure 1, most specimens that were out-gassed did not grow during irradiation, but some did. Specimens that were out-gassed prior to irradiation were more likely to be good (the dependent variable) in these experiments. This relationship is shown in Figure 2.

Figure 1: Plot showing the relationship between out-gassed specimens and growth during irradiation. The bar to the right shows the overall frequency of growth without regard to whether the specimen was out-gassed prior to irradiation. Numerical values are shown in the table.

Figure 2: Results (good vs. bad) plotted against whether the specimens were out-gassed prior to irradiation. The numerical results are shown in the table.

Shown in Figure 3 are the relationship between gas evolved and material form. No gas was evolved during irradiation with the cast material (Ct), whereas all of the crystal LiH (there were only two crystal specimens) evolved gas. For cold pressed LiH (P), some specimens evolved gas and some did not. Gas Evolved and Growth were related, but not perfectly. Most of the specimens that did not grow also did not evolve gas during irradiation. This relationship is shown in Figure 4.

Figure 3: The relationship between gas evolved and material form. All of the crystal specimens evolved gas, none of the cast (Ct) evolved gas, and results were mixed for pressed (P) specimens.

Figure 4: Plot and table showing the relationship between gas evolved and growth.

The dependent variable, identified subjectively as “good” or “bad” by Welch, was found to have a significant relationship with gas evolved. Those specimens that were “good” generally did not evolve gas. Those specimens that were “bad” either evolved gas or possibly evolved gas (Figure 5). Pressed material (P) was more likely to be bad than cast material (Ct) as shown in Figure 6.

Results By Gas Evolved Same comment				
Total %	Maybe	No	Yes	
Bad	9.30	0.00	16.28	25.58
Good	0.00	69.77	4.65	74.42
	9.30	69.77	20.93	

Figure 5: Plot and table showing the relationship between gas evolved and results. Most of the specimens determined to be “good” did not evolve gas.

Material Form By Results			
Total %	Bad	Good	
Crystals	0.00	2.08	2.08
Ct	4.17	31.25	35.42
P	25.00	37.50	62.50
	29.17	70.83	

Figure 6: Plot of the relationship between material form and results (good or bad). Most of the cast specimens were good. Results for the pressed specimens were more evenly mixed. Crystals were not included in the plot.

1.5. Conclusions

Significant insight was obtained from this meta analysis that assists with the understanding and qualification of lithium hydride as a space reactor shield material. The first is that cast LiH is more likely to be “good” (i.e., not swell) than pressed. This is believed to be due to the fundamental difference in processing methods between cast and pressed LiH, and the resulting differences in purity, impurity distribution, and microstructure.

This meta analysis also indicated that out-gassing the specimens prior to irradiation reduced the likelihood of radiation-induced swelling. It is possible that this affect is caused by the removal (i.e., bake-out) of the dissolved gasses (atmospheric gasses, moisture, etc., i.e., LiH is highly hygroscopic) and perhaps other impurities (e.g., LiOH) prior to irradiation. Further discussion on this topic may be found in Enclosure 2.

1.6. References

- (a) Glass, G. V. 1976. Primary, secondary, and meta-analysis of research. *Educational Researcher*, 5, 3-8.
- (b) Welch, F. H. 1967. Lithium Hydride Technology: III. Properties of Lithium Hydride for SNAP Shielding Applications. Atomics International Document NAA-SR-9400 Volume III.

Attachment 4 to Enclosure 2 to MDO-723-0048:

SP-100 Irradiation Experiments

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1. SP-100 LiH Review

Reference (a) details the lithium hydride (LiH) literature review, LiH irradiation testing and analysis, LiH swelling mechanisms, and conclusions from the SP-100 program. Lithium hydride was selected for use in the SP-100 shield based on mass minimization studies. SP-100 conceptual designs and LiH literature review identified a need for several irradiation tests focused on the swelling of LiH under various fluences, fluxes and temperatures. Irradiation test temperatures focused on 600K to 800K full power operations and 400K to 500K for partial power operations. The test specimens were made from Y12 LiH tailings with somewhat depleted Li^6 concentrations. No information is available in Reference (a) as to the mass fraction of LiOH in the samples and it appears that the samples were not out-gassed prior to irradiation. Care was taken during processing to avoid LiH contamination with water but the end specimen LiOH concentration was unknown at the time of issuance of this letter. Reference (b), which contained a final presentation from the SP-100 researchers on actions which might lower LiH swelling in future irradiations, included the recommendation that the samples be out-gassed, which implies the SP-100 samples were not.

Initial neutron testing was performed in the Advanced Test Reactor (ATR) at the Idaho National Engineering Laboratory (INEL). After completion of ATR tests and a more extensive review of the LiH database, additional neutron tests were conducted at the Advanced Reactivity Measurement Facility (ARMF), also located at INEL. Gamma testing was conducted at Georgia Tech Research Reactor (GTRR).

1.1. Mixed Neutron/Gamma

The neutron test performed in the ATR, referred to as B-2A test, is well documented in Reference (a), pgs 34-72. The following are the key aspects of the test.

Test temperatures ranged from ~500-650K. There is question as to the temperature accuracy and usefulness. The temperatures were measured with thermal expansion difference (TED) monitors, which typically only indicate the highest specimen temperature during the entire irradiation exposure time. Given that the specimens expanded significantly, closing the gaps within the test containers, heat transport was likely enhanced, cooling the specimens below the maximum temperatures indicated by the TEDs. Should the swelling mechanisms under mixed neutron and gamma irradiation prove to be a strong function of temperature in this range, this temperature inaccuracy could be significant in the interpretation of the test results.

Neutron fluences and fluxes varied with specimen location. The fluence from neutrons with $E > 1\text{MeV}$ was approximately $1 \times 10^{18} \text{ n/cm}^2$ (~3 Grad). The fast flux ($E > 1\text{MeV}$) ranged from $5 \times 10^{11} \text{ n/cm}^2\text{-s}$ to $3 \times 10^{12} \text{ n/cm}^2\text{-s}$. The thermal flux ranged from $5 \times 10^{12} \text{ n/cm}^2\text{-s}$ to $1 \times 10^{13} \text{ n/cm}^2\text{-s}$.

Specimens exhibited higher than expected swelling. This result was attributed to the accelerated testing via high fluxes to reach prototypical fluences in minimal exposure time. The amount of LiOH in the specimens may have contributed to the higher than expected swelling. The SNAP & ANP exposures (see Attachment 2 to Enclosure 2) were similarly accelerated, with many specimens showing no swelling ("growth"). Several B-2A specimens swelled about 20%, with the remainder swelling about 10%. The container design allowed for approximately 20% volume swelling. The containers were made from aluminum—as were the NARF containers that ruptured during testing. One B-2A container, A-15, ruptured. SP-100 estimated that an internal pressure of 3500 to 4000 psi was required to rupture the container. Several other containers were bowed out, as if due to high internal pressure. The specimen and container A-15 was located in the coolest area in the reactor for this test. LiH specimens showed swelling temperature dependence, with specimens ~500K swelling more than specimens exposed to hotter conditions, ~650K.

Table 1 summarizes several parameters important in the B-2A test and Figure 1 displays swelling results.

Table 1: SP-100 B-2A Mixed Neutron/Gamma ATR Test¹ (Reference (a))

Test Container	Sample # ²	Temperature (K) ³	Average Swelling %	Notes
A-15	RC550WL1	492	Not measured	ruptured
A-16	RR550WL1	504	18.5	
A-17	RR550WL2	505	19.1	
A-10	RC700WL1	637	Not measured	
A-13	RR700WL1	636	9.7	
A-14	RR700WL2	634	7.9	
A-18	RC700OL1	660	13	
A-19	RR700OL1	656	9.2	
A-20	RR700OL2	642	11.8	
A-21	RC550OL1	527	20	
A-22	RR550OL1	529	19.1	
A-23	RR550OL2	497	17.6	

¹ Cycle 86C @ I-1 location; 371.5 EFPH, nominal power of 23 Mwatts for each NE and NW lobes

² Specimens were prepared with and without the SS-316L egg crate and both stoichiometric and non-stoichiometric. Sub-stoichiometric contained ~2% free Li with ~2% Li⁶ from Y-12 stockpile tails. A 2.5" LiH specimen would include at least one lattice cell. Material formed with and without the cell was shown to have similar properties. Sample dimensions varied with test temperature to accommodate a thicker "x" parameter with increasing temperature. Specimen diameter @ 550K, 2.54"; 700K, 2.52"; 850K, 2.50".

³ Measured in the dosimetry package via a thermal expansion difference temperature monitor (TEDs); reported @ SOI conditions, highest specimen temperature within irradiation time.

Figure 1: SP-100 B-2A ATR and B-2F ARMF Neutron/Gamma Tests (Reference (a))

PRE-DECISIONAL - For planning and discussion purposes only

The B-2F ARMF test was another test run by the SP-100 program testing LiH specimens under irradiated conditions. This test is documented in Reference (a), pages 73-86. All specimens demonstrated 0% swelling. The specimens were run at temperature for 24 hours but only exposed to irradiation for ~8 hours per day. Table 2 summarizes the test conditions and results. The SP-100 program believed the zero swelling result was due to annealing of the damage caused by irradiation, i.e. the 16 hours per day when the flux was turned off was when the damage was being annealed. It is not clear whether the 16 hours per day of annealing repaired the damage caused by the flux, or that simply the relatively low averaged fluxes and high temperatures may have combined to minimize the swelling. The ARMF test may be much closer to the typical swelling pure LiH (no LiOH impurities) would see under similar conditions.

Table 2: SP-100 B-2F Mixed Neutron/Gamma ARMF Test (Reference (a))

Sample # ¹	Neutron Flux ²		Neutron Fluence ²	
	$E_n > 0.1 \text{ Mev (n/cm}^2\text{-sec)}$	$E_n > 1.0 \text{ Mev (n/cm}^2\text{-sec)}$	$E_n > 0.1 \text{ Mev (n/cm}^2)$	$E_n > 1.0 \text{ Mev (n/cm}^2)$
850	4.89E+11	2.05E+11	2.04E+17	8.56E+16
RC700OH1	4.89E+11	2.05E+11	2.04E+17	8.56E+16
RC700WH1	4.89E+11	2.05E+11	2.04E+17	8.56E+16
W/O	4.89E+11	2.05E+11	2.04E+17	8.56E+16
			(~0.41 Grad)	(~0.26 Grad)
Sample # ¹	Gamma ²		Gamma ²	
	Temperature (K) ³	Average Swelling % ⁴	Dose Rate (Grads/hr)	Total Dose (Grads)
850	700	0	0.008	0.872
RC700OH1	700	0	0.008	0.872
RC700WH1	625	0	0.008	0.872
W/O	600	0	0.008	0.872
¹ Samples from B-2A ATR test				
² Average predicted rates from nuclear testing.				
³ Controlled temperature of each specimen through use of thermocouples attached to each specimen container and computer control of a series of disk heaters. Individual containers were separated by ceramic insulator disks. Temperatures reported as +/- 17K.				
⁴ Dimensional analysis of the test specimens detected no measurable swelling.				

1.2. Gamma

Gamma testing on LiH specimens was conducted at GTRR in 1992 (Reference (a), pgs 87-100).

- Gamma irradiation emanated from a ⁶⁰Co source at the GTRR facility.
- Test temperatures targeted 400K, 450K, 500K, and 600K, however the lower target temperatures were elevated during testing due to high gamma heating at the higher flux rate of 3.4 Mrad/hr.
- The LiH specimens were tested at two flux rates, 3.4 Mrad/hr and 1.25 Mrad/hr for a total dose of 2.5 Grads. Results showed LiH swelling reached up to ~10% at the 500K, 3.4Mrads/hr condition. All specimens tested at 600K showed no swelling. Specimens exposed to the lower rate of 1.25Mrad/hr measured a maximum swelling of ~7% at 450K.
- Table 3 summarizes the test conditions and results from the GTTR gamma test and Figure 2 shows the results pictorially.

The gamma testing performed by SP-100 is consistent with that reported in Reference (c). Reference (a) suggests that dose rate dependence may be important in LiH swelling as well as the more obvious temperature dependence. Gamma irradiations at as much as 1000 times lower dose rates, which were much more prototypical of Prometheus dose rates than those used in either Reference (a) or (c), were planned but not started prior to Prometheus restructuring. The purpose of this planned testing was to determine whether the Reference (a) minimum design temperature of 600K could be lowered significantly, or perhaps eliminated, which would expand the LiH design space making the use of LiH much more attractive.

Table 3: SP-100 GTRR Gamma Test (Reference (a))

Sample #	Total Dose (Grads)	Temperature (K) ¹	Dose Rate (Mrads/hr)	Average Swelling % ²	notes
3222	2.5	438	3.4	7.7	
3218	2.5	438	3.4	7.95	
3151	2.5	438	3.4	8.6	
3224	2.5	465	3.4	9.05	
3172	2.5	465	3.4	9.45	
3166	2.5	465	3.4	9.15	
3220	2.5	500	3.4	9.5	
3154	2.5	500	3.4	11.15	sample severely damaged, swelling estimated
3164	2.5	500	3.4	10.65	sample severely damaged, swelling estimated
3157	2.5	600	3.4	0	
3174	2.5	600	3.4	0	
3171	2.5	600	3.4	0	
3217	2.5	400	1.25	5.3	
3221	2.5	400	1.25	5.1	
3153	2.5	400	1.25	5.1	
3155	2.5	450	1.25	6.7	
3156	2.5	450	1.25	6.8	
3163	2.5	450	1.25	6.8	
3167	2.5	500	1.25	5.3	
3169	2.5	500	1.25	5.5	
3173	2.5	500	1.25	5.8	
3177	2.5	600	1.25	0	
3178	2.5	600	1.25	0	
3180	2.5	600	1.25	0	

¹ Reported temperatures may not be accurate

² Reported volumetric swelling error +/- 0.15%. Recorded as a min and max % swelling based on dimensional data. Values herein are an average of the min and max reported values. Samples exposed @1.25Mrads/hr only reported 1 swelling values with a +/- 0.3% error.

