Research and Development History of Glass Bubbles Bulk-Fill Thermal Insulation Systems for Large-Scale Cryogenic Liquid Hydrogen Storage Tanks

Based on the published literature record, this document provides an overview of the research and development of glass bubbles bulk-fill thermal insulation systems for cryogenic equipment in general and, in particular, for large-scale cryogenic liquid hydrogen (LH2) storage spheres. Glass bubbles (also known as hollow glass microspheres) are used in place of perlite powder which began use in double-wall cryogenic tanks in the 1930s. Included in this overview is a historical summary, a development timeline, a selected publications list, and the key technical points from those publications.

Introduction

Summarized here is the current state-of-the-art on the subject bulk-fill thermal insulation systems for vacuum-jacketed cryogenic tanks; that is, the use of glass bubbles as the primary component of this type system. This research and development work was performed from about 2000 to 2010 under the leadership of the Cryogenics Test Laboratory team at the NASA Kennedy Space Center (KSC).

For large-scale spherical LH2 storage tanks (that is, above about 100,000-gallon capacity), the evacuated perlite powder system has been used for the last 60 years. Large scale LH2 tanks are site built and can therefore be of a spherical design. The sizes range from about 50,000 gallons up to 2,000,000 gallons, with the upper end limited by the shell thickness of the vacuum jacket. But what about the latest technology for the insulation system? The glass bubbles system has been proven first by NASA/KSC researchers and now by industry in different parts of the world as a cost-effective and reliable alternative to evacuated perlite powder systems. The driver for this adoption has been substantial energy/product savings.

Our technical publications show an average 46% reduction in boiloff over 6 years of field demonstration. This real-world result surpasses the ~35% reduction (compared to perlite powder) found through years of extensive laboratory and sub-scale testing with liquid nitrogen (LN2) and LH2. The field test facility is a 50,000 gallon LH2 tank at Stennis Space Center with a long prior history of excellent vacuum maintenance and a top performing track record with pristine, top specification perlite powder that was removed in 2008 and replaced with 3M K1 series glass bubbles. Why was field performance even better than the markedly improved laboratory performance? Because the real-world vacuum levels are in a range where a performance gap opens between the two materials. Glass bubbles are far less sensitive to vacuum level degradation compared to perlite powder, making the field result even better than the idealized laboratory result

The glass bubbles-based cryogenic insulation system has also been proven for various applications in double-wall tanks and piping. The double-wall construction can be for vacuum or non-vacuum (purged) environment. The environment (vacuum, partial vacuum, or non-vacuum) and the residual gas composition in which the insulation material operates is the key to the level of insulating performance. The lowest possible heat flow into the tank for the least life-cycle cost is always the desired target.

Research & Development Highlights

We worked with K1, K25, and K46 bubbles from 3M. These bubbles have been both coated and uncoated. Coatings included carbon black, titanium dioxide, and other opacifiers. The main purpose of the coatings is to reduce radiant heat transfer in the infra-red range. We have also tested different glass bubbles (microspheres) produced by ThermaCell (no longer in business). The K1 bubbles, shown in Figure 1, were the most economical and shown to perform well in all aspects.

Through Cryostat-100 testing and 1000-liter spherical tanks testing, we produced extensive data on the thermal conductivity and total system thermal performance of glass bubbles-based thermal insulation systems under cryogenic-vacuum conditions. The 1000-liter tanks, shown in Figure 2, are a 1/15th scale version of the 850,000 gallon LH2 storage tanks at KSC. We understand the intricacies of the heat transfer mechanisms and their interactions through the vacuum pressure range. We understand that glass bubbles are better than perlite powder through the entire vacuum pressure range. This performance increase is mainly through the additional radiation scattering afforded by the walls of the bubbles in combination with the low thermal conduction by virtue of the point contacts among adjoining spheres. We understand that bubbles are better than aerogel-based insulations (particle or blanket) under high vacuum, but not as good as aerogels at non-vacuum conditions. We further understand the pros and cons of glass bubbles, for both thermal performance and operational practicalities, in comparison to all other cryogenic insulation systems used in the world today.

