The safe removal of frozen air from the annulus of an LH2 storage tank

A Krenn¹, S Starr², R Youngquist², M Nurge², J Sass³, J Fesmire³, C Cariker⁴ and A Bhattacharya⁴

¹Cryogenic Propulsion Systems Branch, NASA Kennedy Space Center, FL 32899, USA
²Applied Physics Lab, NASA Kennedy Space Center, FL 32899, USA
³Cryogenics Test Lab, NASA Kennedy Space Center, FL 32899, USA
⁴Department of Physics, University of Central Florida, Orlando, FL 32816, USA

Email: angela.g.krenn@nasa.gov

Abstract. Large Liquid Hydrogen (LH2) storage tanks are vital infrastructure for NASA. Eventually, air may leak into the evacuated and perlite filled annular region of these tanks. Although the vacuum level is monitored in this region, the extremely cold temperature causes all but the helium and neon constituents of air to freeze. A small, often unnoticeable pressure rise is the result. As the leak persists, the quantity of frozen air increases, as does the thermal conductivity of the insulation system. Consequently, a notable increase in commodity boil-off is often the first indicator of an air leak. Severe damage can result from normal draining of the tank. The warming air will sublimate which will cause a pressure rise in the annulus. When the pressure increases above the triple point, the frozen air will begin to melt and migrate downward. Collection of liquid air on the carbon steel outer shell may chill it below its ductility range, resulting in fracture. In order to avoid a structural failure, as described above, a method for the safe removal of frozen air is needed. A thermal model of the storage tank has been created using SINDA/FLUINT modeling software. Experimental work is progressing in an attempt to characterize the thermal conductivity of a perlite/frozen nitrogen mixture. A statistical mechanics model is being developed in parallel for comparison to experimental work. The thermal model will be updated using the experimental/statistical mechanical data, and used to simulate potential removal scenarios. This paper will address methodologies and analysis techniques for evaluation of two proposed air removal methods.

1. Introduction

Liquid hydrogen (LH₂) has many industrial uses, and is a primary rocket fuel utilized by the National Aeronautics and Space Administration (NASA). The safe and efficient storage of large quantities of LH₂ is required by suppliers and users, but it is complicated by the extremely low boiling point of LH₂ (20 K). NASA's Kennedy Space Center (KSC) has two 3,218 cubic meter (850,000 gallon) LH₂ storage spheres at Launch Complex 39 (LC-39) which were built in the 1960s and were used in support of both the Apollo and the Space Shuttle Programs. At least one of these is intended for use in future human space flight programs. These storage spheres are representative of large LH₂ tanks and will be used in the proceeding work as the standard for an LH₂ sphere. They are comprised of an 18.7 meter (61.5 foot) diameter 1.75 cm (0.688 inch) thick stainless steel inner sphere suspended inside a 21.6 meter (70 foot) diameter, 2.95 cm (1.16 inch) thick carbon steel outer sphere¹. The 1,642 cubic meter (58,000 cubic foot) annular space contains inner sphere supports as well as liquid and gas lines,

and is filled with perlite powder² for insulation. A vacuum is maintained in the annulus to reduce the overall heat leak minimizing LH_2 losses due to boiloff. The construction of one of these spheres is shown in figure 1.



Figure 1. Construction of an 850,000 gallon LH₂ Sphere at LC-39

Because the outer sphere is made of carbon steel, it is highly susceptible to corrosion. If corrosion penetrates the outer shell, or if soft seals crack or otherwise develop leaks, air will leak into the annulus. Slow air leaks into the annulus are notoriously difficult to identify in a timely manner. Air leaking into a vacuum would typically result in a noticeable pressure rise in the vacuum space. However, in the case of an LH₂ storage tank, the extremely low temperatures cause most of the air constituents to freeze near the inner tank wall, resulting in a pressure increase so slight; it can go unnoticed for months or even years. However, long term monitoring of the annular pressure can provide an estimate of the leak rate because Helium and Neon do not freeze out and their fractional content in the atmosphere is well known. As the annular pressure rises, a residual gas analysis (RGA) may be performed on a gas sample from the annulus to verify the leak is air, and approximate the volume of ingested air. But before a significant pressure increase is noted, a secondary effect often results in the primary diagnosis. As air freezes inside the perlite, the residual gases degrade the thermal performance of the perlite causing more heat from the environment to reach the bulk liquid. The increase in heat leak is significant enough to result in a noticeable increase in the boiloff rate.

