U.S. DEPARTMENT OF
ENERGY

Office of
ENERGY EFFICIENCY &
RENEWABLE ENERGY

Thermodynamic and Economic Modeling of Boil-off Losses in Liquid Hydrogen Handling Processes

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Fuel Cell Technologies Office Webinar

June 26, 2018

Question and Answer

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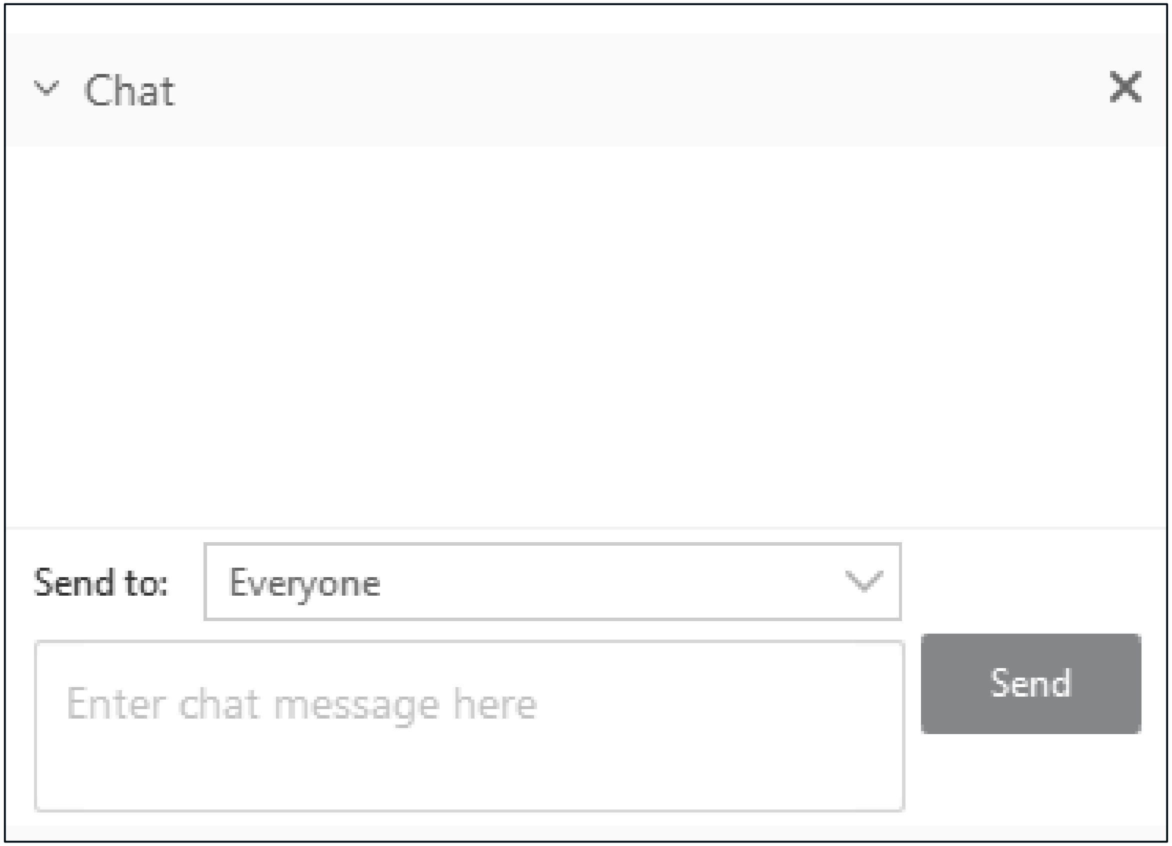


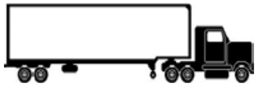
Liquid hydrogen (LH2) has many benefits for the hydrogen infrastructure

Over 14,000 FC forklifts deployed.
Most of them LH_2 supplied

Photo credit: Linde

Photo credit: AC Transit

AC transit owns the largest FC bus fleet in the world and rely on 2 LH_2 based HRS