Perlite powder is the main target for replacement with glass bubbles. Installations can be new construction or retrofits. We understand the vacuum sensitivity of glass bubbles versus perlite and have shown how this feature is a strong cost savings benefit. Large vacuum-jacketed (VJ) perlite tanks around the world are designed for high vacuum (below 0.1 millitorr) but typically operate at up to 10 to 50 millitorr (degraded or partial vacuum) in the real world. The performance benefit (boil-off reduction) is then not 35% (laboratory) but approximately 50% (field) or better.

We performed extensive mechanical testing to verify by scientific materials tests, prototype tank tests, and field tests that the bubbles do not break to any significant amount. The cases include vibration, compaction, installation, and thermal cycling. This fact was established mainly for spherical tanks with some work also applied for cylindrical vertical and cylindrical horizontal tanks. Mechanical prototypes of piping and flexible piping were also built and tested. Granular mechanics analysis and modeling of glass bubbles and systems was also performed in concert with the prototype and lab testing.

We worked out the filtration and vacuum pumping processes that are critical for handling and use of very fine particles. Filtration elements include vacuum-jacket internal devices as well as devices before the vacuum pump suction. The use of other, coarser particles to prevent the unwanted displacement of bubbles has also been shown through lab testing. Pumping and bake-out times, purging cycles, vacuum retention behavior, and other key parameters have been worked out.

The mechanical settling behavior of glass bubbles has been extensively researched, tested, and analyzed in the laboratory. Testing included vibration settling, compaction due to thermal cycling, moving wall tests, and vertical columns tests. We understand that the hydrostatic force equation does not apply, but that forces move through networks of force chains, thus allowing the insulation to stay at a more consistent density from top to bottom. These features are all important to ensure that undue forces are not imposed on the tank structures and that thermal performance is optimized. We performed pneumatic pressure testing that showed the K1 glass bubbles began an onset of breakage between 50 and 100 psi. This pressure is lower than the isostatic crush strength of 250 psi, but still well above the threshold for the actual operational environment.

We have demonstrated the thermal-mechanical performance of glass bubbles for VJ tank insulation in the following cases: Full-scale field demonstration on 50,000-gallon spherical liquid hydrogen tank at Stennis Space Center; research testing using two 1,000-liter spherical tanks (1/15th scale models of 850,000 gallon tanks at LC-39) with LH2 and LN2; industry field demonstration on a pair of 6,000 gallon LN2 tanks (through SBIR project with TAI).

The above listed items are a sampling of some of the work over about a 10-year span. Our papers and publications contain more facets and details, both technical and economic, of the use of glass bubbles for cryogenic insulation systems.

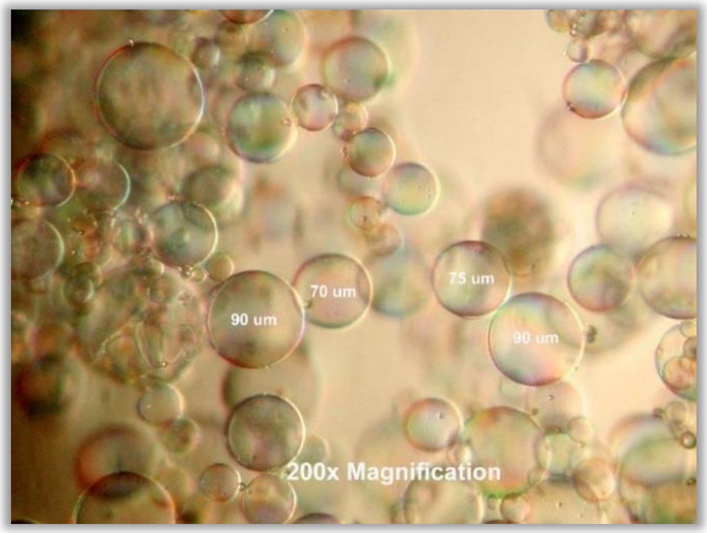

Figure 1. Micrograph photo of glass bubbles, type K1 by 3M. The average diameter is 65 microns.

Figure 2. Liquid hydrogen testing of glass bubbles (and perlite powder) using two 1000-liter spherical tanks.