While RGA data is informative, it does not address the problem of locating or stopping the leak, which can prove very difficult in an operational tank. In industrial applications, storage tanks with air leaks are typically removed from service, repaired via standard mass spectrometer helium leak testing and weld repair techniques, then returned to service. NASA, however, is often in the difficult position of maintaining test and operational programs, and removing these essential assets from service would result in significant schedule and cost impacts. Opportunities for in-service repairs are limited and waiting for a convenient opening in the schedule to bring the vessel down can result in thousands of kilograms of air being ingested and frozen inside the annular space. These large quantities of air cause problems throughout any future repair process.

2. Problem Description

At low pressures of 1.3 - 26.7 Pa (10 – 200 millitorr), the primary constituents in air (nitrogen and oxygen) will freeze at temperatures below 50 K³. When the storage tank is full, those temperatures will be present at some distance from the inner tank wall through the entire height of the liquid column. When the liquid level is reduced for operational purposes, or to facilitate removal from service, the reduction in liquid level will result in warming of some of the areas where frozen air is

present. Due to the low pressure, warming will initially cause the air constituents to sublimate, which will cause the annular pressure to rise. If liquid is not re-introduced before the annular pressure rises above the triple point of any of the constituents, sublimation will turn to liquefaction. As the air begins to liquefy, it will drip from its location near the inner tank wall, down to the inside of the outer tank wall (which is at near ambient temperatures). Liquid air contacting the outer wall will result in a significant drop in the outer wall temperature. If the volume of air is large enough, the temperature of the outer wall may drop below its ductility range which could subsequently result in large cracks on the outer sphere due to embrittlement.

The goal of this work is to establish a method to remove frozen air from the annular space of an LH_2 storage sphere, shown in figure 2, without cracking the outer shell of the vessel. There has been some related, but not directly applicable work studying heat flux in in helium systems with sudden vacuum loss^{4,5}. However, an extensive literature search has revealed no prior work concerning removal of frozen air from an LH_2 storage tank. Two potential methods for removal will be evaluated in this project. First, connecting a vacuum pump to the annular space and pumping in parallel with tank drain could keep the annular pressure below the triple point. This would result in continuous sublimation, thus eliminating the threat that liquefaction poses. The second method to be evaluated is to install heaters to the bottom of the outer tank during the tank drain. Though liquefaction in the annular space will occur, the heaters would be designed to keep the outer shell above the embrittlement temperature, so that cracking will not occur.



Figure 2. LC-39 Pad A LH2 Storage Tank

In order to evaluate methods for air removal, it is first necessary to identify locations within the perlite where the air may freeze. This will be accomplished using thermal modeling of an LH₂ storage tank in SINDA⁶/FLUINT⁷. The results of this model will show the temperature gradient though the extent of the perlite at varying liquid levels. Areas below 50 K will be identified as zones where the primary air constituents can solidify. Additionally, an experiment will be performed to determine the thermal conductivity changes in perlite as nitrogen freezes into the volume of the interstitial spaces. Other work has examined the effect of carbon dioxide (CO_2) on the thermal conductivity of cryogenic insulators, including perlite⁸, but this work was limited to LN₂ temperatures and had only a background of CO₂. The experiment will also attempt to quantify the maximum nitrogen absorption capability of perlite, and may potentially provide some insight into the density of the air-ice. Concurrently, microscopic models of the air flow into the vacuum are being developed. These models will be used to determine the distribution, density, and maximum absorption of the air-ice formation, and can be comparted to the experimental results. The maximum absorption parameter is important because it sets a limit on the total volume of air that can be drawn into the annular space before the situation becomes uncontrollable. Once the perlite is fully saturated and can adsorb no more air, the annular pressure will rise beginning the process which could ultimately lead to cracks. All of the data will be compiled in order to perform a physics based evaluation of the two proposed air removal techniques, and a suggested path forward for tanks in this situation will be outlined.