4,300 kg H_2
capacity
$167/kg
LH_2

800 kg H_2
capacity
$783/kg
350 bar,
composite

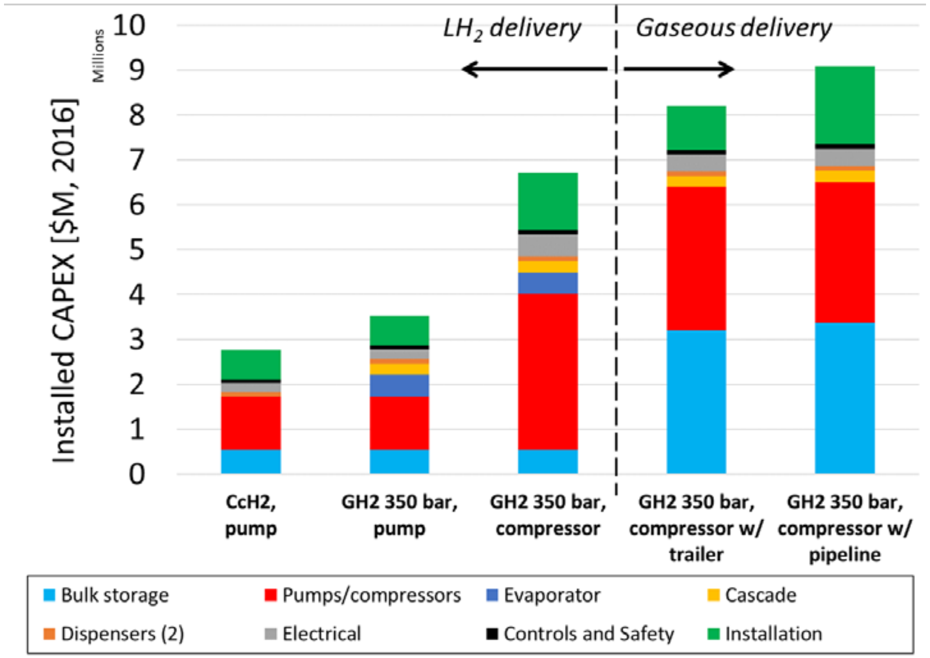
250 kg H_2
capacity
$1000/kg
190 bar, steel

From Reddi *et al*, 2015

Liquid hydrogen (LH2) has many benefits for the hydrogen infrastructure, especially at large scale(s)