Figure 2. SP-100 GTRR Gamma Test (Reference (a))

1.3. References

- (a) Disney, R.K., Draft Issue. "Status Report on the SP-100 Program Investigation of Irradiation-Induced Swelling of Lithium Hydride Shield Materials." Westinghouse Electric Corporation Document SP-GES-93-0005.
- (b) ORNL/LTR-NR-JIMO/04-03 Appendix 3, "Documentation Supporting ATR SP-100 Irradiation Experiments," 2004.
- (c) Souers, P.C., T.S. Blake, R.M. Penpraze, and C. Cline, "Pulsed Nuclear Magnetic Resonance of Gamma-Irradiated Lithium Hydride," J. Phys. Chem. Solids, Vol. 30, pp 2649-2656, 1969.

Attachment 5 to Enclosure 2 to MDO-723-0048:

**Atomistic and Mechanistic Modeling of Irradiation Induced Swelling of
Lithium Hydride**

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SIGNIFICANCE TO NR PROGRAM:

The quantum mechanical methodology used to investigate swelling in LiH is a powerful and generally applicable tool to better understand irradiation damage in materials. Work to date has defined the energies of defect formation and the kinetic barriers to defect migration as well as the likely mechanisms of hydrogen gas generation. These findings provide insight into the mechanisms of irradiation induced swelling and can be further assessed should LiH be considered for future application as a neutron shield material.

ABSTRACT

Lithium Hydride (LiH) was a promising neutron shielding material being considered for the Prometheus Project; however, excessive irradiation induced swelling was identified as a factor potentially hampering its usefulness. There are numerous historical studies demonstrating minimal volumetric swelling of LiH under mixed neutron-gamma irradiation (Reference (a)), but there are also many gamma and mixed neutron-gamma irradiation studies demonstrating significant (up to 25%) volumetric swelling (References (b) and (a)). In an attempt to better anticipate the expected swelling of LiH under Prometheus operating conditions, quantum mechanical methods have been used to estimate the energetics and rates of reactions that occur during irradiation of LiH, with particular emphasis on potential reactions leading to formation of H₂. These formation energy and rate estimates are the basic inputs required for a planned integrated rate model, which would attempt to predict concentrations of the chemical species (H₂ in particular) as a function of temperature, time, and irradiation. Conditions that favor significant H₂ production could potentially lead to swelling of the LiH under irradiation.

1.0 BACKGROUND

Lithium Hydride (LiH) has a long history as an attractive primary neutron shielding material for nuclear space reactor applications, including the Aircraft Nuclear Propulsion (ANP) program, the Space Nuclear Auxiliary Power (SNAP) program, and the SP-100 program. Most recently, lithium hydride was also one of the more attractive candidates considered for the Prometheus project. There has been concern over uncertainties in the degree of irradiation induced swelling that would occur in the material under operating conditions. Past gamma irradiation experiments observed irradiation induced swelling as high as (25%) (Reference (b)); however, there is considerable discrepancy over the degree of swelling caused by neutron irradiation (References (a), (c)). In an attempt to better understand irradiation induced swelling of LiH, quantum mechanical methods have been used to predict the formation energies and diffusion rates for point defects that are expected to occur under irradiation, as well as to explore mechanisms for the formation of H₂ gas, which is expected to be the prime contributor to the irradiation induced swelling. These formation energies and rate predictions would be the main inputs for a planned integrated model, which would attempt to predict concentrations of the chemical species as a function of temperature, time, and irradiation. Such predictions could be used to better assess irradiation induced swelling as a function of these conditions, as well as the potential to anneal out this damage at elevated temperatures.

2.0 COMPUTATIONAL METHODS

All quantum mechanical calculations were performed with version 4.6.19 of the Vienna ab initio Simulation Package (VASP) (References (d), (e), (f)). VASP predicts the total energies and forces for the systems of interest by solving the Kohn-Sham equations for density functional theory (DFT). Electron-electron exchange and correlation effects were treated by the generalized gradient approximation (GGA) (References (g), (h)) using the PBE functional (References (i), (j)). Core

electrons are represented by projector-augmented-wave (PAW) potentials (Reference (k)), and valence electrons are represented by a variational plane wave basis set, as implemented in VASP. A plane wave cut-off energy (ENCUT) of 250 eV was used for all calculations, and k-point spacings of $0.399 \text{ \AA}^{-1}$ and $0.266 \text{ \AA}^{-1}$ were used for the $\text{Li}_{32}\text{H}_{32}$ and $\text{Li}_{108}\text{H}_{108}$ supercells, respectively.

Geometry optimizations were performed to identify minimum energy configurations for each of the species of interest using a conjugate gradient method based on the forces and total energies. Transition state geometries were found by using a “nudged elastic band” (Reference (l)) methodology. In this method, the known initial (reactants) and final (products) states are connected by a series of intermediate trial structures. These trial structures are optimized in parallel, with the “elastic band” helping to maintain their relative separation from each other along the trial reaction path. The maximum along this approximate minimum energy path corresponds to the first-order saddle point (transition state), which sets the lower energetic limit the reactants must possess to successfully react. Reaction and diffusion kinetics can be estimated by the barrier height of the identified transition state relative to the reactants.

Auxiliary electronic structure calculations were performed using the Gaussian03 program (Reference (m)). In contrast to VASP, Gaussian is a molecular cluster method: discrete basis functions are placed on each atom, and the cluster is built up atom-by-atom until the results converge upon the bulk properties. Periodic boundary conditions were not applied, which made possible the calculation of alternate electron density analyses and ionization processes, which are not readily performed with the periodic methods. A general basis set was used, with 6-31G applied to the Li atoms and 6-31G(d,p) to the H atoms. The non-local BLYP pure density functional was used to compute exchange and correlation energies; the use of a pure density functional enabled efficient integral evaluations through use of the DGA1 charge fitting function basis. Electronic properties (energies, polarizabilities, and CHELPG atomic charges) were computed for the molecular cluster corresponding to the $3 \times 3 \times 3$ supercell, at geometries optimized in the previous VASP calculations.

3.0 RESULTS

Quantum mechanical methods were used to estimate the optimized geometries and formation energies for isolated defects that are expected to form in the LiH under irradiation. Specifically, the formation of Li and H vacancies, interstitials, and substitutions were considered, as well as the formation of combined Li and H vacancy/interstitial pairs. The details of these findings are presented in section 3.1. In section 3.2, mechanisms are considered for the formation of molecular H_2 within the irradiated LiH, along with the corresponding energetics and reaction barriers for these processes. In section 3.3 the interaction of H_2 with isolated defect sites is predicted to assess the relative stability of these molecules within the LiH lattice. The intragranular diffusion of H_2 within the LiH, as well as the diffusion of Li and H vacancies and interstitials is evaluated in section 3.4 to assess the mobility of these defect species. Section 3.5 discusses the charge distribution for identified defect sites within the LiH, as well as predicted ionization and electron attachment energies. The plan is to eventually incorporate all of these thermodynamic and mobility predictions into an integrated rate model in an attempt to assess the evolution of the LiH as a function of irradiation and temperature, with special attention to the formation of H_2 , due to its expected role in the swelling of LiH. These results will be presented in a future report (Reference (n)).

3.1 ISOLATED DEFECTS

The two supercells used to model the LiH are presented in Figure 1. Initially, the smaller $2 \times 2 \times 2$ ($\text{Li}_{32}\text{H}_{32}$) supercell was used to identify the stable defect structures, but the calculations were then refined using the larger $3 \times 3 \times 3$ ($\text{Li}_{108}\text{H}_{108}$) supercell in an attempt to minimize self interactions with the periodic images of the isolated defects. Because of the ionic nature of the LiH, there is concern of

introducing isolated interstitials or vacancies into the lattice, since a charged defect is being introduced into the system, yet the system is forced to be neutral within the calculation. To overcome this difficulty, only neutral defect pairs (vacancy/interstitial and di-vacancy/di-interstitial pairs) were considered, so that the charge neutrality of the system was maintained. In Table 1 the predicted formation energies for the formation of a Li interstitial/Li vacancy pair (referred to as $\text{Li}_{\text{int}}/\text{Li}_{\text{vac}}$ pair or Li Frenkel pair), a H interstitial/H vacancy pair (referred to as $\text{H}_{\text{int}}/\text{H}_{\text{vac}}$ pair or H Frenkel pair), and a LiH di-vacancy with the balancing Li and H interstitials (referred to as $\text{Li}_{\text{int}}\text{H}_{\text{int}}/\text{Li}_{\text{vac}}\text{H}_{\text{vac}}$ pair or LiH di-vacancy/di-interstitial pair) are presented. The optimized structures, using the larger $\text{Li}_{108}\text{H}_{108}$ supercell, for all of these species are presented in Figure 2. For these predictions the formation energy corresponds to the difference in energy between the optimized supercell with the defect(s) of interest and the original defect-free supercell:

$$\text{Formation Energy (LiH}_{\text{Defect}}) = \text{Electronic Energy (LiH}_{\text{Defect}}) - \text{Electronic Energy (LiH}_{\text{Supercell}}) \quad (1)$$

There is good agreement between the $\text{Li}_{32}\text{H}_{32}$ and $\text{Li}_{108}\text{H}_{108}$ supercell predictions for the formation energies of these defect pairs, lying within 6 kJ/mol of each other for the Li Frenkel defect pair, and within ~1 kJ/mol of each other for the H Frenkel defect pair. In performing the interstitial diffusion calculations for the $\text{Li}_{108}\text{H}_{108}$ supercell it became apparent that there is a relatively strong attraction at close distances between the vacancy and its corresponding ion. For example, for the Li Frenkel pair the relative formation energy is reduced by ~13 kJ/mol when the Li interstitial is moved closer to the Li vacancy site ($\text{Li}_{\text{int}}/\text{Li}_{\text{vac}}$ Pair2 in Table 1). A comparable effect is found for the H Frenkel pair where the formation energy for the H interstitial in the next-nearest neighbor position ($\text{H}_{\text{int}}/\text{H}_{\text{vac}}$ Pair2 in Table 1) is ~21 kJ/mol lower in energy than when it is further from the vacancy site. This finding is consistent with the vacancy providing more room for lattice relaxation to accommodate the interstitial atom, when the interstitial atom is near the vacancy site. It is also reasonable that a larger relaxation energy is found for the H Frenkel pair, since the H^- anion has a larger radius than the Li^+ cations. The formation energies found for the di-vacancy/di-interstitial pair ($\text{LiH}_{\text{int}}/\text{LiH}_{\text{vac}}$) is much larger than the formation energies for the Frenkel pair defects (440 – 485 kJ/mol); however, they are less than the sum of the Li and H Frenkel pair formation energies (520 – 547 kJ/mol), which is reasonable since the adjacent vacancy sites allow for additional relaxation of the lattice to help accommodate the Li and H interstitials.

The optimized cell dimensions are also presented in Table 1 for these point defects. The dimensions were kept fixed for the smaller $\text{Li}_{32}\text{H}_{32}$ supercell for all calculations, so no change in cell volume can occur due to the formation of the point defects. The cell dimensions were allowed to vary for the larger $\text{Li}_{108}\text{H}_{108}$ supercell calculations in order to see the approximate change in volume due to the formation of these point defects. As a reference, the defect free $\text{Li}_{108}\text{H}_{108}$ supercell was found to have 11.84 Å x 11.84 Å x 11.84 Å cell dimensions. In the formation of these defects it was often found that the cell became slightly smaller in the **a** and **b** directions, while expanding in the **c** direction, giving negligible overall changes in the total volume of the cell. The exception to this trend was found for the $\text{H}_{\text{int}}/\text{H}_{\text{vac}}$ Pair2 and $\text{LiH}_{\text{int}}/\text{LiH}_{\text{vac}}$ Pair structures, where a 1.4 Å³ and 19.7 Å³, respectively, increase in total cell volume was found due to the formation of the point defects.

Figure 1. LiH supercells used to model isolated defect formation energies and migration rates: **a)** smaller $\text{Li}_{32}\text{H}_{32}$ supercell used, corresponding to $2 \times 2 \times 2$ LiH unit cells; **b)** larger $\text{Li}_{108}\text{H}_{108}$ supercell used, corresponding to $3 \times 3 \times 3$ LiH unit cells. Note that the image atoms are not displayed in the figure.

Table 1. Formation Energies for Possible Irradiation Induced Defects in LiH

Defect	# H Atoms	# Li Atoms	Relative Energy ^a (kJ/mol)	Total Electronic Energy (eV) ^b	Cell Dimensions ^c (Å)
Li _{int} /Li _{vac} Pair	32	32	249.9	-192.006361	7.88x7.88x7.88
Li _{int} /Li _{vac} Pair1	108	108	255.9	-653.722741	11.83x11.83x11.86
Li _{int} /Li _{vac} Pair2 ^d	108	108	242.8	-653.858612	11.83x11.83x11.86
H _{int} /H _{vac} Pair	32	32	297.5	-191.51314	7.88x7.88x7.88
H _{int} /H _{vac} Pair1	108	108	298.7	-653.27882	11.83x11.83x11.86
H _{int} /H _{vac} Pair2 ^d	108	108	277.4	-653.499931	11.82x11.82x11.89
LiH _{int} /LiH _{vac} Pair	32	32	439.3	-190.043764	7.88x7.88x7.88
LiH _{int} /LiH _{vac} Pair	108	108	484.7	-651.350642	11.87x11.90x11.89

^a Energies are relative to the corresponding defect-free LiH supercells.

^b The total electronic energy of the reference Li₃₂H₃₂ and Li₁₀₈H₁₀₈ supercells are -194.596538 eV and -656.37473 eV, respectively.

^c The cell dimensions were not allowed to vary during the course of the calculation for the smaller Li₃₂H₃₂ supercell calculations, so the cell dimensions remain equivalent to the defect free supercell (7.88 Å x 7.88 Å x 7.88 Å). The dimensions for the defect free Li₁₀₈H₁₀₈ supercell were found to be 11.84 Å x 11.84 Å x 11.84 Å.

^d Lower energy configurations were found when the interstitial atom is moved closer to the vacancy site.

3.2 H₂ FORMATION MECHANISMS

Prior experimentation identified H₂ gas to be the dominant contributor to LiH swelling (References (b), (c), (o), (p)). Therefore, effort was spent attempting to identify reasonable H₂ formation mechanisms that could occur under irradiation, as well as assess the relative energetics and kinetics for these mechanisms. Three potential mechanisms were identified: 1) creation of a Li vacancy site provides a pathway between two hydrogen sites, which given enough energy could react to form H₂; 2) if two H interstitials are created they could potentially combine to form an interstitial H₂ molecule; and 3) if a H interstitial could substitute into a Li vacancy site, it could readily combine with any of the adjacent H sites to form H₂. The last mechanism has been discarded since all attempts to substitute an H atom for a Li site have failed to converge to the desired geometry; instead the H atom placed in the Li vacancy site rapidly moves to an interstitial position during the course of the geometry optimization.