3. Historical Information

In late 2011, the LH₂ tank at Stennis Space Center's (SSC) B-1 Test Facility experienced a significant vacuum leak which eventually led to major cracks in the bottom of the outer shell due to a similar sequence of events as those described in the problem description. The B-1 tank is a 340.7 cubic meter (90,000 gallon) cylindrical tank that was built in 1962 by Chicago Bridge & Iron. Two rupture disc assemblies at the top of the tank developed leaks and a pressure rise was noted in the annular space. Additional testing requirements drove users to re-fill and continue operating the tank. Liquid top-off spurred cryo-pumping which resulted in an annular space pressure drop from approximately 9332.6 Pa (70,000 millitorr) to 3.1 Pa (23 millitorr). During test runs, operational constraints were implemented to prevent shifting/damage of the inner vessel, and after testing was completed, the tank was drained to facilitate repair of the leaking rupture disk assemblies. However, two days after the tank had been completely emptied, heavy frost developed on the bottom of the outer vessel. Temperature sensors indicated the outer jacket was between 77.8 – 88.9 K at the bottom which is well below the ductility range for carbon steel (244 K)⁹. Additional vacuum pumping was attempted, but proved difficult due to small port sizes and/or perlite intrusion into the pumping system. Eighteen days after tank drain, the outer vessel cracked. Damage can be seen in figures 3 & 4.



Figure 3. Picture of B-1 tank cracks



Figure 4. Bottom view of B-1 tank with cracks in bold

Currently, there is a large LH_2 storage tank that has had a small air leak for at least two years, and is estimated to have several thousand kilograms of air frozen inside its annulus. Further details cannot be divulged due to contractual issues, but it is hoped that the work described in this paper can be completed prior to draining this tank so that major damage, like that seen at SSC, can be avoided.

4. Thermal model

A thermal model of a typical, large LH₂ storage tank was created using Thermal Desktop¹⁰ as an interface to SINDA/FLUINT. This model employs a finite difference solver to determine the steadystate temperature profile of the inner wall and perlite filled annulus. Each $\frac{1}{2}$ shell of perlite "solid" was subdivided into 8 equally spaced angular nodes (divisional lines extend pole-to-pole), 8 equally space radial nodes (divisional lines are shells within the perlite), and 15 equally spaced beta nodes (divisional lines are horizontal slices through the perlite shell). These divisions provided adequate temperature resolution while keeping model run times reasonable. The thermal conductivity of perlite is a function of both temperature and pressure. Because the perlite was modeled in SINDA as a solid, changes in pressure cannot be considered. However, a pressure can be "set" by choosing the thermal conductivity which corresponds to the desired pressure using existing, published thermal conductivity data^{11,12}. The temperature dependency is included in the inputs and is fully accounted for. The liquid inside the tank, which provides the cold boundary, was created in SINDA, but will be transitioned to FLUINT. Modeling the liquid in SINDA allows for ease in reflecting temperate gradients in the gas section, but varying the liquid level becomes quite laborious. Once the liquid is fully transitioned into FLUINT, the liquid level will be adjustable and temperature changes with liquid level changes will be observable.

Results from the initial, 50% full, SINDA model are shown in figures 5 and 6. A freezable zone (<50 K) of approximately 6.88 cm (2.71 inches) is shown to extend the entire height of the liquid. It begins to taper off at the upper limit of the liquid and diminishes to zero after approximately 79.2 cm (2.6 feet). According to the model results, at steady-state and 50% full, approximately 38.2 cubic meters (1,350 cubic feet) of annular space is cold enough to freeze air. This value corresponds to 2.3% of the total annular volume.



Figure 5. Thermal model, 50% full case

Figure 6. Zoomed view with freezable zone shown in bold

5. Experimental work

An experiment was designed to determine thermal conductivity changes in perlite that has nitrogen frozen into it. Nitrogen was used instead of air to avoid any potential safety concerns using oxygen. Because air is 78.1% nitrogen, this simplification is considered to be representative of the thermal conductivity changes that would occur in a storage tank leaking air into its annulus. The test set-up is shown in figures 7 & 8 and includes a Cryomech AL230 Cold head covered by 12.7 cm (5 inches) of perlite. Eight silicon diode temperature sensors (Scientific Instruments Model 410AA) were installed in the center of the perlite at distances shown in figure 9. A radiation shield was fabricated out of 0.318 cm (1/8 inch) copper plate sandwiched by 0.635 cm (1/4 inch) copper tubing runs in a waffle pattern. The radiation shield, intended to minimize the total temperature change in the perlite sample, was positioned approximately two inches above the top of the perlite sample and was fed by LN₂. A multi-layer insulation (MLI) lined vacuum can was then installed over the sample assembly.