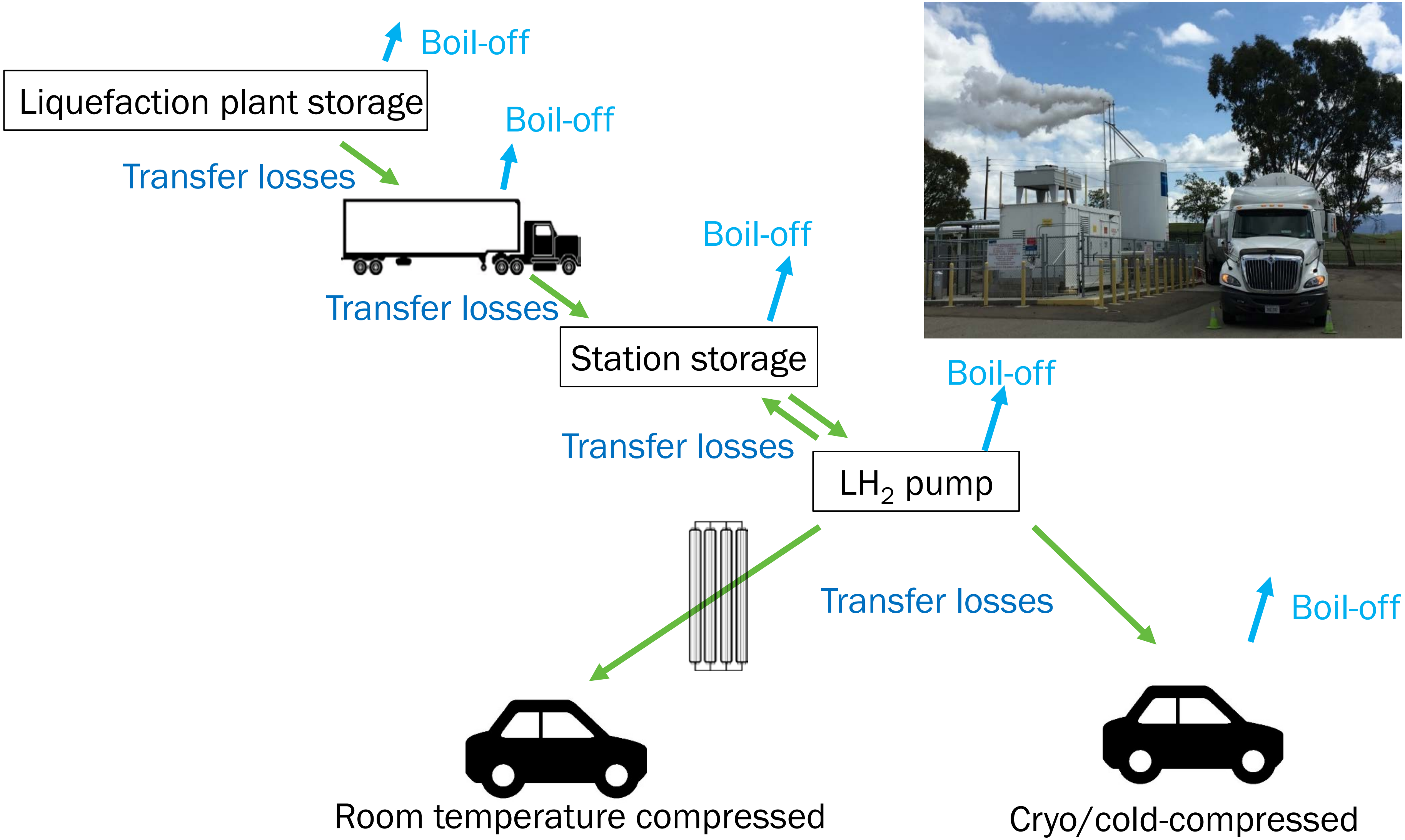
- High density LH_2 allows *minimum* footprint and cost
- High capacity per truck & short transfer times *minimize* delivery logistics/scheduling
- *Low* potential burst energy: 20 K and <6 bar vs. 300 K and >200 bar
- LH_2 pumps provide *high* throughputs at *low* dispensing costs
- High density of LH_2 can be transferred to compact onboard solutions (cryo/cold)

Comparison with 350 bar dispensed to vehicles



- Cost projections from ANL (HDSAM)
- Station designed for 80 trucks or buses per day, 50 kg capacity each (**4,000 kg/day**)
- Assumes high volume production
- Pipeline has high transmission costs ($500k-$1m per mile)

Transfer and boil-off losses can occur all along the LH2 pathway



Boil-off

Liquefaction plant storage

Boil-off

Transfer losses

Boil-off

Transfer losses

Station storage

Boil-off

Transfer losses

LH_2 pump

Transfer losses

Boil-off

Room temperature compressed

Cryo/cold-compressed

Boil-off along LH_2 pathway needs to be better understood

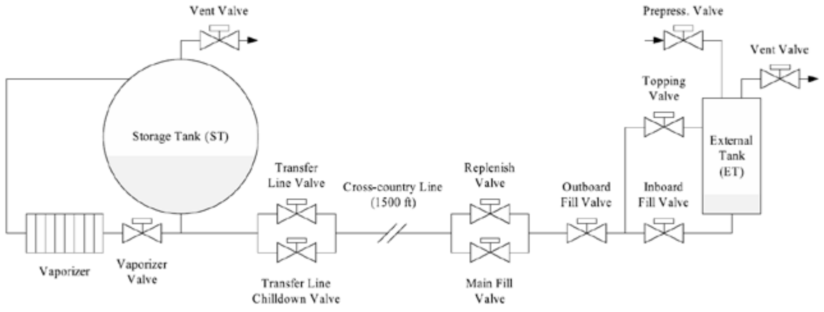
Overview of the presentation

1. Early-stage R&D to develop a thermodynamic model that simulates liquid hydrogen transfers, accounting for real gas equation of states and 2-phase behavior,
2. Analysis of current liquid hydrogen handling practices and requirements of U.S. Department of Transportation regulations,
3. Collection of data on boil-off rates at a fueling facility at LLNL
4. Predictions of boil-off losses for given station designs and capacities