An approximation to a minimum energy path was optimized for the first reaction mechanism (see Figure 3), where once a Li vacancy is created, neighboring H sites can combine across the vacancy to form H₂. The maximum along this approximate minimum energy path corresponds to the transition state, which defines the energetic barrier the reactants must overcome to successfully react. The predicted barrier to reaction is approximately 103 kJ/mol, relative to the isolated Li vacancy, with the net reaction being endothermic by 21.9 kJ/mol. The reaction of two gas-phase H atoms to form H₂ has no barrier; however, that is for the reaction of two neutral H radicals, versus the energy required to overcome the coulombic repulsion of forcing to H anions together. Presumably the bulk of this

Figure 2. Optimized point defect structures for $\text{Li}_{108}\text{H}_{108}$ supercell. Li atoms are purple, H atoms are white, and vacancies are black in the figure. **a)** $\text{Li}_{\text{int}}/\text{Li}_{\text{vac}}$ Pair1; **b)** $\text{Li}_{\text{int}}/\text{Li}_{\text{vac}}$ Pair2; **c)** $\text{H}_{\text{int}}/\text{H}_{\text{vac}}$ Pair1; **d)** $\text{H}_{\text{int}}/\text{H}_{\text{vac}}$ Pair2; and **e)** $\text{LiH}_{\text{int}}/\text{LiH}_{\text{vac}}$ Pair. The various defect features are more clearly identified in **2e**.

Figure 3. Approximate minimum energy path (MEP) for reaction between 2 adjacent H anions across a Li vacancy. MEP is not yet fully optimized.

barrier is due to the energy required to transfer the extra electrons from the reacting H anions to the LiH lattice, allowing the reaction to proceed. The ability of the LiH lattice to accept these extra electrons are examined in more detail in Section 3.5, where predictions of the electron attachment energy of LiH are discussed.

A local minimum was also found where the formed H₂ molecule is centered in the Li vacancy versus keeping a H atom localized at one of the original H lattice sites; however, the net reaction would be endothermic by 73.8 kJ/mol versus the original 21.9 kJ/mol found for the H₂ molecule sited at one of the H lattice positions. This reaction path was found with the smaller Li₃₂H₃₂ supercell. The stable H₂ minimum corresponding to the product of this reaction has not yet been identified with the larger Li₁₀₈H₁₀₈ supercell.

A minimum energy path was identified for the second reaction mechanism, where adjacent H interstitials could combine to form an interstitial H₂ molecule (see Figure 4). The predicted barrier to this reaction is approximately 108 kJ/mol, in close agreement with the first reaction. It is reasonable that the predicted barriers to reaction are consistent between the first and second reaction mechanisms if the largest energetic penalty is due the electron transfer from the reacting H anions to the LiH lattice framework. Unlike the first reaction mechanism, this reaction is exothermic, gaining approximately 83 kJ/mol by formation of the H–H bond. In the gas-phase, reaction of two H atoms to form H₂ is exothermic by 436 kJ/mol (Reference (q)); however, a large energetic penalty must be paid to force the H₂ molecule into the interstitial site of the LiH, which partially explains why the reaction is not nearly as exothermic when it occurs within the LiH. The nudged-elastic-band calculations are not yet completely converged for either the first or second reaction mechanisms; however, they have proceeded for several hundred cycles without changing significantly, so these approximate barrier predictions are not expected to change significantly.

3.3 INTERACTION OF H₂ WITH DEFECT SITES

It is important to gain an understanding of the relative stability of H₂ within the LiH lattice to assess the solubility of H₂ within the lattice versus the likelihood of it diffusing to grain boundaries and other release pathways, or alternatively to combine with other H₂ molecules to nucleate and grow H₂ bubbles, which would promote swelling of the LiH. In Table 2 the relative interaction energies for H₂ with various defect sites within the LiH lattice are presented, and the corresponding optimized structures are presented in Figure 5. These energies are relative to an isolated H₂ molecule and the defect site of interest. The predicted interaction energies are consistent with the physical understanding of the system where the least energy (8.9 kJ/mol) is required to force the H₂ molecule into the site with the most empty space (the LiH di-vacancy site), and the most energy (177 – 201 kJ/mol) is required for the site with the least empty space (the interstitial site), with the H-vacancy and Li-vacancy sites lying intermediate to these two extremes.

These interaction energies alone may be misleading since they assume the defect sites of interest have already been created; however, from Table 1 it is apparent that considerable energy is required to create these vacancy sites (~250 kJ/mol to create a Li Frenkel pair and ~300 kJ/mol to create a H Frenkel pair). These defects naturally occur under irradiation, and will be readily available for the H₂ molecule to react with; however, the sum of the formation energies and the H₂ interaction energies (~350 kJ/mol for H₂ at a Li vacancy and ~330 to 370 kJ/mol for H₂ at a H vacancy) are much higher than the ~200 kJ/mol required to place H₂ at an interstitial site in defect free LiH. This implies that the system will be minimizing its total energy by “healing” the defects as they form, and force the H₂ into interstitial sites. These results, however, only include energetic contributions. A more disordered system would be favored entropically, so there is actually a competition between the desire of the

Figure 4. Approximate minimum energy path (MEP) for reaction between 2 adjacent H interstitial atoms. MEP is not yet fully optimized.

system to minimize its total energy by healing these defects as they form with its desire to maximize its entropy by creating as much disorder as possible. A prediction of the free energy of the system would account for both of these competing factors; however, it has not been feasible to perform these computationally intensive free energy calculations in the time available. In general, increasing the temperature of the system should favor increasing disorder.

Very little energy is required to force a H₂ molecule into the larger LiH di-vacancy site (8.9 kJ/mol); however, again the sum of the di-vacancy formation energy (440 – 485 kJ/mol) and H₂ interaction energy (8.9 kJ/mol) is much higher than the energy required to heal the di-vacancy and force the H₂ molecule into an interstitial site. Again, entropy effects must be included before any definitive conclusions can be drawn about the absolute stability of H₂ within this vacancy site.

Table 2. Interaction Energies of H₂ with Various Sites in LiH

Defect	# H Atoms	# Li Atoms	Interaction energy ^a (kJ/mol)	Total Electronic Energy (eV)	Cell Dimensions ^b (Å)
H ₂ + Int	34	32	201.3	-199.206871	7.88x7.88x7.88
H ₂ + Int	110	108	176.7	-661.240234	11.79x11.86x11.87
H ₂ + Li _{vac}	34	32	99.9	-197.668123	7.88x7.88x7.88
H ₂ + Li _{vac}	110	108	102.8	-659.354421	11.86x11.87x11.85
H ₂ + H _{vac}	34	32	28.8	-197.911355	7.88x7.88x7.88
H ₂ + H _{vac}	110	108	66.5	-659.286248	11.87x11.84x11.85
H ₂ + LiH _{vac}	34	32	—	—	—
H ₂ + LiH _{vac}	110	108	8.9	-657.954876	11.87x11.92x11.88

^a Energies are relative to the isolated defect site and an isolated H₂ molecule.

^b The cell dimensions were not allowed to vary during the course of the calculation for the smaller Li₃₂H₃₂ supercell calculations, so the cell dimensions remain equivalent to the defect free supercell (7.88 Å x 7.88 Å x 7.88 Å). The dimensions for the defect free Li₁₀₈H₁₀₈ supercell were found to be 11.84 Å x 11.84 Å x 11.84 Å.

In order to see the start of bubble formation, additional calculations were performed where increasing numbers (2 to 4) of H₂ molecules were forced into the same LiH di-vacancy site. These results are summarized in Table 3, and the optimized structures are illustrated in Figure 6. These calculations can only give some insight into the initial nucleation of the bubble, since an actual gas bubble would require a significantly larger supercell. Olander (Reference (r)) cites bubbles with a radius less than ~10 Å as being small enough to behave as “constant-density condensed phases.” The bubbles must actually get much larger than this 10 Å (roughly 500 - 1000 Å) before their size is primarily governed by the internal gas pressure versus the surface tension of the LiH. It is at these larger sizes of bubbles, where the gas laws begin to dictate the size of the bubbles, where significant swelling is expected to occur. These sizes are consistent with a previous study (Reference (s)) where NMR and electron microscopy were used on gamma-irradiated LiH, which demonstrated as much as 25 volume per cent swelling after irradiation, to deduce that on average the gas bubbles ranged in size from 80 to 1500 Å. For perspective, the large Li₁₀₈H₁₀₈ super cell has cell dimensions of approximately 12 Å, so combining 8 of these supercells worth of vacancies would approximate a cavity with the ~10 Å radius cited by Olander as the minimum where the internal gas pressure begins to play some role in the size of the bubbles. A large enough supercell must then be created around this cavity to

Figure 5. Optimized structures for H_2 interaction within $Li_{108}H_{108}$ supercell. Li lattice atoms are purple, H lattice atoms are white, and H_2 molecules are blue in the figure. **a)** H_2 sitting in an interstitial site; **b)** Li_{int}/Li_{vac} Pair + H_2 ; **c)** H_{int}/H_{vac} Pair + H_2 ; and **d)** LiH_{int}/LiH_{vac} Pair + H_2 .

Table 3. Interaction Energies for Multiple H₂ Molecules at a LiH Di-Vacancy Site

Defect	# H Atoms	# Li Atoms	Interaction energy ^a (kJ/mol)	Total Electronic Energy ^b (eV)	Cell Dimensions ^c (Å)
H ₂ + LiH _{vac}	110	108	8.9	-657.954876	11.87x11.92x11.88
2H ₂ + LiH _{vac}	112	108	-30.2	-665.057635	11.97x11.87x11.86
3H ₂ + LiH _{vac}	114	108	78.4	-670.627939	12.07x11.85x11.86
4H ₂ + LiH _{vac}	116	108	216.4	-675.894517	12.10x11.91x11.85

^a Energies are relative to the isolated defect site and an isolated H₂ molecule.

^b The total electronic energies of the isolated H₂ reference molecule and LiH di-vacancy site are -6.69673957 eV and -651.350642 eV, respectively.

^c The dimensions for the defect free Li₁₀₈H₁₀₈ supercell were found to be 11.84 Å x 11.84 Å x 11.84 Å. The dimensions of the Li₁₀₈H₁₀₈ supercell with a LiH di-vacancy and corresponding Li and H interstitials were found to be 11.87 Å x 11.90 Å x 11.89 Å.

approximate the bulk LiH. It becomes readily apparent that treating a realistic gas bubble quantum mechanically is beyond the scope of current computing resources.

The situation is not quite as difficult as it may first seem, since the nucleation and growth of the gas bubbles depend on a series of atomistic events: 1) vacancy/interstitial pairs are created, 2) H₂ molecules diffuse to and bind to the vacancy sites, preventing recombination of the interstitial with the vacancy, and 3) additional vacancies and H₂ molecules diffuse to the initial vacancy allowing the bubble to grow. Quantum mechanic methods can be used to estimate the relative energetics and kinetics involved for each of these processes, which can then be fed into larger scale models (kinetic Monte Carlo or a coupled rate equation model) to anticipate the actual growth of these larger bubbles as a function of conditions. Seeing how many H₂ molecules can readily fit into a LiH di-vacancy site gives an indication of the number of H₂ molecules required to stabilize the bubble cavity as it forms. In general, the trend holds that increasing energy is required to force an increasing number of H₂ molecules into the di-vacancy site, with the exception of 2 H₂ molecules. For this case the unexpected result was found that it is actually more favorable for the 2 H₂ molecules to be forced into the di-vacancy site than to be at infinite separation. This could be due to the slight attractive interaction between the 2 H₂ molecules properly oriented within the cavity, as well as due to the effect they may have to actually stabilize the di-vacancy site. As more molecules are forced into the di-vacancy site, an energetic penalty arises due to forcing the H₂ molecules closer to each other than they would prefer, as well as due to distortion of the LiH lattice to accommodate the additional molecules.

Examining the increases in cell volumes with the increasing number of H₂ molecules gives some indication of the strain placed on the total system by forcing these H₂ molecules into the di-vacancy site. Inserting 1 H₂ molecule into the di-vacancy site increases the cell volume by only 19.7 Å³. Inserting 2 H₂ molecules increases the total cell volume by 23.9 Å³, with much larger “swelling” predicted for 3 and 4 H₂ molecules (35.1 Å³ and 46.5 Å³, respectively). Based on these predictions, it seems most likely that 2 H₂ molecules per LiH di-vacancy would be the most favorable configuration.

Figure 6. Optimized structures for interaction of multiple H_2 molecules at a LiH di-vacancy site within the $\text{Li}_{108}\text{H}_{108}$ supercell. Li lattice atoms are purple, H lattice atoms are white, and H_2 molecules are blue in the figure. **a)** 1H_2 molecule; **b)** 2H_2 molecules; **c)** 3H_2 molecules; and **d)** 4H_2 molecules.

3.4 DIFFUSION OF DEFECTS

Minimum energy paths were optimized for the diffusion of Li and H interstitials and vacancies to adjacent sites within the LiH models. Due to the small model size of the $\text{Li}_{32}\text{H}_{32}$ supercell, it was difficult to keep the interstitial/vacancy pairs far enough apart while diffusing to prevent them from annihilating each other during the course of the geometry optimization. It was found that when the pairs were within one lattice spacing of each other ($\sim 2.16 \text{ \AA}$) there were no energetic barriers preventing recombination. For this reason, non-stoichiometric models were used for the smaller $\text{Li}_{32}\text{H}_{32}$ supercell calculations, where only a single defect (interstitial or vacancy) was included. Stoichiometric defect pairs were still used for the larger $\text{Li}_{108}\text{H}_{108}$ supercell calculations. The predicted barrier heights for these diffusion processes are summarized in Table 4.