Historical Summary

The research and development for the use of glass bubbles bulk-fill material as part of a cryogenic tank insulation system began in the early 1970s by Dr. George Cunnington (Lockheed Palo Alto Research Laboratory) and Professor C. L. Tien (University of California, Berkeley). The literature record shows that they worked with K1 glass bubbles manufactured by 3M. The potential for the use of these hollow, spherical, micro-sized glass bubbles was introduced to me in about 1998 by Dr. Paul Mueller of Utah State University Space Dynamics Laboratory for a Mars Surface Storage of Cryogens application. While our collaboration project proposal did not receive funding, I began initial experimentation with glass bubbles as part of the Cryogenics Test Laboratory (CTL) internal research work at the NASA Kennedy Space Center (KSC). The starting point was the K1 Glass Bubble product by 3M as this was the material successfully used and characterized for thermal and mechanical performance data by the prior and substantial work of Cunnington and Tien.

Soon after, in 2000, the CTL added a new insulation test cryostat (now called Cryostat-200) to enable the thermal performance testing of bulk-fill materials. We needed a material to calibrate this instrument and naturally chose 3M K1 glass bubbles because of the important cryogenic-vacuum thermal data provided by the literature. Other manufacturers were also researched at that time and on-going for the next 5 years as work progressed. Products by two other companies, ThermaCell and Emerson & Cuming Composite Materials, were tested to a preliminary degree. However, these products were only available in limited quantities and were more expensive.

The next phase of the work was funded by a series of projects for NASA Stennis Space Center (SSC). The R&D continued with cryostat lab testing and small vacuum-jacketed tanks testing. All work was done using 3M K1 in comparison with perlite powder. In parallel, several NASA SBIR projects on different cryogenic-vacuum insulation projects were awarded to Technology Applications Inc. from 2001 to 2005. Again, the long list of publications shows that 3M K1 bubbles were used because of the technical pedigree, wide availability, large-scale production, and low cost.

In 2004, my team won major multi-year NASA IR&D funding from the Space Operations Mission Directorate with a project called *New Materials & Technologies for Cost-Efficient Cryogenic Storage & Transfer (CESAT)*. Our job was to prove out the glass bubbles system for large-scale spherical liquid hydrogen tanks. The return on investment and cost-benefit analysis was an essential component of the System Studies deliverable of the project. Again, other commercially available glass bubble products were examined from the market study aspect, but none were found to be suitable for consideration. The CESAT project culminated in late 2007 with the publication of several key technical articles. In parallel, R&D work was also being conducted for the Rocket Propulsion Test Program at NASA Stennis Space Center. All work was entirely centered on using 3M K1 glass bubbles as the bulk-fill material. In addition, an industry-based field demonstration was successfully completed on a vertical 6000-gallon cryogenic tank at Acme Cryogenics in Allentown, PA in 2005.

Following the success of the CESAT project, an industry partnership project among KSC, SSC, and 3M, and again led by the CTL, went forward in 2008. Field performance data and cost-effective retrofit of spherical LH2 tanks was the target. A perfect condition 50,000 gallon LH2 tank was selected, the perlite was removed, and 3M K1 glass bubbles were installed by the industry team provided by 3M. The glass bubbles installation process is shown in Figure 3. This field demo went on to enormous success as three complete thermal cycles were completed over a six-year period with no vacuum problems and an average 46% reduction in boiloff.

In the last decade, other laboratories and institutions around the world have tested the 3M K1 Glass Bubbles for different thermo-mechanical characterizations in cryogenic-vacuum applications. They are building on the work of the CryoTestLab as we built on the original work of Cunnington and Tien. The KSC-led work totals to about $6M investment over the 10 years from 1998 to 2008. All work was centered around and steadily building the technical database and practical field experience for the use of 3M K1 Glass Bubbles. Although there are many aspects of any such complex cryogenic-vacuum thermal insulation system, this product was a key part.