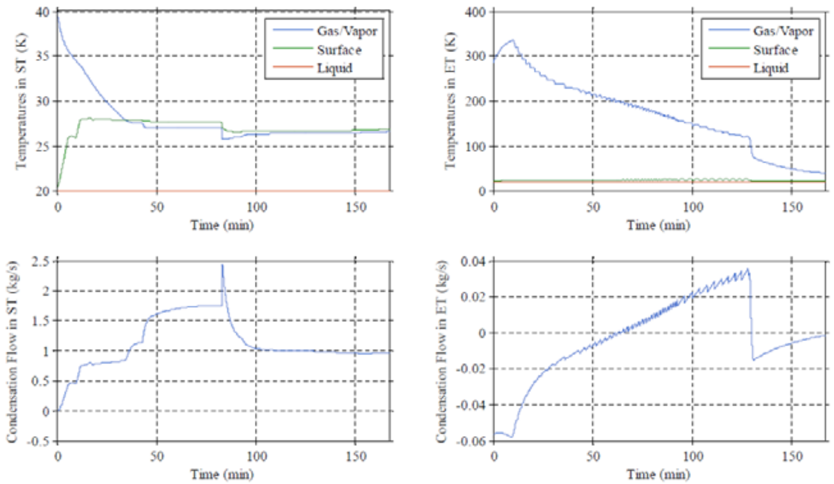
Modeling entire LH_2 pathway enables quantitative understanding

Thermodynamic Model

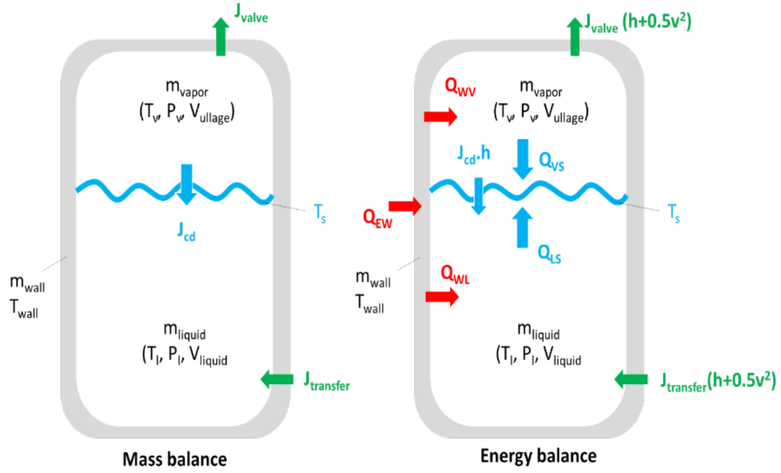
Simulate H2 losses using existing NASA code initially written for rocket loading with LH2