Extremely low barriers (4.3 to 24.7 kJ/mol) to diffusion were found for the diffusion of the Li and H interstitials between adjacent sites. The predicted barriers for Li interstitial diffusion are in good agreement for both supercell models; however, the low magnitude of these predicted barriers (7.0 and 9.0 kJ/mol) are approaching the uncertainty of the computational methods ($\sim 10 \text{ kJ/mol}$) so they should be used with some caution until they can be validated with more accurate methods or experimental verification. There is a larger discrepancy in the predicted barrier heights for diffusion of the H interstitial (4.3 and 24.7 kJ/mol). Of the predicted barrier heights, the lower 4.3 kJ/mol value found for the larger $\text{Li}_{108}\text{H}_{108}$ supercell is particularly suspicious, since it implies that the larger H interstitial anion is able to diffuse more readily than the smaller Li interstitial cation. Typically, the larger supercell would be expected to yield more reliable results; however, there is some concern since the cell dimensions were allowed to vary for the larger supercell calculations, in an attempt to see what role the formation and migration of these defects may have on swelling. There is the potential for increased numerical uncertainties occurring in the density functional calculations when the cell dimensions are allowed to change during the course of the geometry optimization, so this may be the explanation for this unexpected discrepancy.

The predicted barriers to diffusion are much higher (57.1 to 91.0 kJ/mol) for diffusion of the Li and H vacancies between adjacent sites than was found for interstitial diffusion. Both supercell models are consistent in the prediction that the small Li cation vacancy has a smaller barrier to diffusion (43.7 to 57.1 kJ/mol) than that found for the larger H anion vacancy (84.1 to 91.0 kJ/mol). There is some discrepancy in the magnitude of these predicted barriers for the different supercell models; however, the agreement is reasonable considering the differences between the models (size, non-stoichiometric versus stoichiometric system, and fixed cell dimensions versus relaxed cell dimensions). Overall, although the vibration frequency (and consequently the attempted jump frequency) of the lighter H anion is much higher than the Li cation frequency the much higher barrier for H vacancy diffusion implies a much slower diffusion rate for H vacancies than for Li vacancies.

A minimum energy path was also identified for diffusion of an interstitial H_2 molecule between adjacent sites (see Figure 7). There is an interesting rocking/twisting motion of the H_2 molecule as it diffuses between the adjacent sites. One end of the H_2 molecule inserts between two Li sites, partially forcing the H anion off of its lattice site (see Figure 7). The opposite end of the H_2 molecule then swings up into the next interstitial site, leading the molecule's diffusion into the site. The predicted barrier for interstitial H_2 migration is approximately 72 kJ/mol, which is between the predicted barriers to diffusion for the Li and H vacancies.

To help put these relative barrier heights into perspective, included in Table 4 is an analysis of the fraction of diffusing species with sufficient energy to overcome the barrier and successfully diffuse at 400 K, 500 K, and 600 K, based on Boltzmann's distribution. The fraction of vacancy species with sufficient energy to overcome the predicted barriers is extremely small; however, the species are

Table 4. Barriers to Diffusion for Li and H Interstitials and Vacancies Between Adjacent Sites in LiH, and an Estimate of the Successful Movements Per Second

Diffusing Defect	# H Atoms	# Li Atoms	Barrier Height ($E^\ddagger$) ^a (kJ/mol)	$\exp(-E^\ddagger/(RT))$			$\exp(E^\ddagger/(R \cdot 500K)) \cdot \nu$ (sec ⁻¹) ^b
				400K	500K	600K	
Li _{int}	32	33	7.0	1.22E-01	1.86E-01	2.46E-01	3.3E10
Li _{int}	108	108	9.0	6.68E-02	1.15E-01	1.65E-01	2.0E10
H _{int}	33	32	24.7	5.95E-04	2.63E-03	7.07E-03	8.8E8
H _{int}	108	108	4.3	2.74E-01	3.55E-01	4.22E-01	1.2E11
Li _{vac}	32	31	57.1	3.50E-08	1.08E-06	1.07E-05	1.9E5
Li _{vac}	108	108	43.7	1.97E-06	2.72E-05	1.57E-04	4.8E6
H _{vac}	31	32	84.1	1.04E-11	1.64E-09	4.77E-08	5.5E2
H _{vac}	108	108	91.0	1.31E-12	3.11E-10	1.20E-08	1.0E2
H _{2 int}	108	108	72.3	3.62E-10	2.80E-8	5.08E-7	9.4E3

^a Energies are relative to the isolated defect site.

^b Product of Boltzmann distribution (at 500K) with approximate jump frequency (1.77E11 attempted jumps/sec⁻¹ for Li and 3.36E11 attempted jumps/sec⁻¹ for H) for respective diffusion species.

attempting to jump the barrier multiple times per second. The lattice vibrations give an estimate of how many times the species will try to jump over the diffusion barrier. Messer (Reference (t)) reports infrared absorption studies on LiH yielding absorption peaks centered at 1120 cm⁻¹ and 590 cm⁻¹. Assuming the higher frequency peak (1120 cm⁻¹) corresponds to the lighter H species and the 590 cm⁻¹ peak to the heavier Li species approximate attempted jump frequencies (ν) of 3.36E11 sec⁻¹ and 1.77E11 sec⁻¹ for H and Li species, respectively, are expected. Multiplying the Boltzmann factor with the attempted jump frequency gives an estimate of the fraction of successful jumps per second (see $\exp(E^\ddagger/(R \cdot 500K)) \cdot \nu$ in Table 4 for these estimates at 500 K). This shows that in spite of the relatively high barriers predicted for H vacancy and H₂ interstitial diffusion, hundreds (1.0E2 – 5.5E2) or thousands (9.4E3) of successful jumps per molecule/ion per second are expected at 500 K.

3.5 PREDICTED CHARGE DISTRIBUTION

The possibility that two H interstitial anions combine to form an interstitial H₂ molecule runs contrary to conventional chemical understanding. In an attempt to better understand this phenomenon, as well as the ionization process for LiH, molecular cluster calculations were performed. These calculations were performed by constructing a 216 atom molecular cluster, which corresponds to the 3x3x3 supercell of the solid state calculations. Because there is no periodic lattice, a charge can be introduced which interacts only with the local atoms and not with a periodic image of itself. Electron attachment was modeled by adding one electron to the results of the neutral calculation, resulting in a net negative charge; likewise, ionization was modeled by removing one electron to give a net positive charge. The energy differences for attachment and ionization are given in Table 5.

Figure 7. Minimum energy path (MEP) for H₂ interstitial diffusion. Note the twisting motion of the H₂ molecule as it diffuses between the adjacent interstitial sites.

Table 5. Molecular Cluster Estimates for Electron Attachment and Ionization Energies

Charge	Total Energy (au) ^a	Relative Energy (eV)
Cation (+1)	-879.190830796	5.221
Neutral	-879.382825130	0.000
Anion (-1)	-879.402553268	-0.536

^a Absolute electronic energies are quoted in atomic units (1 au equals 27.2114 eV).

The use of a finite cluster introduces edge effects into the calculation. The CHELPG electrostatic fitting method was used to estimate charges on the atoms, as a tool to investigate the electron distribution and its change upon the addition or subtraction of an electron. The use of quantum mechanical tools to predict effective charges on atoms is a notoriously finicky process due to the difficulty of partitioning the space around the nuclei and properly assigning the electron density to the respective atoms, so these charges are only qualitative. The charges computed for some representative atoms are presented in Table 6. The edge effect appears in the way the atoms in the interior have charges of larger magnitude than the atoms on the face, on the edge, and at the corner of the cube. This is consistent with the presence of decreasing numbers of nearest neighbors to stabilize the charge on an ion as one passes from the interior to the exterior of the cluster.

Note that the transition from neutral to cation draws electron density from the hydrogen ions, in a manner that is fairly smooth across the entire cluster. By contrast, the transition from neutral to anion concentrates the charge at the corners of the cube. This suggests that the electron attachment energy of -0.536 eV may be inaccurate due to the edge effect, which would be absent from the bulk crystal, while the ionization energy of 5.221 eV should be more reliable. If it is confirmed, the negative electron attachment energy indicates that the LiH lattice can readily accommodate the excess charge of the combining H⁻ anions during H₂ formation, which is a bit surprising. This prediction should be verified with other methods before any definitive conclusions can be drawn.

Table 6. Electronic Charges within the LiH Cluster, Showing the Edge Effect of Decreasing Charge as the Number of Nearest-Neighbors Decreases

Position	Cation	Neutral	Anion
H Corner	-0.68	-0.74	-0.77
H Edge	-0.72	-0.74	-0.73
H Face	-0.74	-0.74	-0.74
H Interior	-0.84	-0.87	-0.87
Li Corner	0.78	0.76	0.43
Li Edge	0.74	0.73	0.66
Li Face	0.72	0.71	0.68
Li Interior	0.81	0.83	0.82

Point defects were probed by computing the charges associated with single atoms that had been moved from the crystal lattice position to a neighboring interstitial position. The results are presented in Table 7. The point defects, both Li and H, act as electron concentrators and are more negatively charged than the unperturbed atoms on the regular lattice sites. The prediction that the H interstitial has a charge more negative than -1.0 is unrealistic, and is most likely an artifact of the charge distribution analysis. Examining the structure for the H interstitial, the neighboring Li sites are closely

Table 7. Charges on Interstitial Defect Atoms

Point Defect	Charge
Li interstitial	Li -0.22
H interstitial	H -1.72
LiH Di-vacancy and Li,H Interstitials	Li +0.77; H -1.46

associated with the H interstitial, with some of their electron density most likely getting assigned to the H interstitial during the charge distribution analysis. Likewise, the negative charge found for the Li interstitial is also questionable, and is most likely the result of the neighboring H anion lattice sites getting part of their electron density added to the Li interstitial in the charge distribution analysis.

The same charge analysis was applied to the geometries computed during the transition state search discussed in section 3.2, with the results presented in Table 8. The difficulty presented by H₂ formation is that two negatively charged ions come together to form a neutral molecule. In the process, the repulsive coulombic force must be overcome and the electronic structure must relax in such a way as to redistribute the excess electrons into the lattice. As in the previous example of point defects, the hydrogen pair begins the process with charges that are negative but less so than for an isolated H point defect. At the point of maximum charge accumulations, when the ions are separated by 2.62 angstroms, each ion becomes highly localized with a unit negative charge. Examination of the surrounding lattice reveals that each ion is closely associated with a Li cation, with separations of 1.80 and 1.84 angstroms respectively that are significantly shorter than the 1.97 angstrom separation between pairs of ions on the lattice. These interactions both stabilize the concentration of negative charge during the reaction, in a manner analogous to the stabilization of charges by a polar solvent. They also facilitate the transfer of electrons back into the lattice, as the Li cations can pick up the excess charge as it is shed by the reacting hydrogen ions.

Table 8. Total Charge as a Function of Hydrogen Atom Separation, for Two Interstitial Ions Combining to Form a Neutral Hydrogen Molecule

H-H Separation (Å)	Total Charge
4.17	-1.000
3.31	-1.595
2.62	-2.087
1.97	-1.108
0.80	-0.346

4.0 CONCLUSIONS

Due to the large number of competing processes that occur during irradiation of LiH it is not possible to make any conclusions on the rate of H₂ production, and its impact on swelling, without an integrated rate model that attempts to take into account all of these competing interdependencies. An integrated model has not yet been developed, but some initial conclusions can be made based on these quantum mechanical results:

- It is predicted that less energy is required to knock Li ions off of their lattice (250 – 260 kJ/mol) sites to form vacancy/interstitial pairs than for the H ions (298 – 299 kJ/mol).
- Once formed, interstitial defects are expected to diffuse rapidly, with very low calculated barriers to diffusion (7 – 25 kJ/mol).
- The corresponding vacancies are expected to diffuse much more slowly, with much higher barriers to diffusion (43.7 – 57.1 kJ/mol for Li and 84.1 - 91.0 kJ/mol for H). The larger predicted barriers to diffusion for H are consistent with the larger radii for the H anions than for the Li cations.
- Two feasible mechanisms were identified for H₂ formation during irradiation: 1) reaction of adjacent H atoms across a Li vacancy, and 2) reaction between two interstitial H atoms to form an interstitial H₂ molecule. The predicted barriers to reaction are approximately 100 kJ/mol for both reaction mechanisms.
- An unusually favorable interaction energy was found for placing two H₂ molecules within the same LiH di-vacancy site.

5.0 FUTURE WORK

Due to the restructuring of the Prometheus project, many planned modeling activities were not yet completed. Below is a description of the additional modeling work originally planned to help support development of LiH as a shield material, as well as some discussion of what insight was hoped to be gained by the specific tasks. Final results from any further studies will be incorporated in Reference (n).

- Complete quantum mechanical calculations to finish assessing relative stability of point defect stabilities and mobilities, as well as explore additional H₂ formation mechanisms, and further explore impact of larger k-point meshes and a larger number of plane waves in the calculations.
- Perform phonon calculations for the identified stable structures to include thermal and entropic contributions in the evaluation of the relative stability and mobility of the point defects.
- Couple predicted formation energies and mobility predictions into an integrated rate model, and examine the predicted H₂ production rates as a function of irradiation damage, temperature, and time.
- Perform molecular dynamic simulations to predict displacement threshold energies of Li and H within the LiH, as well as to examine cascade events.

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Attachment 6 to Enclosure 2 to MDO-723-0048:

X-ray Irradiation Testing of Lithium Hydride

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1. X-ray Irradiation Testing of Lithium Hydride

This attachment describes in greater detail the x-ray irradiation testing discussed in Enclosure 2 Section 8. X-ray testing will provide early insight into LiH irradiation performance at lower cost. This section discusses the irradiation testing plans for this material as part of the overall qualification.

2. Qualification Approach

The path toward qualifying LiH consists of taking the present state of material knowledge and expanding it to a fuller understanding of irradiation induced affects on LiH. The overall approach includes:

1. Mixed neutron/gamma irradiation, as close to the correct neutron/gamma ratio as possible to generate close to prototypical LiH performance compared to the actual shielding application. Several irradiation rates should be tested to determine the effect. One rate should be less than 10x of the actual application rate, preferably using in-situ monitoring of swelling and gas evolution. Most tests, however, should be accelerated to achieve total predicted dose, similar to the successful SNAP/ANP tests.
2. The effects of neutron spectrum (fast-vs-thermal) must be understood relative to the source spectrum, and likely shifts in the spectrum within the shield.
3. X-ray irradiation to quickly screen various parameters prior to gamma testing, e.g. dose, dose rate, impurities, temperature, processing, etc.
4. Gamma irradiation to generate confirmatory data compared with past gamma tests. Again, several rates should be tested including one rate less than 10x of the actual application rate.