All along, from the 1970s work through the CTL work in the 2000s, the goal has been a cost-effective, reliable, and higher performance thermal insulation system compared to perlite powder. Perlite is inexpensive, but the total cost of a vacuum-jacketed thermal insulation system is very expensive no matter what filler is put into the annular space. Because 3M began large scale production decades ago, and for many other applications besides an insulation material, the low cost K1 product benefits from the economies of scale for common industrial uses. The goal of a higher performance, cost-effective bulk-fill vacuum insulation system has thus been met by the concerted effort of many people through millions of dollars of investment.

Glass bubbles thermal insulation data are now included in ASTM C1774 *Standard Guide for Thermal Performance Testing of Cryogenic Insulation Systems* for reference, calibration, and engineered applications in cryogenic systems.

Figure 3. Field demonstration in a 50,000-gallon LH2 storage sphere at NASA Stennis Space Center. Shown is the process of loading glass bubbles into the annular space of the vacuum-jacketed tank.

Development Timeline

Late 1950s – Hollow glass microspheres found floating in tanks of solid glass microsphere production

Early 1960s – first purpose- made hollow glass microspheres made at 3M Cottage Grove

Early 1970s – Glass Bubbles production starts at Guin, Alabama

Mid 1970s – Cryogenic research testing by G.R. Cunnington and C.L. Tien

Mid 1980s – 3M K Series Glass Bubbles production starts with K1 and other density/strength products

Late 1990s – Bulk delivery of 3M Glass Bubbles starts in nominal 2500 ft^3 pressure differential trailers

1998 Met P. Mueller of Utah State University at KSC meeting of Cryogenic Fluid Management team

1999 CryoTestLab proposal with P. Mueller for Mars application

2000 CryoTestLab meetings with ThermaCell and Cryostat-2 testing of material VXL-14

2001 NASA SBIR Phase I, *Evacuated Microsphere Insulation Panels*, Technology Applications Inc. (TAI)

2003 NASA SBIR Phase II, *Evacuated Microsphere Insulation Panels*, Technology Applications Inc. (TAI)

2003 Proposal to Rocket Propulsion Technology Development Board, NASA Stennis Space Center, *Glass Bubbles Retrofit of Perlite Insulated Cryogenic Storage Tanks*, January 2003

2003 *Comparison of Perlite and Glass Microsphere Insulation Using 10-liter Cryogenic Dewar Testing*, NASA/KSC Cryogenics Test Laboratory Test Summary Report #1, June 2003

2003 *Development of Thermal Insulation Systems for Cryogenic Storage Tanks Using Bulk—Fill Materials*, proposal to NASA Stennis Space Center, August 2003

2003 NASA/HQ Office of Space Flight (OSF) IR&D solicitation, November 2003 and Proposal, *New Materials & Technologies for Cost-Efficient Cryogenic Storage & Transfer (CESAT)* by NASA/KSC Cryogenics Test Laboratory

2003 NASA SBIR Phase I, *Cryogenic Propellant Insulation Project*, Technology Applications Inc. (TAI)

2004 *Cost-Efficient Storage and Transfer (CESAT)* proposal accepted in April, start of major NASA/HQ IR&D funded project

2004 Field demonstration of piping insulation panels at Complex 20 Liquid Nitrogen cryogenic loading system (TAI SBIR follow-on work in collaboration with NASA/KSC Cryogenics Test Laboratory)

2004 *Glass Microspheres for Retrofit of Perlite Insulated Cryogenic Storage Tanks, Phase I, Part 1*, NASA/KSC Cryogenics Test Laboratory Test Summary Report, April 2004, for NASA Stennis Space Center, National Rocket Propulsion Test Alliance, Rocket Propulsion Technology Mgt Board

2004 NASA SBIR Phase II, Cryogenic Propellant Insulation Project, Technology Applications Inc. (TAI)

2005 *Glass Microspheres for Retrofit of Perlite Insulated Cryogenic Storage Tanks, Phase I, Part 2*, NASA/KSC Cryogenics Test Laboratory Test Summary Report, June 2005, for NASA Stennis Space Center, National Rocket Propulsion Test Alliance, Rocket Propulsion Technology Mgt Board

2005 NASA/KSC Center Director's Discretionary Fund (CDDF) project, *Bulk-Fill Insulation Systems for Cryogenic Storage Tanks – Phase II*

2005 Field demonstration of 6000-gallon Liquid Nitrogen tank insulation system at Acme Cryogenics in Allentown, PA (TAI, SBIR).