Figure 7. Schematic of test set-up

Figure 8. Test set-up

After evacuation to approximately 2.67 Pa (20 millitorr), the cold head was activated and liquid nitrogen flow was initiated through the radiation shield. Vacuum pressure was then increased to 867 Pa (6500 millitorr) in order to increase the heat flow so that the time-scale of the experiment would be days instead of weeks. A flow controller maintained the pressure at 867 Pa (6500 millitorr) throughout the test and a flowmeter recorded the flow required to maintain that pressure. All temperatures were recorded, a sample of which is shown in figure 10. An interesting feature of this data is that change in temperature slope seen by T01, T02, and T03 (bottom 3 lines). This change in slope is due to the change in thermal properties after the nitrogen has frozen into the interstitial space. At the end of the test, all of the temperatures approached steady state, meaning there was equal energy flow through all of the perlite surfaces. With known temperatures and spacing, the thermal conductivity of the layers with frozen air can be calculated using equation 1, where k1 thru k7 represent the thermal conductivities of the layers between the temperature sensors. Likewise, 11 thru 17 represent the distance between the temperature sensors and $\Delta T1$ thru $\Delta T7$ represent the changes in temperature. A complete discussion of the testing and analysis of the results will be published in the future.

Temp Measurement	Distance from cold head
	in cm (+/- 0.15)
T08	12.67
T07	10.26
T06	7.54
T05	6.17
T04	5.16
T03	3.73
T02	2.39
T01	0.00

Figure 9. Temperature senor locations



Figure 10. T01 – T08 shown bottom to top after GN₂ introduction

$$\frac{k1\Delta T1}{l1} = \frac{k2\Delta T2}{l2} = \frac{k3\Delta T3}{l3} = \frac{k4\Delta T4}{l4} = \frac{k5\Delta T5}{l5} = \frac{k6\Delta T6}{l6} = \frac{k7\Delta T7}{l7}$$
(1)

6. Statistical mechanics model

The dynamics of fluid transport within the annular region of the LH_2 tank are not entirely known. To be able to model the spatial evolution of fluid distribution in the annulus, important details that remain unknown are the absorptive capacity of the insular region (along with any hysteresis in the absorption isotherms) as well as the fluid's ability to percolate through the insular medium. These characteristics are dependent on the specific microporous structure of the insulating medium and are not readily measured by experiment. However, numerical simulations have been successfully used in the past to forecast these characteristics¹³. A molecular simulation that predicts the absorption isotherms of gas molecules in perlite is being developed. This model simulates a system of gas atoms in a Grand Canonical ensemble and uses the Monte Carlo algorithm¹⁴, which is carried out by sampling the phase space of the system by means of trial particle displacements, insertions, and removals, using the Boltzmann weight to determine the probability of move acceptance. Now that a working code implementing this algorithm has been developed and debugged, a modification of the simulation cell to reflect the microporous structure of perlite is underway. A comparison of simulation results with measurable physical quantities can then verify the usefulness of the simulation, which can then be used provide data for absorption at low temperatures and pressures, where experimental observations of the same are difficult to obtain.

7. Proposed air removal methods

During the anomaly with the B-1 tank at SSC, active pumping immediately following tank drain was performed and was not successful at controlling the annular pressure. However, post-test inspection revealed that the annular evacuation system had been damaged making pumping efforts ineffective. If a tank's pumping system is intact, one should be able to lower the liquid level slowly enough that air can be pumped out as it sublimates. Therefore, as the tank warms, the annular pressure could be maintained below 133.3 Pa (1000 microns), which is the triple point for oxygen - the lowest of the air constituents. However, the time-scales for this type of process are unknown. Evacuation rates can be obtained using data from the recent evacuation of the LC-39 Pad B LH₂ tank, which has been out of service undergoing refurbishment since the end of the Space Shuttle program. Calculations will be performed using results from the thermal model and the experimental work in order to quantify sublimation rates. These two rates can then be compared in order to determine how long it would take to execute removing a tank from service in this manner.