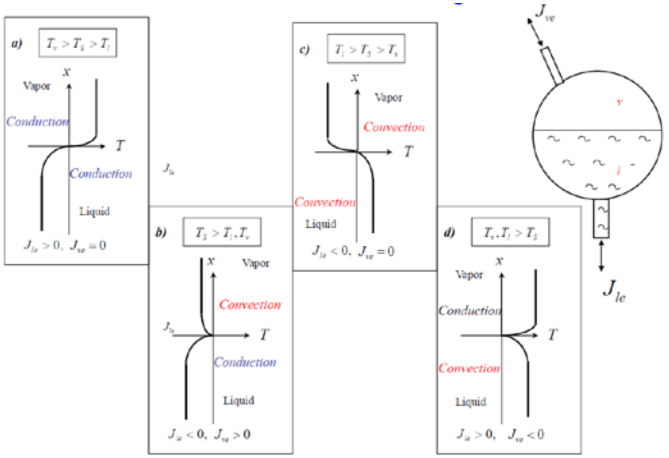
From Osipov and Daigle, 2011



Interaction between two LH_2 volumes and dynamic effects



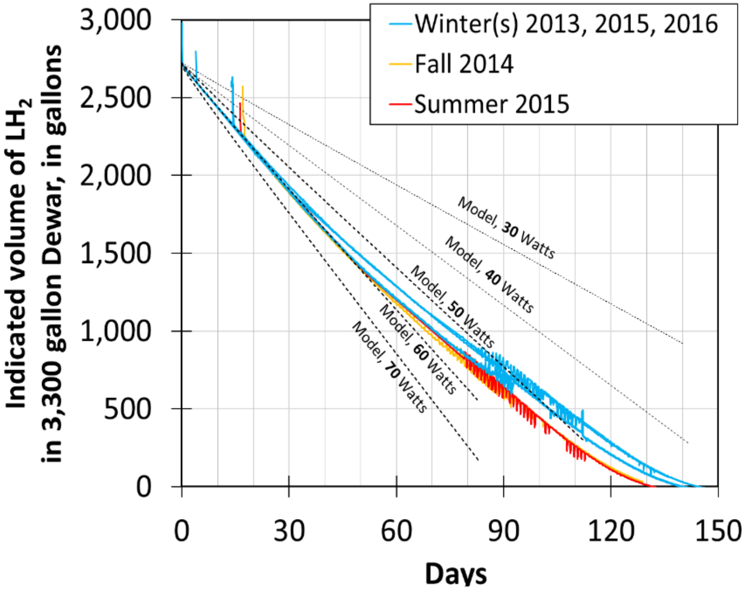
Condensation/evaporation, energy balance