2007 Completion of CESAT project and presentation of six papers at the Cryogenic Engineering Conference in Chattanooga, TN for publication in *Advances in Cryogenic Engineering*

2008 Field demonstration number one of a 50,000-gallon LH2 spherical tank insulation system at NASA/SSC, starting in September 2008.

2014 Completion of field demonstrations of NASA/SSC 50,000-gallon tank with three complete thermal cycles (three fill up and boiloff) over a six-year time period

2016 Study of implementation of glass bubbles insulation system in the vacuum annulus of the planned new 1,4000,000 gallon LH2 storage tank for NASA/KSC Launch Complex 39B with full technical acceptance obtained as part of engineering process

Selected Publications

1. Fesmire, J.E., “**Standardization in cryogenic insulation systems testing and performance data**,” Physics Procedia 67 (2015) 1089 – 1097.
2. Fesmire, J.E., Johnson, W.L., Meneghelli, B., and Coffman, B.E., “**Cylindrical boiloff calorimeters for testing of thermal insulations**,” IOP Conf. Series: Materials Science & Eng. 101 (2015).
3. *Sass, J.P. Johnson, Fesmire, J.E., Meneghelli, B., Carmouche, G., Obregon, R, and Hunter, R., “**Operational history of liquid hydrogen tank with glass bubbles insulation**,” Cryogenic Engineering Conference, Tucson, Arizona, July 2015 [presentation only]
4. Werlink, R.W., Fesmire, J.E., and Sass, J.P., "**Vibration Considerations for Cryogenic Tanks Using Glass Bubbles Insulation**," Advances in Cryogenic Engineering, AIP Conference Proceedings, Vol. 1434, pp. 265-272 (2012).
5. **Sass, J.P., Fesmire, J.E., St. Cyr, W.W., Lott, J.W., Barrett, T.M., Baumgartner, R.G., “**Glass bubbles insulation for liquid hydrogen storage tanks**,” *Advances in Cryogenic Engineering*, AIP Conference Proceedings, Vol. 1218, pp. 772-779 (2010).
6. Helenbrook, B., Powers, M., Shen, H., and Metzger, P. (2009). "**Continuum Modeling and Discrete Element Simulations of Elastic-Quasi-Static Granular Flow in a Compressing Slot**." J. Aerospace. Eng., 10.1061/(ASCE)0893-1321(2009)22:4(415), 415-422.
7. Fesmire, J., “**KSC Tests Glass Bubbles as Insulation**,” Cold Facts, Cryogenic Society of America, 2009, Vol. 25, No. 2, pp. 20-21, 35.
8. Scholtens, B.E., Fesmire, J.E., Sass, J.P., and Augustynowicz, S.D., “**Cryogenic thermal performance testing of bulk-fill and aerogel insulation materials**,” in Advances in Cryogenic Engineering, Vol. 53A, American Institute of Physics, New York, 2008, pp. 152-159.
9. ***Fesmire, J.E., Sass, J.P., Nagy, Z.F., Sojourner, S.J., Morris, D.L., and Augustynowicz, S.D., “**Cost-efficient storage of cryogens**,” in Advances in Cryogenic Engineering, Vol. 53B, American Institute of Physics, New York, 2008, pp. 1383-1391. ***
10. Sass, J.P., Fesmire, J.E., Nagy, Z.F., Sojourner, S.J., Morris, D.L. and Augustynowicz, S.D., “**Thermal performance comparison of glass microsphere and perlite insulation systems for**

liquid hydrogen storage tanks," in Advances in Cryogenic Engineering, Vol. 53B, American Institute of Physics, New York, 2008, pp. 1375-1382.