The second method under consideration is the application of heat to the exterior of the outer jacket in order to keep the jacket from dropping below its ductility range. Data from testing and modeling can again be used, to analyze the heat flow into the system. This heat flow can be used to estimate the time required to melt a given mass of nitrogen. A calculation of the amount of heat required to maintain the carbon steel within its ductility range (>244 K) over that period of time will quantify the heating power required to successfully remove a tank from service in this way. Once an estimate of the required heating power is obtained, all that remains is to determine if there are commercial heating devices that could provide the required heating power, and to verify sufficient electrical power is available at the location of the storage tank. This scenario would provide a more rapid approach for removing the frozen air however, there are additional safety concerns. These areas are classified as Class 1 Division 2 and there are restrictions on electrical wiring and equipment which need to also be considered¹⁵. Further analysis is needed to produce a recommended course of action.

8. Conclusion

It has been shown that the problem of air leaking into the annulus of a large LH_2 storage tank has resulted in severe damage to national assets in the past, is a current obstacle to operations in the present, and can be expected to present challenges in the future. Despite this, no guidance on methods to address this problem was found in literature searches. Two methods have been proposed here, each

with their own unique challenges for execution. However, the combined micro and macro level models along with the testing data should yield enough information for the evaluation of both methods. Further work is planned to produce detailed analysis and recommended guidelines for the safe removal of frozen air.

Acknowledgements

A special thanks to Craig Fortier and Jared Congiardo for helping with the ins and outs of SINDA/FLUINT. And testing would not have been possible without the support of Kevin Jumper and the team of the Cryogenics Test Laboratory. Bartt Hebert, Harry Ryan, and Haynes Haselmaier produced an unpublished overview of the events that took place at Stennis Space Center which provided important details in understanding the air leak problem.

References

- Chicago Bridge & Iron Company, 1965 Drawing Number LHCD-40862, General Plan 850 MG LH2 Sphere Launch Complex 39-B for Catalytic Co.
- [2] R H Kropschot and RW Burgess 1963 Perlite for cryogenic insulation, Advances in Cryogenic Engineering 8 ed K D Timmerhaus (Los Angeles, California: Plenum Press) 425-436
- [3] E W Lemmon, M L Huber and M O McLinden 2013 Reference Fluid Thermodynamic and Transport Properties (REFPROP), NIST Standard Reference Database 23, Version 9.1
- [4] E S Bosque, R C Dhuley and S W Van Sciver 2014 Transient heat transfer in helium II due to a sudden vacuum break, Advances in Cryogenic Engineering: Transactions of the Cryogenic Engineering Conference-CEC 1573 (AIP Publishing) 260-267
- [5] T Boeckman, D Hoppe, K Jensch, R Lange, W Maschmann, B Petersen and T Schnautz 2008 Experimental tests of fault conditions during the cryogenic operation of a XFEL prototype cryomodule *Proceedings of International Cryogenic Engineering Conference* 22 (Seoul: H M Chang et al) 723-728
- [6] C&R Technologies 2012 Introduction to SINDA, Version 5.6 Revision 1
- [7] C&R Technologies 2012 Introduction to FLUINT, Version 5.6 Revision 1
- [8] J Maximilians 2010 Thermal Characterization by Freezing of Carbon Dioxide as a Filler Gas, Disseration to the Department of Physics and Astronomy at the University Wurzburg, Germany
- [9] P Mittal 2011 Part 2: Low temperature ductility and ductile crack arrest properties of high strength low alloy steel, *Pipeline & Gas Journal* **238**
- [10] C&R Technologies 2014 Thermal Desktop User's Manual, Version 5.7
- [11] L Adams 1965 Thermal conductivity of evacuated perlite, Cryogenic Technology 1 249-251
- [12] L Adams 1965 Thermal conductivity of perlite at low temperatures, Cryogenic Technology
- [13] F Romm 2004 Microporous media: synthesis, properties, and modeling *CRC Press* **120**
- [14] D Frenkel and B Smit 2001 Understanding molecular simulation: from algorithms to applications vol 1 (Academic Press)
- [15] NFPA 55 2010 Compressed Gases and Cryogenic Fluids Code