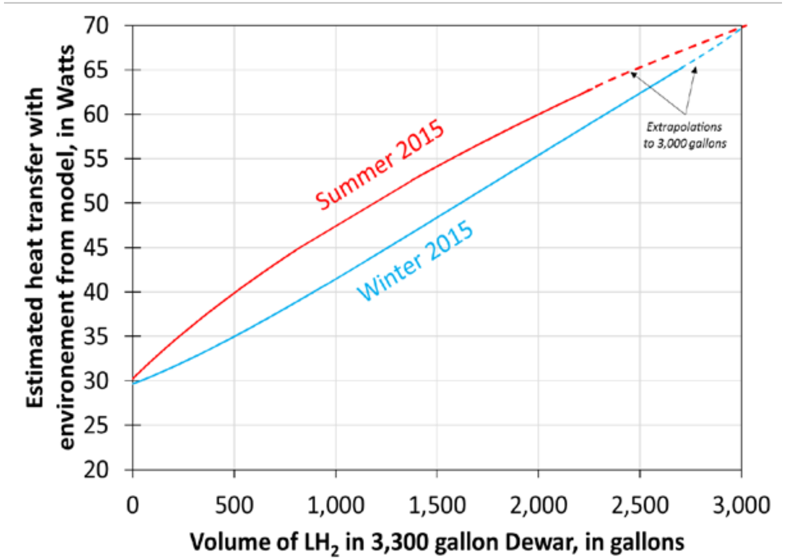


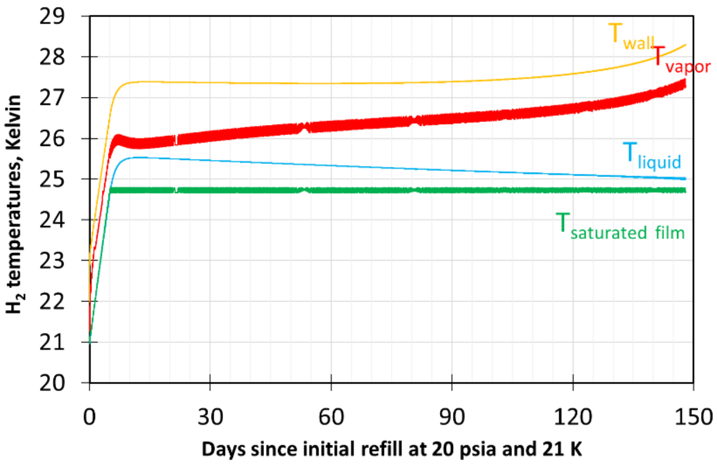
Heat transfer modes with saturated film

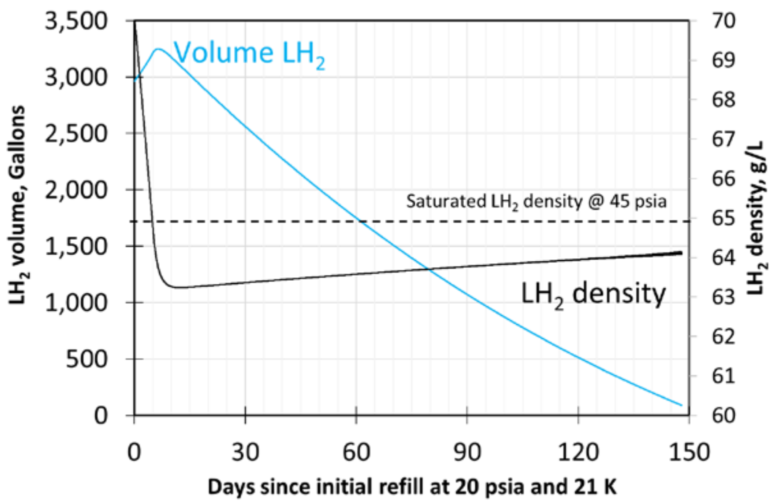
Existing code from NASA provides framework for LH_2 transfer analysis