11. Majumdar, A.K., Steadman, T.E., Maroney, J.L., Sass, J.P., and Fesmire, J.E., "**Numerical modeling of propellant boil-off in a cryogenic storage tank**," in Advances in Cryogenic Engineering, Vol. 53B, American Institute of Physics, New York, 2008, pp. 1507-1514.
12. Fesmire, J.E., Morris, D.L., Augustynowicz, S.D., Nagy, Z.F., Sojourner, S.J., "**Vibration and thermal cycling effects on bulk-fill Insulation materials for cryogenic tanks**," in *Advances in Cryogenic Engineering*, Vol. 51B, American Institute of Physics, New York, 2006, pp. 1359-1366.
13. Baumgartner, R.G., Myers, E.A., Fesmire, J.E., Morris, D.L., Sokalski, E.R., "**Demonstration of microsphere insulation in cryogenic vessels**," in *Advances in Cryogenic Engineering*, Vol. 51B, American Institute of Physics, New York, 2006, pp. 1351-1358.
14. Allen, M.A., Baumgartner, R.G., Fesmire, J.E., and Augustynowicz, S.D., "**Advances in Microsphere Insulation Systems**," in *Advances in Cryogenic Engineering*, Vol. 49, American Institute of Physics, New York, 2004, pp. 619-626.
15. Fesmire, J.E., and Augustynowicz, S.D, "**Thermal Performance Testing of Glass Microspheres under Cryogenic-Vacuum Conditions**," in *Advances in Cryogenic Engineering*, Vol. 49, American Institute of Physics, New York, 2004, pp. 612-618.
16. Cunnington and Tien, "**Apparent Thermal Conductivity of Uncoated Microsphere Cryogenic Insulation**," *Advances in Cryogenic Engineering*, Vol. 22, Plenum Press, New York, 1977, pp. 263-270.

Key Technical Points from Publications

*Key point 1: Six years of testing of a 50,000-gallon spherical tank at Stennis Space Center. Three complete thermal cycles. Perlite baseline boiloff of LH2 was 386 liters/day. Perlite removed was in pristine condition and density for optimum thermal performance. Bubbles test 1 (2009) was 216 liters/day (44% reduction). Bubbles test 2 (2011-2013) was 208 liters/day (46% reduction). Bubbles test 3 (2015) was 201 liters/day (48% reduction). There were complete thermal cycles between the tests.

**Key point 2: Shipping of two identical VJ tanks, one with bubbles and one with perlite, from Ohio to Florida is described. The perlite tank compacted, the bubbles tank did not. Vibrational loads, such as from over the road transport to annular pipe chattering, generally serve to fluidize (fluff up) the bubbles rather than compact. Twenty-two complete thermal cycles performed on a 1000-liter spherical tank insulated with bubbles. There was zero bubble breakage (gas SO2) detected using an RGA instrument.

***Key point 3: Total system studies including bubble breakage, corrosion, oxygen compatibility, granular particle modeling, etc. For the 850,000-gallon LH2 tank, the maximum pressure on the bubbles at the bottom was calculated to be 3 psi. This was from the granular physics work we did with Clarkson University and Dr. Phil Metzger. The crush resistance is much greater than 10X (the onset of breakage was somewhere between 50 psi and 100 psi).

The thermal data below (Figure 4) are from tests using the Cryostat-100 insulation test instrument (see references 1 and 2 above for details). The data include thermal performance numbers for perlite powder, glass bubbles, and several different multilayer insulation (MLI) systems for general reference. The boundary temperatures are 78 K and 293 K; the residual gas is nitrogen. These data are absolute thermal data and are apples-to-apples in the practical sense. For engineering calculations, the heat flux numbers for a specific system design with specific shapes, thicknesses, and 20 K cold boundary temperature can be estimated using our design tool called TISCALC.