3 X-ray irradiation scoping study

This research will narrow the required follow-on irradiation testing by providing early, low cost insight into irradiation induced swelling. These data will also be used to characterize the veracity of the atomistic modeling.

3.1 Assumptions

The gamma spectrum from a typical fast reactor is shown in Figure 1. Overlaid on this plot is the spectrum from a 300 KeV X-ray tube. The fast reactor spectrum is markedly different from the X-ray spectrum generated by a rotating tungsten anode X-ray tube.

Figure 1: Conceptual plot of the gamma/x-ray spectrum for a hypothetical fast nuclear reactor, X-ray source, and cobalt-60 source. The units for flux are photons/cm²/sec. Reference (a).

Employing X-rays to evaluate radiation-induced damage assumes that LiH damage is not highly spectrum-dependent, and that X-rays from a 300 KeV tube are of sufficient energy to generate the desired material changes in LiH. This assumption was being evaluated at the time of project restructuring, and therefore further study is required before this approach should be applied.

While not prototypical, the use of X-rays to irradiation test lithium hydride has several advantages. Foremost is the opportunity to obtain irradiation data rapidly and at low cost. Due to its self contained nature, transportation, setup, and use are less cumbersome than traditional irradiation testing equipment, including isotope sources. Furthermore, government regulations covering cabinet X-ray equipment are well understood by commercial suppliers, versus the case-by-case issues that arise with non-cabinet systems. Cabinet X-ray equipment of this type are regulated by the US Food and Drug Administration (FDA) under Title 21 Code of Federal Regulations (CFR) 1010.40. Personnel monitoring equipment is not required by Federal regulation for operators of cabinet X-ray systems.

X-ray irradiation testing is synergistic with the atomistic modeling described in Attachment 5. Results of this testing will then be used to direct follow-on irradiation testing.

3.2 X-ray Vice Fast Reactor Spectrum

X-rays are created by the process of electrons decelerating in the target of an X-ray tube and transferring their energy to single photons. The resulting radiation is termed Bremsstrahlung radiation, and is the German word for decelerating (braking) radiation. The highest photon energy equals the whole kinetic energy of the electron. Therefore, the smallest possible wavelength is inversely proportional to the anode voltage. The equation for X-ray wavelength ($\lambda_{\min}$) is:

$$\lambda_{\min} = \frac{hc}{eV}$$

where:

h = Planck's constant

c = speed of light

e = electron charge

V = anode voltage

The kinetic energy of the incident electron is the product of electron charge and anode voltage (eV). This equation illustrates that the short-wavelength limit of an X-ray tube is proportional to the anode voltage supplied to the tube.

Only a small portion (under 1%) of the energy supplied to a tube is converted into X-ray photons; the remaining energy is dissipated as heat. It is this heat that limits the maximum power output (dose rate) of an X-ray tube.

The relationship between the initial Bremsstrahlung and the actual output of the tube is shown in Figure 2. The change in spectrum is due to characteristic X-ray peaks caused by photon-electron interactions in the target material (in this case tungsten), and filtering caused by the X-ray tube envelope and tube-head components. The spectrum from a rotating anode tube extends up to the supplied voltage, and drops off rapidly below about 20 KeV due to the inherent shielding/filtration of the tube envelope, cooling/dielectric oil, tube head, and tube window (typically glass or beryllium depending on the manufacture). A rotating anode X-ray tube contained in its tube head is shown in Figure 3.

Figure 2: X-ray final and initial spectrum

Figure 3: An X-ray tube in its tube-head. Reference (b).

3.3 Experimental Setup and Equipment

The X-ray machine used to perform the irradiation testing consists of a rotating anode X-ray tube and power supply combined with a shielded cabinet. Equipment of this general type is frequently used in industrial X-ray radiography. For irradiation testing, however, a much higher dose rate (at the same KeV range) is necessary. This requires the use of a rotation anode vice the traditional fixed anode X-ray tube.

Rotating anode X-ray tubes are commonly used in radiotherapy. These tubes consist of a tungsten anode (target) that is rotated on a molybdenum shaft (molybdenum is used for its high melting temperature combined with poor thermal conductivity). Motion is provided by an induction motor that is built integral to the tube envelope. By rotating the target, heat is more effectively dissipated and allows for higher X-ray tube power and therefore higher dose rates. Voltages of up to 300 KeV and currents of up to 200 mA are typical with these tubes. This represents an increase in tube power of two orders of magnitude over fixed focus tubes. The consequence of this higher X-ray tube power is a substantially shorter irradiation test and higher radiation dose rates. The experimental setup is shown in Figure 4.

Figure 4: X-ray irradiation experimental setup showing cabinet X-ray machine employing a rotating anode X-ray tube

The LiH specimens are contained in an aluminum can. The can is highly transparent to high energy X-rays and provides an atmosphere of high purity anhydrous hydrogen around the test specimens to prevent the formation of oxides and other impurities. The can could be sealed or provided with flowing hydrogen. If flowing hydrogen were used, it could be supplied from a 2,000 psi high pressure bottle. The hydrogen flows through the can at a low rate, controlled by a pressure regulator. Flow is observed by a bubbler connected to the can's exhaust tube. This setup allows the can to be open to the atmosphere at all times, and eliminates the possibility of pressure buildup during the test.

As an additional safety measure, a burst diaphragm is mounted to one end of the can. This diaphragm is made from an aluminum foil sheet, is only a few mils thick, and is fastened over a large hole using an adhesive such as room temperature vulcanization (rtv) silicone rubber. If an explosive mixture of hydrogen gas were to ignite inside the can, the burst diaphragm would safely release the pressure to the surroundings. If desired, to prevent an explosive mixture of hydrogen from collecting inside the cabinet X-ray machine due to, for example, a small leak, inert gas could be fed into the cabinet, which could also contain a hydrogen sniffer.

Specimen temperature is controlled by a proportional temperature controller, with feedback provided by a wire-beaded type K (chromel-alumel) thermocouple. Heating rope (a nichrome resistive heating wire contained in a quartz-fiber sheath) is wrapped around the can to heat the specimens during

irradiation. External heating is preferred to internal due to the presence of hydrogen. An internal heater could act as an ignition source in the event of a short circuit or similar fault.

X-ray energy and dose rate are set by the X-ray machine's controller. Peak photon energy is determined by the voltage applied between the anode and cathode of the X-ray tube, and dose rate is controlled by the tube's filament current. Dose rate could conceptually be monitored using a metal oxide surface field effect transistor (MOSFET) dosimeter having an active area approximately 0.2mm x 0.3 mm, mounted adjacent to the LiH specimens. A bias supply provides bias voltage to the MOSFETs during irradiation. These dosimeters are typically used in patients undergoing radiotherapy, and the life of these devices needs to be determined under this high level of irradiation. Temperature set point and x-ray dose rate are set by the operator according to the statistical experimental design shown in Table 1.

3.4 Statistical Experimental Design

An experiment was designed to evaluate the affect of X-ray irradiation and elevated temperatures on the swelling of LiH. This approach creates a mathematical model (multiple regression equation) that can then be used to predict swelling.

The dependent and independent variables are shown in Table 1. Temperatures from 450 to 550 K are combined with dose rates of 0.05 to 0.5 mega Rad per hour. Total exposure is from 50 to 200 mega Rad.

Table 1: LiH X-ray Irradiation Screening Experimental Matrix

Random Run sequence	Run number	Temperature (K)	Dose rate (Mega Rad/hr)	Total dose (M Rad)	Total hours
6	0	450	0.05	50	1000
5	1	450	0.05	200	4000
7	2	450	0.5	50	100
3	3	450	0.5	200	400
0	4	550	0.05	50	1000
1	5	550	0.05	200	4000
2	6	550	0.5	50	100
4	7	550	0.5	200	400

Randomization is employed to minimize the affect of unknown sources of experimental error. An Analysis of Variance (ANOVA) statistical analysis is used to build the multiple regression equation, evaluate interactions, and check model adequacy. Sources of experimental error have been identified to be photon energy, composition, fabrication method, the X-ray machine, the machine operator, and the LiH container and its temperature control system. These factors are controlled to improve the statistical power of the experiment.

Sufficient replicates are required to achieve the statistical power needed to draw meaningful conclusions. This cannot be determined a-priori due to the sample variance not being previously known. Therefore, an iterative experimental approach is employed both to quantify sample variance (for use in determining sample sizes for follow-on experiments) and also to provide insight into the experimental volume.

The dependent variable in this experiment is swelling. Past researchers have measured swelling by measuring the change in length between two scribe marks on the LiH specimens. For consistency the same or a similar method would be employed for this experiment. The resulting measurements would be used in the statistical analysis.

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Attachment 7 to Enclosure 2 to MDO-723-0048:

**Shield and Reflector Irradiated
Materials Testing Laboratory at ORNL for Project Prometheus**

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**Reviewed by:
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1. Introduction

Planned funding would have allowed Oak Ridge National Laboratory (ORNL) to modify an existing laboratory to carry out materials property measurements on unirradiated and irradiated reflector and shielding materials for Project Prometheus. The "Space Irradiated Materials Laboratory" (SIML) would have been capable of handling low external radiation level irradiated materials, e.g., Be, BeO, B₄C and LiH. BeO specimens irradiated in the JOYO Experimental Fast Reactor, operated by JNC, located in O-arai, Japan were also to be tested in the proposed ORNL facility (Reference (a)). The total planned funding for the SIML was \$1,496K.

1.1 Extensibility to Lunar Surface Missions

Although significant differences in the shield and reflector designs are likely between the deep space and lunar surface missions, some of the materials will likely be the same. For a surface mission, the volume of the shield may be larger than the deep space reactor shadow shield, so the density of the material may become even more important, increasing the desire to test LiH, which is the lowest density hydrogenous material under consideration. From a reflector standpoint, Be and BeO remain the primary material candidates.

1.2 Selection of ORNL as the Vendor:

As discussed herein, ORNL was to be recommended as the vendor due to unique expertise in handling irradiated Be and Li-bearing materials as well as its capability to perform irradiations in the HFIR. ORNL was planning on sharing the costs of this effort as well.

2. Background

Beryllium-bearing materials were being considered for use in the Prometheus reflectors (Be and BeO) and shield (Be). Irradiated material properties were required to ensure the designs would meet performance requirements. The initial review of Be indicated that irradiated material properties were known within the Prometheus design space, however, a comprehensive review was required. Beryllium oxide irradiated material properties were less certain, primarily due to a difference in the grain size of current commercial materials versus historical materials (literature indicates that swelling is a strong function of grain size). BeO specimens planned for insertion into the JOYO reactor in FY06 would have been shipped after irradiation to ORNL for testing. To complement the JOYO irradiation test a set of BeO samples were planned to be irradiation tested in the High Flux Isotope Reactor (HFIR) at ORNL (Reference (a)).

Boron carbide may also have required irradiated materials testing. A comprehensive review of B₄C properties was planned for FY06. Enclosure 2 and Attachments 1 - 6 provide detailed discussions of the planned irradiation testing of LiH.

3. Discussion

The proposed Space Irradiated Materials Laboratory (SIML) was intended to meet the materials testing needs for several of the Prometheus shield and reflector materials, e.g., Be, BeO, B₄C and LiH, as well as be available to test other low dose materials.

The strategy for testing select shield and reflector irradiated materials was as follows:

- Test JOYO-irradiated BeO samples in the SIML.
- Irradiate BeO samples in HFIR, and test them in the SIML.

- Potentially irradiate B₄C samples in HFIR (or JOYO), and test them in the SIML.
- Potentially irradiate Be samples in HFIR and test them in the SIML (not considered likely).
- Perform gamma and x-ray irradiations of LiH samples and test them in the SIML.
- Perform mixed gamma and neutron irradiation of LiH samples in HFIR (and potentially the ORNL Californium User Facility (CUF) for lower fluences) and test them in the SIML.

3.1 Justification to establish the SIML at ORNL

Material property testing was needed on irradiated BeO for reflector and potentially fuel element application, and LiH for shield application. Irradiated materials testing was potentially also going to be performed on Be and B₄C as well. Beryllium-bearing materials require special controls due to toxicity, but Be and BeO were not expected to present any special requirements from a radiological standpoint. Although not as hazardous as Be-bearing materials, LiH reacts with water, air and other chemicals, requiring safety precautions. However, ⁶Li-bearing materials absorb neutrons producing significant amounts of tritium (³H), which has a long half life (12.3 years), and emits a low energy beta particle (18.6 keV max) not detectable by most standard contamination detection equipment. The envisioned LiH neutron-irradiated specimens were predicted to contain significant (~.18Ci per gram) quantities of ³H. ORNL had previously handled irradiated Be-bearing materials and irradiated LiH.

Due to the limited irradiation data available on BeO, as well as the need to supplement the data available on LiH (and possibly Be and B₄C), a program to perform additional testing and a facility to test necessary properties (Table 1) needed to be established. No existing facilities with the capability for carrying out thermal and physical property measurements in the controlled environment required for irradiated Li and Be-bearing materials were identified. ORNL was expected to be funded to lead the irradiated materials testing of LiH, and possibly additional BeO irradiations, as well as perform the irradiated materials testing of the BeO samples planned for irradiation in JOYO in FY06.

In subcontracting one organization to perform the envisioned shield and reflector irradiated materials testing, the NRPCT expected to get the needed information: (1) sooner than if separate facilities are involved; (2) at lower cost than using separate facilities due to elimination of transportation costs, extra contract administration, and duplicate overhead; and (3) potentially more precise data by utilizing the same test equipment for pre- and post-irradiation testing. ORNL was planning to share the costs of this effort as discussed below.

ORNL was judged to be the best location to sponsor the shield and reflector irradiation program and to house the associated irradiation property testing facility for the following reasons:

- ORNL had tested irradiated Be and BeO, and irradiated LiH (one time campaign). Trained personnel and procedures were still in place at ORNL (per L. Snead, 6/22/05). However, the prior testing facilities did not exist for the LiH (ORNL originally bagged the equipment as a control method, which is unacceptable for a long duration test program) or for Be testing (current toxicity controls require a dedicated clean room approach, which was not the case during prior testing). ORNL performed material testing of LiH in support of the SP-100 program, including some testing of gamma-irradiated LiH, which was directly applicable to the Prometheus shield materials program.
- The prime candidate facilities for neutron irradiation were HFIR (for LiH, and to complement JOYO BeO testing) and the CUF (for LiH, if needed), both located at ORNL—although the ATR was also being considered as an alternative to the HFIR.