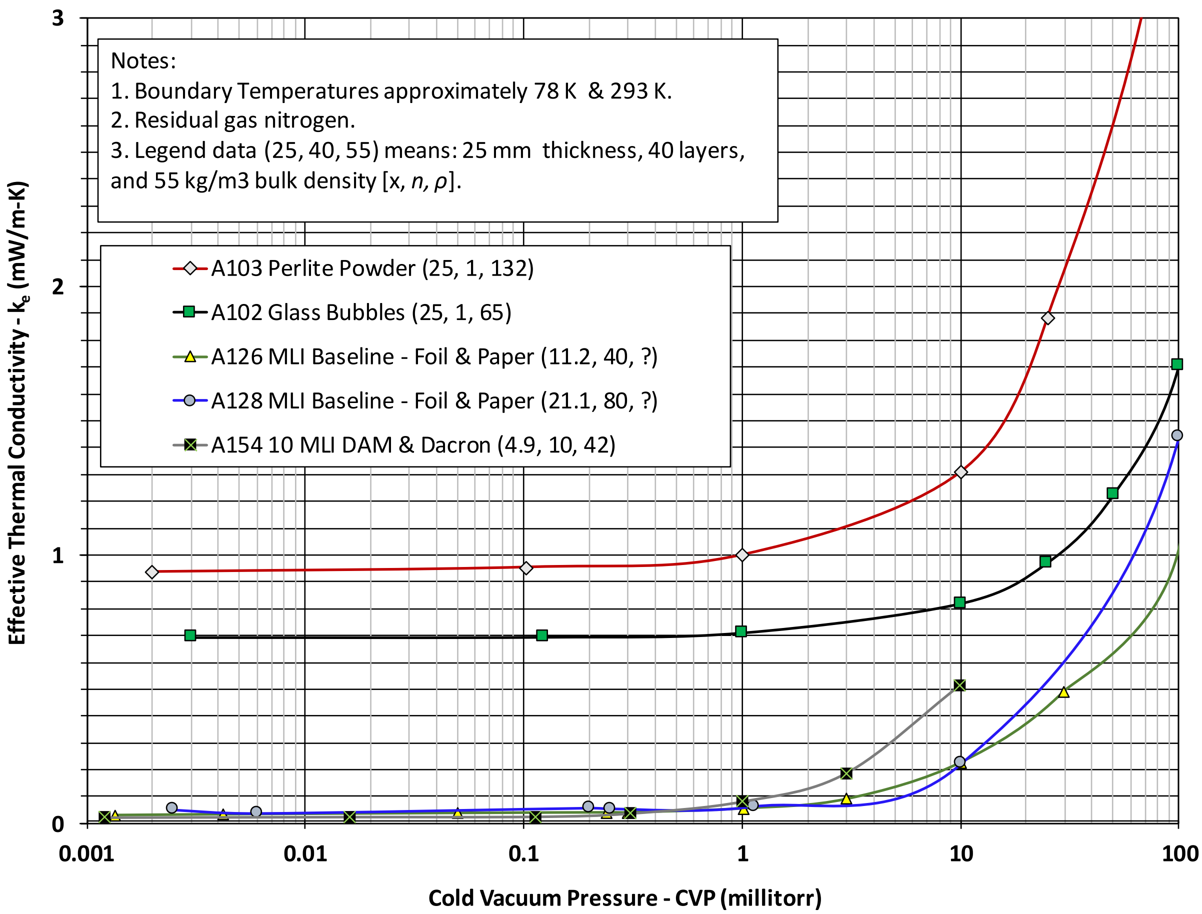

Figure 4. Effective thermal conductivity of perlite compared to bubbles under laboratory conditions using Cryostat-100. Bubbles are the lowest thermal conductivity for any evacuated bulk-fill material. Bubbles are also less sensitive to vacuum degradation compared to perlite.

Glass Bubbles Important Points

- Proven **46%** reduced LH2 boil-off over perlite in the field
  - Glass bubbles have been in-use in a 50,000-gallon sphere at SSC for 9 years (including three thermal cycles of tank)
  - About one half the bulk density of cryogenic grade perlite
- Bubbles do not break for application within annular space systems
  - Extensive crush testing was conducted, both isostatic and point-to-point
  - Based on 15 years of testing and development by numerous parties
  - Stored at 3M in a silo ~80 ft tall. Estimated "hydrostatic" crush head ~1500 ft
- Bubbles do not compact due to vibration or thermal cycling
  - Bulk product does settle after filling, but remains free-flowing under stress
  - 1000-liter spheres endured 20+ cycles in the lab, and SSC sphere has gone through numerous with no degradation
  - Settled bubbles out performed settled perlite by **51%** in lab tests.
- Better real-world vacuum level observed
  - 10 millitorr vs. 34 millitorr witnessed on the SSC tank
- Bulk supply is no issue, per the 3M representative
  - Delivery and offloading from standard tanker trailers

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