Having one laboratory in charge of both specimen irradiation testing and pre- and post-irradiation property measurements was expected to reduce overall costs and time and reduce or eliminate transportation of radioactive materials outside facility borders.

- ORNL was expected to provide a principal investigator to coordinate the irradiations and testing programs, and provide analysis of the resulting data, thereby accelerating the program and significantly lowering the burden on the NRPCT.
- The fact that ORNL had procedures and controls as well as expertise in place for tritium-bearing materials as well as irradiated Be-bearing materials represents a significant cost savings relative to having to establish these capabilities simultaneously at another facility—which could have resulted in unacceptable delays to the shielding and reflector materials programs, as well as duplication of costs already incurred by the government.
- ORNL had laboratory space and some equipment reserved for this facility. They had renovated the facility (floors, lighting, clean up, painting, etc.), added a state of the art glove box with environmental controls, and were procuring the required clean room. They would have provided the required labor resources to set up equipment and perform tie-ins at their cost. The total ORNL contribution to the SIML is estimated at \$500K.
- ORNL had expertise and resources to design and deliver irradiation test hardware for both the CUF and HFIR. It was not clear who would be the design agency if the ATR were used.

3.2 Proposed SIML Facility and Equipment

ORNL had an identified lab space for the SIML, and reviewed the safety and handling requirements for Be-bearing and LiH materials. Besides providing recently renovated laboratory space, ORNL would have provided the clean room and an environmentally controlled glove box. The SIML would also be on the same site as the HFIR, CUF and principal investigator, which would minimize radioactive shipping and general travel.

ORNL proposed to install a pre-fabricated clean-room (funded by ORNL) within the lab to provide controlled environmental conditions, including low humidity (target 10%), a filtration system able to handle radioactive material needs and non-water-based fire suppression equipment—LiH reacts exothermically with water. The clean room would also serve as a control boundary for contamination when the lab handled irradiated specimens.

Within the clean room, samples would have been stored under an argon cover-gas in humidity and oxygen controlled/monitored glove boxes (<10ppm oxygen). Samples would have been transferred from the storage glove box to other control boxes or environmental chambers in a sealed container under argon. All thermophysical property measurements would have been carried out in vacuum or in inert-gas environmental chambers as appropriate. Originally, the samples were allowed to see the reduced-humidity lab-air (~10% humidity) when a sample was removed from the carrying container and placed in the environmental chamber of a piece of test equipment. After review of the SNAP data, the requirement would need to have been changed to only allow the samples to be exposed to <10ppm oxygen at all times. Transfer from one piece of equipment to another needed to be done within an enclosed glove box accessible to the measurement equipment, or via another transfer method that limits oxygen exposure appropriately.

Given the factors stated above, the NRPCT planned to establish this facility at ORNL.

Table 1: Estimated Costs for Facility to Test Irradiated BeO and LiH Specimens

Item	Reason	Cost FY06	Cost FY07
Clean Room modifications	Humidity control, radiation boundary	\$180K	--
Glove Boxes	Tightly control environment around LiH specimens	\$10K	\$195K
Metallography Equipment	Prepare specimens to examine LiH structure	\$60K	\$40K
Optical Microscope	Examine LiH structure	\$15K	--
Differential Scanning Calorimeter	Measure specific heat. Use in calculating thermal conductivity.	\$65K	--
Thermal Diffusivity Equipment	Measure thermal diffusivity. Use in calculating thermal conductivity.	\$110K	--
Thermal Expansion Equipment	Measure thermal expansion.	\$40K	--
Creep Test Frame	Measure material creep	--	\$140K
Tensile Test Frame	Measure yield strength, ductility.	--	\$185K
Gas Evolution Detection	Measure gas production in LiH specimen containers to help determine swelling mechanism	--	\$105K
Miscellaneous Laboratory Equipment	General fund to allow for small start-up costs and associated laboratory equipment	\$50K	\$50K
Upgrade Lab for Radioactive Material Handling	Ability to measure irradiated LiH specimens.	--	\$115K
Subtotal by Fiscal Year		\$530K	\$830K
10% contingency by Fiscal Year		\$53K	\$83K
Total by Fiscal Year		\$583K	\$913K
Total		\$1496K	

4. References

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Attachment 8 to Enclosure 2 to MDO-723-0048:

LiH Containment System

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1. **LiH Containment System**

A lithium hydride containment system will isolate the LiH from the surrounding environment, protect against loss of hydrogen, improve the mechanical properties of the LiH system, and potentially provide a heat rejection path to space for the shield.

1.1. **Isolation from Surrounding Environment**

It is necessary to prevent LiH from coming in contact with air, water, and certain metals. LiH reactions and reaction rates in each of these environments vary, as do the results. A containment system should allow for the assembled LiH shield components to be handled in an uncontrolled environment, reducing the complexity and resources required to manufacture/assemble the shield.

At room temperature in air, lithium hydride will quickly form a thin film of lithium hydroxide which crystallizes and protects the hydride from further rapid oxidation. In low humidity air, diatomic oxygen reacts with LiH to form Li₂O, LiOH, or Li₂CO₃. At elevated temperatures (400-800 K), LiH can react with diatomic nitrogen to form LiNH₂, Li₂NH, or Li₃N (Reference (a)).

Lithium hydride reacts with water and water vapor vigorously at room temperature, but without ignition (LiH + H₂O → LiOH + H₂). The presence of LiOH inside LiH blocks may increase swelling in a radiation environment (see Enclosure 2, Section 10).

The containment system must protect the LiH, and not be subject to corrosive attack by it. Small quantities of free metals can frequently be found in lithium hydride (see Attachment 1). At temperatures greater than the melting temperature of the impurity, spot corrosion, decarburization, or intergranular penetration is common. Mueller (Reference (a)) provides a schematic (Figure 1) depicting the resistance of materials to attack by liquid lithium, which can exist at temperatures greater than 454 K. Molten lithium will decarburize steels at temperatures greater than 773 K. However, iron, niobium, tantalum, and molybdenum have good corrosion resistance even at high temperatures.

Figure 1: Resistance of Materials to Liquid Lithium

Small amounts of hydroxides, oxides, nitrides, or chlorides will form eutectics with LiH causing the LiH to become corrosive. Lithium chloride (LiCl) forms as a eutectic at 759 K, which is corrosive to stainless steels and nickel-base alloys. Lithium oxide (Li₂O) forms as a eutectic at 927 K, which is close to the melting point of LiH.

1.2. Protection Against Hydrogen Loss

A partial pressure of hydrogen, dependent on temperature and pressure of the system, is required to prevent hydrogen loss from pure LiH. To maintain stoichiometric LiH and prevent dissociation of LiH, the operating temperature and pressure must remain within the shaded region of Figure 2 (Reference (b)).

Figure 2: Dissociation Pressure of Lithium Hydride and Vapor Pressure of Lithium

Containing an overpressure of hydrogen greater than the partial pressure from LiH should prevent dissociation of the LiH. The ability of the can/clad material to contain hydrogen is a combination of the ability of the material to diffuse and dissolve hydrogen. Permeability of the can/clad material is defined as the product of the diffusivity and solubility (Reference (c)). The hydrogen permeability of potential canning/cladding materials is shown in Figure 3.

Stainless steels provide superior hydrogen loss protection when compared to the other materials evaluated. Furthermore, long missions might require a more complicated containment system than just a single material; multi-layered systems should be considered to reduce the permeability of the containment system. Alternatively, a material that slowly breaks down to produce (replenish) hydrogen gas and other benign chemicals could be considered.

Oxide films provide superior hydrogen barriers on the order of 10³ times greater than steel. Unfortunately, oxides produced on most alloys are typically reduced to some extent by hydrogen. Therefore, they must be continually replenished to mitigate barrier degradation. Designing a system with reserve oxygen to replenish the oxide is extremely difficult, especially because LiH reacts at room temperature with oxygen, which may drive irradiation-induced swelling.

Other options exist, but they all involve complicated designs. Refractory metals provide a hydrogen barrier on the order of 10X greater than stainless steels, due to the low hydrogen solubility. SNAP-

10A used an enamel coating on Hastelloy-N for the fuel elements. Glass coatings on Haynes 25 have been fabricated, but the glass is incompatible with lithium hydride (Figure 1).

Figure 3: Hydrogen Permeability of Selected Potential Canning/Cladding Materials (Reference (c))

1.3. Improvement in Mechanical Properties

The mechanical properties of LiH are not well understood, particularly in a radiation environment. For example, at room temperature (corresponding to launch), the Young's Modulus of LiH is ~266 MPa, and significantly less at operational temperatures, compared to stainless steel which is ~175 GPa. The strength of LiH is such that it can support its own weight, but should not be considered a load bearing material. Therefore, the containment system, either clad or canning, would provide the means to transmit load.

The NRPCT has performed preliminary calculations that determined that the launch loads are much greater than the mechanical loads due to the pressure of the contained gas during operation of the Prometheus reactor shield. The spacecraft launch loads are a function of spacecraft weight, stiffness, and lateral/axial coupling as well as booster configuration and forcing functions and are estimated to be in the order of 10 g's (Reference (d)). According to Figure 2, at a design temperature of 650 K the required H pressure in the containment system would be less than 1 Pa. Based upon pressure sizing calculations alone, the required containment system thickness would be significantly less than 1 mm.

SP-100 containment system utilized material thickness of 3.8 mm, which was presumably sized appropriately for launch loads. From this comparison it is concluded that the structural design of the containment system would be driven by launch loads.

1.4. Design of System

The design of the containment system is driven by the requirements of the Prometheus reactor shield subsystem. Fabricability and minimizing the mass of the shield were considered defined requirements for the Prometheus reactor shield. The shield must be able to be manufactured and it must be able to be launched. Other factors should be considered when designing a LiH containment system, which are not specifically addressed herein because the NRPCT did not study the containment system thoroughly. These factors include, but are not limited to, thermal management, swelling accommodation, endurance, and metallurgical compatibility.

One of the shield requirements is fabricability. A simplified design results in an easier manufacturing process. For example, consider choosing a cast shield over a cold-pressed shield. While the casting process requires zone melting and controlled cooling, virtually no machining of the shield is required. At room temperature in air, fine particles (< 60 mesh) of LiH can ignite spontaneously and potentially explode. All machining operations that produce dust must be performed in a controlled environment. A cast shield may allow the elimination of the requirement for a controlled machining environment.

Depending on the thermal management requirements of the shield, canning or cladding should be considered. The can contains a gap insulating the LiH from the can. The gap reduces the heat transfer to the can, thus increasing the temperature of the LiH. Cladding would be in contact with the LiH, improving heat conduction from the LiH to the clad material. This would reduce the temperature of the LiH, but increase the temperature gradient. The temperature gradient could be of concern relative to the mobility of the hydrogen within the crystalline structure (see Enclosure 2, Section 3 and Attachment 1). The NRPCT did not investigate the benefits and disadvantages of either a can or a clad containment system. However, a clad system, where the material is bonded to the LiH is considered to be an unlikely choice for a LiH shield due to the thermal and irradiation induced swelling.

The complexity of the shield design could also complicate the thermal management of the shield. Figure 4 shows a preliminary finite element analysis of a monolithic lithium hydride shield. The inclusion of a containment system, independent of type, would complicate this model. If the lithium hydride was divided into more than one section, the contact resistance between all of the segments would be critical to obtaining an accurate temperature prediction. Cladding would be easier to model because coincident nodes could be modeled at the LiH/clad interface. However, canning systems provide an additional challenge because the gap between the LiH and the containment system should be modeled, as well as some contact, which can be expected.

Thus far, the NRPCT has been unable to fully understand the swelling mechanisms of LiH in a radiation environment. It is clear that some specimens have swelled and others have not (see Attachment 2). At this time, if a LiH containment system was to be designed, swelling and thermal expansion of the LiH must be considered. A canning system must contain enough void volume to accommodate the swelling, while maintaining sufficiently low pressures to avoid creep concerns, and control LiH temperatures and differential temperatures throughout life. A clad containment system must be designed to grow with the LiH, which becomes more complicated than just matching the CTE of the clad material with LiH.

Layered designs, which complicate the fabrication and analysis of the shield, might need to be considered to protect the LiH from the containment system and the containment system from the LiH. If a single layer design is considered, then the containment material must be compatible with LiH and prevent (or slow, depending on the design requirements) hydrogen diffusion and interaction. The following metals do not easily form hydrides: Mo, Fe, W, Mn, Te, Re, Ru, Os, Cr, Rh, Ir, Pt, Ag, Au (Reference (a)). All previous space shield containment system designs used stainless steel. However, lithium leaches chromium from the stainless steel (Reference (e)). In the case of multi-layer designs, chemical and mechanical compatibility between the layers must be considered as well.

Although at the time of publication, the NRPCT had not studied shield structural materials or a LiH containment system in depth, the NRPCT believes that designing a successful containment system is crucial to the success of a LiH shield.

Figure 4: Thermal Analysis of LiH (temperature range shown = 650-690K)

2. References

- (a) Mueller, William M., James P. Blackedge, and George G. Libowitz. 1968. *Metal Hydrides*. New York: Academic Press.
- (b) Welch, F.H. 1964. Lithium Hydride Technology I. Properties of Lithium Hydride and Corrosion Studies. Atomics International Document NAA-SR-9400.
- (c) Shelby, J.E. 1996. *Handbook of Gas Diffusion in Solids and Melts*. ASM International.
- (d) Evolved Expendable Launch Vehicle Standard Interface Specification. Version 6, September 5, 2000: EELV Standard Interface Working Group.
- (e) Snead, Lance. 2004. ORNL Presentation: JIMO Shield.ppt. September 9, 2004.

Attachment 9 to Enclosure 2 to MDO-723-0048:
Annotated Bibliography of LiH Related Resources

Authors:
Brain Campbell
Barri Gurau
Rose Lewis
Beth Lugert

Reviewed by:
James Nash

Author: Aitken, E.A., and D.L. Henry
Title: Radiation Damage to Lithium Hydride
Reference: General Electric Document APEX-323
Date: 1956
Key Words: Lithium Hydride, Testing, Radiation

Summary

Aitken and Henry irradiated three samples: constrained cast, constrained cold-pressed, and unconstrained cold-pressed LiH. They noted some damage, evident at the microscopic scale, is produced by radiation, such as microcrystalline fracturing and helium retention in vacant lattice sites, and also apparent annealing effects. Unfortunately, no micrographs are included.

Author: Bauer, P., F.H. Welch, and E.P. Kilb
Title: Irradiation Testing of XMA-1A Shield Materials
Reference: GE Document DC 59-5-81
Date: 1959
Key Words: Lithium Hydride, ANP, Testing, Radiation

Summary

This document includes irradiation test results for beryllium-boron, tungsten-boron alloy, boron stainless steel, beryllium oxide-boron, and lithium hydride. A three page table is provided summarizing the data, which despite the brevity, is the most informative document located by the NRPCT associated with these tests.

Author: Baxter, W.G., and F.H. Welch
Title: Comprehensive Technical Report, General Electric Direct-Air-Cycle Aircraft Nuclear Propulsion Program – Shield Materials
Reference: GE Document APEX-915
Date: 1962
Key Words: Lithium Hydride, Beryllia, Beryllium, Shield Materials, Cold Pressing, Honeycomb, Casting, Austenitic Steel, Irradiation Damage

Summary

“This is one of twenty-one volumes summarizing the Aircraft Nuclear Propulsion Program of the General Electric Company. This portion discusses the shielding materials development, which was begun in 1956. Specialized materials, which would provide the most efficient neutron and gamma shielding per unit weight and would be capable of high temperature (755-1144 K) operation under the thermo-mechano-nuclear environment associated with the direct-cycle reactor power plant, are presented.

Primary development effort was focused on three neutron shielding materials: (1) beryllia plus boron, (2) beryllium plus boron, and (3) lithium hydride. In addition, stainless steel plus boron and tungsten-base alloys with boron additions were evaluated as combined gamma-neutron shielding materials.

Fabrication technologies that were developed, physical and mechanical properties that were determined, and the environmental testing programs, including radiation stability studies used to prove the usefulness of the materials under simulated operating conditions, are discussed in their respective sections.” ~ Baxter

Baxter provides some details regarding the 23 ANP irradiation specimens. A summary table of the ANP data is also provided. Furthermore, Baxter provides a half page summary on an out-gassing

study that he performed to support his theory. In the theory, LiOH reacting with LiH will evolve Li₂O and H₂ gas, which will cause the LiH to swell in a radiation environment.

Author: Bowman, C.R. Jr, A. Attalla, P.C. Souers, C.L. Folkers, T McCreary, G.D. Snider, Vanderhoofven, and R.T. Tsugawa

Title: Density of Trapped Gas in Heavily-Irradiated Lithium Hydride

Reference: Journal of Nuclear Materials Volume 154 pp 318-331

Date: 1988

Key Words:

Summary:

"We review old gamma-irradiated lithium hydride data and also display much new bulk and gas-displacement density and nuclear magnetic resonance data on Li(D,T) and LiT at 296 to 373K. We find that : (1) Li(D,T) swells because of the formation of internal D-T and ³He gas bubbles, but probably not because of precipitation of lithium metal; (2) the gas bubbles are at densities of at least 3 to 4x10⁴ mol/m³, i.e. thousands of atmospheres; (3) out-gassing may be largely the result of bubbles rupturing, although diffusion of ³He as atoms may occur at long times." ~Bowman

Bowman presented data indicating there was 10-14% hydrogen retention in LiH. This surprised Bowman, as well as contributes to the theory that LiOH may be causing swelling. In particular, this implies that if LiOH reacts with LiH the LiH crystal will be "charged" with hydrogen, and may retain 10-14% of the hydrogen. Under irradiation, this may then play a role which leads to swelling.

Author: Brasier, J.E., Sr.

Title: INEL LIH Irradiation Testing, SP-100 Final Report

Reference: INEL – 95/0278

Date: February 28, 1995

Key Words:

Summary:

This paper discussed LiH micro-cracking under gamma irradiation as a function of temperature. Brasier is believed to have produced other valuable information, including microstructural analysis of irradiated LiH samples, but these were not obtained by the prior to issuance of this letter.

Author: Dinwiddie, R.B., W.D. Porter, S.C. Beecher, and J.R. DiStefano

Title: The Effect of Gamma Irradiation on the Thermophysical Properties of LiH + 2% Li

Reference: ORNL Document, ORNL/TM-12766

Date: 1994

Key Words: Lithium Hydride, Stoichiometry, Material Properties, Gamma Irradiation, Density, Thermal Expansion, Specific Heat, Thermal Diffusivity, Thermal Conductivity

Summary

"The thermophysical properties of gamma-irradiated lithium hydride + 2% Li have been measured. These properties include density, thermal expansion, specific heat capacity, and thermal diffusivity. Thermal conductivity was calculated from density, specific heat, and thermal diffusivity data. Seven irradiated specimens and one unirradiated specimen were provided for this study. The irradiation temperatures ranged from 400 to 600 K. The temperature dependence of thermal conductivity shows a small depression near the melting point of lithium (453 K). At low irradiation temperatures, the LiH + 2% Li specimens have a lower thermal conductivity than the unirradiated specimens. The thermal conductivity increases as the irradiation temperature increases. The thermal conductivity of the sample irradiated at 600 K has a value significantly higher than the unirradiated specimen. Thermal

expansion and specific heat capacity data indicate that the amount of free lithium varies greatly among the test specimens and that there is very little free lithium in the specimen irradiated at 600 K.”
~Dinwiddie

This document provides material property information for non-stoichiometric LiH, which is useful for comparison to stoichiometric LiH.

Author: Disney, R.K.
Title: Status Report on the SP-100 Program Investigation of Irradiation-Induced Swelling of Lithium Hydride Shield Materials
Reference: SP-GES-93-0005 Advanced Technology Nuclear and Advanced Technology Division, Westinghouse Electric Corporation
Date: 1993
Key Words: Lithium Hydride, Irradiation Testing, ATR, ARMF, Swelling Mechanisms

Summary

Lithium Hydride was selected for use in the SP-100 shield as a result of mass minimization studies. Based on SP-100 conceptual designs and LiH literature review, several irradiation tests of LiH were planned to test LiH properties focusing on swelling under various fluences, fluxes and temperatures. Data from test B-2A in the ATR indicated irradiation induced swelling depended on flux in the operating temperature range of the SP-100 shield (600K to 800K) and enhanced swelling at temperatures below 600K, with a maximum volumetric swelling of 25%. Swelling mechanisms are discussed in the article. An overview of the literature used in facilitating an understanding of LiH was given.

Author: Hamill, C.W., and F.B. Waldrop
Title: Shielding Studies: Neutron Irradiation Damage to a Lithium Hydride Compact
Reference: Union Carbide Corporation, Y-12 Plant Document Y-1454
Date: 1964
Key Words: Lithium Hydride, SNAP, NARF, Testing

Summary

Hamill and Waldrop performed irradiation experiments on lithium hydride to understand the phenomena that caused the aluminum can rupture and thus the NARF irradiation experiments to fail. Hamill and Waldrop concluded that the only significant radiation-induced damage in their experiment was the 2.4% expansion noted by the dimensional analysis. The initial NARF failure was caused by a test design flaw, and the second NARF failure was caused by improper environmental controls while handling LiH. They conclude that proper handling of LiH in a dry atmosphere would prevent the formation of LiOH and prevent significant gas evolution.

Author: Lundberg, L.B.
Title: Mechanical Properties of LiH: Part I – Compression Tests
Reference: NAA-SR-MEMO-7991
Date: 1962
Key Words: Lithium Hydride, Shielding Materials, Testing, Compression, Young's Modulus, Ultimate Compressive Strength

Summary

“The compressive properties of cold pressed lithium hydride have been measured over the temperature range 150°F to 750°F in a dynamic helium atmosphere. The ultimate compressive

strength was found to decrease from 14,300 psi at the lower temperature to 2,190 psi at 780°F. Compressive Young's moduli were observed to decrease by an order of magnitude over the temperature range studied." ~ Lundberg

This document provides ultimate compressive strength data, which is helpful during a mechanical analysis of the shield.

Author: Mel'nikova, T.N., and K.A. Yakimovich
Title: Thermal Properties of Lithium Hydride and Its Isotopic Modifications in a Crystalline State
Reference: High Temperature Volume 18 pp 250-256
Date: 1980
Key Words: Lithium Hydride, Thermal Expansion

Summary

"A general theoretical examination and specific calculation of the coefficient of linear expansion, lattice constant, and density of lithium hydride and all its isotopic modifications in the solid phase in the entire temperature range up to the melting point are presented. Special attention is devoted to isotope effects. It is shown that, unlike the predictions of the simplest theory, at high temperatures (near T_m) the lattice constant of various isotopic modifications of lithium hydride become practically the same."
~Mel'nikova

The thermal expansion expression provided by Mel'nikova is only limited in temperature range by the validity of the specific heat used to compute the thermal expansion.

Author: Minushkin, B.
Title: Final Report: Lithium Hydride Radiation Stability
Reference: Nuclear Development Corporation of America Document NDA-23
Date: 1956
Key Words: Lithium Hydride, ANP, Testing, Growth, Gas Evolution

Summary

"Several cold-pressed compacts of LiH, enclosed in capsules having a volume several times the sample volume, were irradiated in the Brookhaven National Laboratory reactor for 10 to 14 days at thermal neutron fluxes of 10^9 to 10^{12} n/cm²-sec and temperatures from 297 to 594 K. Some gas evolution took place in each test, and the samples, examined after removal from the pile, showed considerable disintegration and growth. The disintegration and growth were such that completely unconfined compacts of LiH do not appear suitable for high flux regions of an ANP reactor neutron shield.

The present hypothesis is that the disintegration and growth were caused by reactor radiation rather than by elevated temperatures, whereas the gas evolution was caused by reaction of impurities in the LiH at elevated temperatures, and was possibly influenced by the radiation. The gas evolution is not believed to be a serious problem. It can be handled by pretreatment of the LiH or by venting the evolved gas. The disintegration and growth of the samples represents a serious design and development problem.

X-ray diffraction data indicate that there was no change in the LiH crystal structure, and this suggests that it may be possible to contain the LiH to prevent disintegration. However, in order for LiH to remain attractive for ANP neutron shields, the containers must be quite thin-walled." ~ Minushkin

Minushkin's report is the most detailed from the pre-SNAP era. Minushkin irradiated six specimens, one of which was a single crystal (which was not examined at the time of publication). Two control specimens were heated in a furnace to segregate thermodynamic effects from radiation effects.

Author: Mueller, W.M., J.P. Blackedge, and G.G. Libowitz
Title: Metal Hydrides
Reference: Academic Press, New York, Library of Congress Catalog Card Number 68-26631
Date: 1968
Key Words: Lithium Hydride, Canning, Manufacturing, Dissociation Pressure, Phase Diagram

Summary

Mueller provides a good overview of lithium hydride, along with other saline hydrides. He includes dissociation pressure, density, fabrication techniques of LiH, and containment strategies. Mueller provides some design concerns and provides a good starting point for the containment system. Furthermore, Mueller covers chemical reactions fairly extensively.

Author: Pretzel, F.E., D.T. Vier, E. G. Szklarz, and W. B. Lewis
Title: Radiation Effects on Lithium Hydride
Reference: Los Alamos Scientific Laboratory Document LA-2463
Date: 1961
Key Words: Lithium Hydride, Mechanical Properties, Phase Separation, Gas Evolution

Summary

"Extensive measurements of the effects of radiation have been made on various compositions of Li hydrides containing combined T. The isothermal expansion of samples exposed to a flux of tritium β radiation equivalent to 16.8 Mr/hr have been observed at 12 temperatures between 77 and 673 K for maximum exposures up to 7 years. The results of these measurements are correlated with other data and are used to formulate a model for radiation damage in the Li hydrides.

That the Li hydrides are essentially ionic in character is shown by various properties. Single crystals of Li hydrides of various compositions were prepared from the melt. These were used to measure various physical properties, such as electrical conductivity, and to study radiation effects on the optical absorption of plates cleaved from the single crystals. The Li hydrides conduct electricity primarily by cation diffusion through a lattice-vacancy mechanism with an activation energy of 0.53 eV in a manner completely consistent with results obtained from the Li halides. The color-center model, which has been proposed to explain the effects of radiation damage to the alkali halides, is shown also to be suitable to explain the radiation-induced optical and electron-spin paramagnetic-resonance absorption observed in the Li hydrides.

Mechanical properties, phase separation, gas evolution, and other properties of the sample exposed to intense β radiation from combined T were also observed and correlated with the isothermal expansion data to formulate a model for the radiation effects. Equations are presented for the mechanisms involved, and comparisons between simplified calculations based on the model and observed expansion rates are given. One interesting conclusion obtained from these studies is the result that little dissociation and cavitation occurs in samples stored at temperatures below 266 K, whereas these effects are extensive and tend to lead to the disintegration of samples stored at 296 K or higher." ~Pretzel

Pretzel provides an explanation for many swelling mechanisms at the ion level. The description provided is more fundamental than any other authors description of LiH irradiation-induced swelling.

Author: Reagan, M.P.
Title: Radiation Testing of Shield Specimen: Test LTH_x-5 and 6
Reference: GE Document DC 58-1-211
Date: 1958
Key Words: Lithium Hydride, ANP, Testing, Radiation

Summary

The title of the document indicates that the information provided is for LTH_x – 5 and -6. However, the reactor operator's notes provided in the Appendix are for LTH_x -4 and -5. LTH_x-4 and -5 are the only two (of 23) specimens that experienced swelling. The notes indicate that air was intentionally injected into the primary irradiation capsule to cool the specimen during a “reactor setback”. This information is helpful in trying to understand LiH behavior in a radiation environment.

Author: Smith, R.L., and J.W. Miser
Title: Compilation of the Properties of Lithium Hydride
Reference: NASA Technical Memorandum, X-483
Date: 1963
Key Words: Lithium Hydride, Material Properties, Thermal Conductivity, Density, Linear Thermal Expansion Coefficient, Heat Capacity, Corrosion

Summary

“The properties of lithium hydride, as published in the classified and the unclassified literature through February 1962, are presented. There are five main categories: chemical, physical, nuclear engineering, and thermodynamic properties, and manufacture and related subjects.” ~ Smith

NASA X-483 provides data for several material properties (specific heat, density, thermal conductivity), as well as some corrosion information. Many of the references provided by the authors were traced. Some information provided herein cannot be corroborated.

Author: Souers, P.C., T.S. Blake, R.M. Penpraze and C. Cline
Title: Pulsed Nuclear Magnetic Resonance of Gamma-Irradiated Lithium Hydride
Reference: Journal of Physical Chemistry, Solids Volume 30 pp 2649-2656
Date: 1969
Key Words: Lithium Hydride, ⁶⁰Co Gamma Irradiation, Swelling

Summary

Data from BNL ⁶⁰Co gamma irradiation testing is presented and discussed. All specimens were tested at 15 MRad/hr gamma dose rate. Total gamma dose rates achieved were 0.5, 1.3, 3.5, 14, 28, and 47 Grads. The document contains a discussion of the experiment and results including atomic percent hydrogen and ⁷Li counted determined from NMR studies.

Author: Souers, P.C., T. Imai, T.S. Blake, R.M. Penpraze and H.R. Leider
Title: NMR and Electron Microscopy Studies on Irradiated Lithium Hydride
Reference: Journal of Physical Chemistry, Solids Volume 31 pp 1461-1466
Date: 1970
Key Words: Lithium Hydride, ⁶⁰Co Gamma Irradiation, Hydrogen gas bubbles
Summary:

Lithium hydride specimens tested in a ^{60}Co Gamma irradiated environment were studied with pulsed NMR and electron microscopy. Cubic voids in the irradiated LiH specimens were shown to be hydrogen gas bubbles. Hydrogen bubble size is related to irradiation temperature.

Author: Terry, R.E.
Title: Lithium Hydride Debris Shields for Plasma Radiation Sources
Reference: NRL/MR/67620-96-7868
Date: 1996
Key Words: Lithium Hydride, Debris Migration, Specific Heat

Summary

"The use of lithium hydride (LiH) for both return current structures and initial debris shielding is explored and a general set of design criteria is derived. It is found that, particularly when the testing requirement is for argon K shell radiation, LiH shields can improve the expected fluence on a test object over present or recently proposed technologies. The concept rests upon a tradeoff between the proximity of a test object to the plasma radiation source (PRS) and the opacity of any shielding that is interposed. Because a larger mass of intervening shield material is possible with LiH, the expected debris velocities are 100 times or more slower than current measurements. A cold press technique for the fabrication of the shield and its electrical connection to a pulser is specified." ~ Terry

Terry fundamentally derives the heat capacity of crystalline LiH using the superposition of the acoustic and optical lattice vibrations.

Author: Welch, F.H.
Title: Lithium Hydride Technology I. Properties of Lithium Hydride and Corrosion Studies
Reference: Atomics International Document NAA-SR-9400, Volume I
Date: 1964
Key Words: Lithium Hydride, Shielding Materials, Material Properties, Corrosion, Neutrons, Testing, SNAP, Ultimate Tensile Strength, UTS

Summary

"The physico-chemical, mechanical, and nuclear properties, and corrosion effects of lithium hydride are described in a three part report for SNAP systems application.

The first section presents new data on the physical, mechanical, and chemical properties of various forms of lithium hydride, and also confirms previously reported data from other sources.

The second section describes the results of 1000-, 2000-, and 4000-hr exposures of selected stainless steels to both solid and liquid lithium hydride. No deleterious corrosion effects were noted on the materials examined.

The third section reviews the effects of nuclear reactor radiation exposure to lithium hydride and lithium (-7 isotope) hydride based on a new radiation effects theory. No significant radiation damage effects are expected during the current SNAP reactor shield lifetime." ~ Welch

Volume I of the Welch tome provides material properties (e.g., dissociation pressure, thermal expansion, Young's modulus, ultimate tensile strength (UTS), and compressive creep). Based on the NRPCT literature review, Welch Volume I is the only source for UTS and compressive creep data.

Author: Welch, F.H.
Title: Lithium Hydride Technology II. Fabrication of Shadow Shields for SNAP Applications

Reference: Atomics International Document NAA-SR-9400, Volume II

Date: 1965

Key Words: Lithium Hydride, Shielding Materials, Fabrication, SNAP

Summary

"The technology of lithium hydride casting is described as a method for fabricating SNAP reactor neutron shielding. The background, development, and current status are present. The casting process and the shield casting hardware are described in detail.

All SNAP systems shields and test specimens produced to date by the casting process are described individually. The method is capable of repetitively producing high-purity (> 97.5 wt % LiH), high-density (~94% of theoretical density) lithium hydride shields rapidly and economically." ~ Welch

Welch, Volume II, provides a good overview of the SNAP investigation into LiH shield fabrication processes. It compares cold-pressing and casting, as well as describes the process of zone melting and controlled cooling required to reduce the shrinkage of the finished product. Additionally, the first few pages of this document provide an extremely high level overview of the SNAP reactor shield (function and selection of material), which the NRPCT found to be helpful early in the Prometheus reactor design cycle.

Author: Welch, F. H.

Title: Lithium Hydride Technology: III. Properties of Lithium Hydride for SNAP Shielding Applications

Reference: Atomics International Document NAA-SR-9400 Volume III

Date: 1967

Key Words: Lithium Hydride, Shielding Materials, Material Properties, Corrosion, Radiation Damage, Testing, SNAP

Summary

"The physico-chemical and mechanical properties, the corrosivity, and the radiation damage characteristics of lithium hydride are described in this three-part report covering the work performed from 1964 through 1966 which was funded by the SNAP General Supporting Technology Program. This report is the third in a series about the LiH shield materials program and is a companion to Volume I which describes the earlier property and corrosion studies. Volume II is about fabrication and casting of the SNAP reactor LiH neutron shields.

The first section of Volume III presents new data from laboratory studies on LiH such as hydrogen migration in LiH, the effect of LiH on the diffusion of hydrogen through stainless steel, the rate of hydriding of metallic lithium, and many other subjects related to SNAP shielding application. The second section describes the effect of LiH on braze alloys, and SNAP 8 emissive coatings. The effects of mixtures of Li and LiH on stainless steel are also described.

The third section reviews the recent irradiation tests on LiH and theories to explain the observed behavior. A number of postulates are made predicting the types of behavior which should be expected under various irradiation conditions." ~Welch

Volume III of the Welch document is by far the most referenced section. This volume contains a summary of the irradiations tests performed to date (1967) and the references associated with those tests. Furthermore, Welch describes the NARF, STIR, and SNAP 10A Reactor Experiment in detail. This summary includes 47 specimens irradiated under a variety of conditions. Furthermore, this document includes the only study of hydrogen migration in LiH known to the NRPCT. Corrosion

studies with potential canning materials are also included, which would be helpful when designing the LiH containment system.

Author: Welch, F. H.
Title: Lithium Hydride Technology: IV. A Novel Neutron-Gamma Material for SNAP Shielding Applications
Reference: Atomics International Document NAA-SR-9400 Volume IV
Date: 1967
Key Words: Lithium Hydride, Shielding Materials, Fabrication, Material Properties, SNAP
Summary

"A novel neutron-gamma shielding material was conceived which consists of a matrix of cast lithium hydride, containing a crushed, granular gamma shielding material. The concept was tried with two different gamma materials. In one version tungsten alloy was used; in the other zirconium hydride was the gamma material; in both cases the less expensive, most available form of the gamma material was used. Densities, compositions, and N_H 's of the two shielding combinations were determined. Modulus of rupture tests indicated that both cast aggregate material combinations were weaker than the cast lithium hydride.

An experimental shield was successfully fabricated containing a 200-lb layer of tungsten alloy, infiltrated with cast lithium hydride. The process is believed feasible for the fabrication of future large reactor shields." ~Welch

This volume of the Welch document explores interesting ways to improve upon one of the most efficient neutron attenuating materials by adding gamma attenuating materials. Creating a homogenous shield material that attenuates both neutron and gamma radiation was considered, but has not been investigated by the NRPCT, due to time constraints and the additional complexity of creating a homogeneous mixture of low and high density materials. However, it is worth reading.

Author: Welch, F. H.
Title: Lithium Hydride Technology: V. Testing and Examination of SNAP Shadow Shields
Reference: Atomics International Document NAA-SR-9400 Volume V
Date: 1967
Key Words: Lithium Hydride, Shielding Materials, Testing, SNAP
Summary

"The results of the X-ray examination, dimensional measurements, shock and vibration testing, and thermal cycle testing are described for each of twelve shields and test specimens. This work is a follow up of the fabrication and casting program, described in NAA-SR-9400 Volume II. The final destructive examinations which were made on seven of the twelve are described and an attempt is made to correlate the findings of the final examinations with observations made during the testing period.

The special equipment and methods used to conduct the testing and examination program are also described." ~Welch

The final volume of NAA-SR-9400 provides an overview of shield assembly testing. Perhaps the most interesting aspect early in the Prometheus reactor design cycle is the lessons learned through experimenting with 10 shield assemblies.

Author: Zalkin, Allan
Title: The Thermal Expansion of LiH
Reference: USAEC Report URCL-4239
Date: 1953
Key Words: Lithium Hydride, Material Properties, Thermal Expansion

Summary

"The thermal expansion of LiH was studied in the temperature range of 298 to 798 K by means of x-ray diffraction. The coefficients of linear expansion were determined as $\alpha = 4.2 \times 10^{-5}$ and $\beta = 1.9 \times 10^{-8}$. There is no evidence of any structure transitions in this range. The cell constant for LiH at 298 K is $a_0 = 4.083 \text{ \AA}$." ~ Zalkin

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CONCURRENCE/DESIGN CHECK FORM FOR DOCUMENT NO. MDO-723-0048 Date: 12/09/05

DOCUMENT TITLE: The Evaluation of Lithium Hydride for Use in a Space Nuclear Reactor Shield, Including a Historical Perspective, For NR Information.

REFERENCES: _____ ENCLOSURES: (1) A Perspective on the Use of Lithium Hydride in a Space Nuclear Reactor Shield
(2) Summary of Lithium Hydride Material Performance and Issues in a Space Nuclear Reactor Shield

1. ADSARS: PERMANENT RECORD: Yes ☒ No ☐ Repository MFLIB Corporate Author: KAPL NR PROGRAM _____

Key Words: Space Reactor, LiH, lithium hydride, irradiated materials, material properties, Prometheus
Need to Know Categories REP SGN
Available Sites: PRNR
Design File Location(s) _____

2. DESIGN CHECK

Type of Check	Signature(s)	Comments: (Including Reference to Check Document If Appropriate)
A. No check considered necessary		
B. Check vs. previous results/issues	<i>[Signature]</i>	
C. Checked calculations made	<i>[Signature]</i>	
D. Checked computer input and/or output	<i>[Signature]</i>	
E. Computer Programs approved/qualified		
F. Performed independent audit		
G. Spot checked significant points	<i>[Signature]</i>	<u>ECPhed BSG (Enc. 1, AH 3, 4) RL (Enc 1, AH 2)</u>
H. Reviewed methods used	<i>[Signature]</i>	<u>ECPhed</u>
I. Reviewed results for reasonableness	<i>[Signature]</i>	<u>ECPhed BSG (Enc. 1, AH 3, 4) RL (Enc 1, AH 2) DP (Enc 1, AH 2)</u>
J. Comparison with test data	<i>[Signature]</i>	<u>BSG (Enc. 1, AH 3, 4) RL (Enc 1, AH 2)</u>
K. Reviewed vs. drawings		
L. Verified procedures		
M. Technical content reviewed	<i>[Signature]</i>	<u>BSG (Enc. 1, AH 3, 4) RL (Enc 1, AH 2) DP (Enc 1)</u>
N. Management verification of adequate review by others		
O. Performed Lessons Learned Search		
P. Used Measurement Uncertainty Methods		
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3. CONCURRENCE REQUIREMENTS:

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☐ SPP MANAGER	☐ ADVANCED CONCEPTS	☐ FLUID DYNAM
☐ NUCLEAR ENGINEERING	☒ SHIELDING <i>[Signature]</i>	☐ STRUC. ENGRG
☐ REACTOR TH/MECH DESIGN	☐ REACTOR SAFETY <i>[Signature]</i>	☐ DRAFTING
☒ REACTOR EQUIPMENT	☐ TO	☐ QA
☐ SPP POWER PLANT SYSTEMS	☐ RSO	☐ OTHER
☐ SPP ELECTRICAL	☐ FSO	☒ BETTIS <i>[Signature]</i>
☐ FINANCE	☐ MDO	☐ BPMI <i>[Signature]</i>
☐ PROJECT OFFICE	☐ ARP	☒ ADMIN REVIEW <i>[Signature]</i>
☐ ENERGY CONVERSION		

Cognizant Manager *[Signature]* ACTING for SA Simonson
(SA Simonson)

4. AUTHORIZED CLASSIFIER: _____ Reviewed By: *[Signature]* CLASSIFICATION: Unclassified

5. RELATED SUBJECTS:
UTRS Implication (Y/N) N Commitment Made (Y/N) N Commitment Complete (Y/N) Y
Safety Council Review (Y/N) N Design Basis Info. (Y/N) N UTRS Doc. # N/A
Design Review (Y/N) N

Distribution:

NR

DI Curtis, 08S, For NR Information
TJ Mueller, 08R, For NR Information
S. Bell, 08I/8024
JP Mosquera, 08C/8017
CH Oosterman, 08C/8017
JD Yoxtheimer, 08S/8034
JM Crye, 08R
L McMichael 08S

SNR

D. Clapper, 065
GM Millis, 065
DJ Potts, 065

BETTIS

J.E. Hack
R Baranwal
W Ohlinger
V Munne
DC Noe
HA Karnes ZAP 31Q
RS Amato ZAP 31Q
JL Bowman ZAP 36E
CD Eshelman ZAP 36E

PNR

J. Andes
JF Koury

KAPL

JW Prybylowski Bin 96
PF Baldasaro Bin 111
MJ Wollman Bin 111
H Schwartzman Bin 132
F Pineau Bin 098
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E Pheil Bin 132
PA Diloranzo Bin 132
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G Newsome Bin 92
Y Ballout Bin 92
W Johnson Bin 157
ER Venerus Bin 157
G Stasik B 132
L Kolaya Bin 92
DF McCoy Bin 111
JK Witter Bin 111
W Gideon Bin 111
BS Gurau Bin 92
DF Poeth Bin 92
R Lewis Bin 92
J Nash Bin 92
B Lugert Bin 92
BC Campbell Bin 92
G Young Bin 163
J Vollmer Bin 102
R Najafabadi Bin 102
D Barnes Bin 154
G Dansfield Bin 154
R Grossman Bin 154
C Regan Bin 092
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