Early-stage R&D to Develop Model for heat entry only to 3,300 gallon vessel



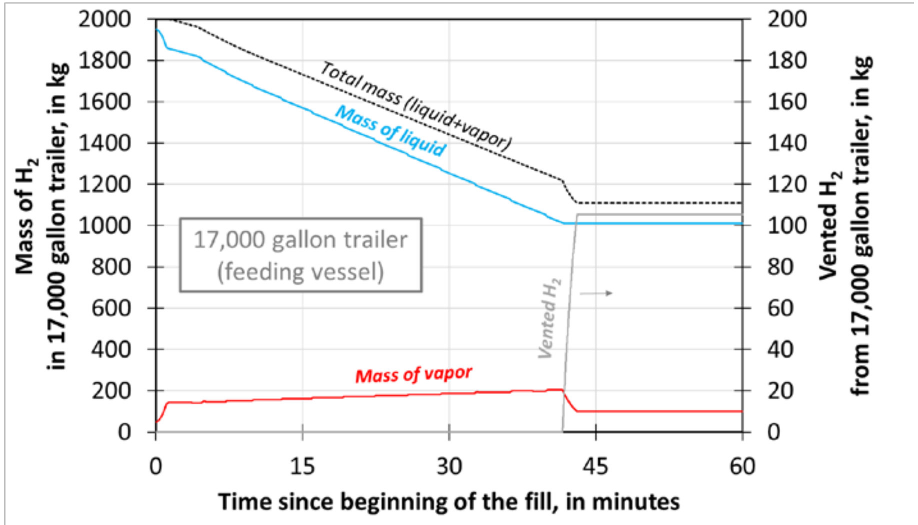


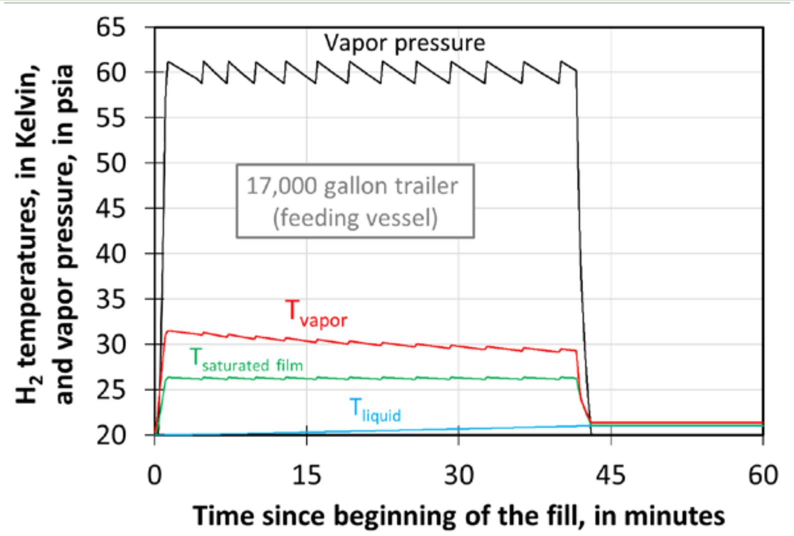


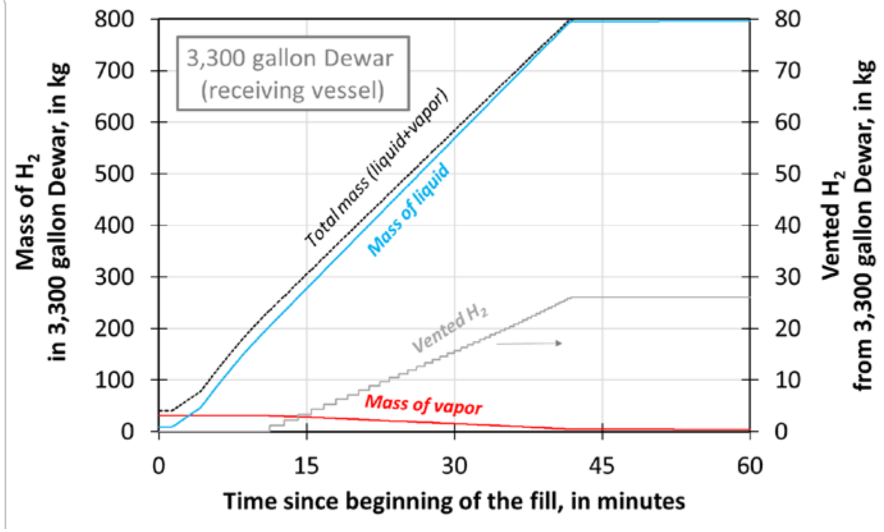


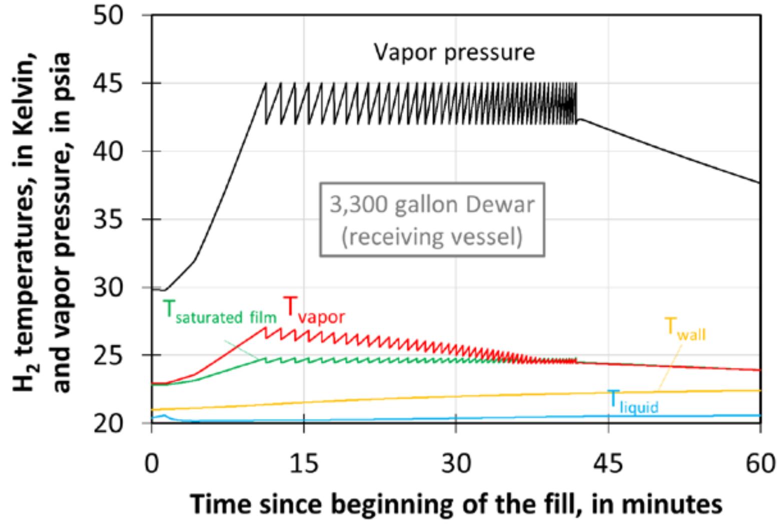
Model enables estimates of heat transfer profile & LH$_2$ density

Model results for liquid transfer from LH2 trailer to stationary vessel (bottom fill)



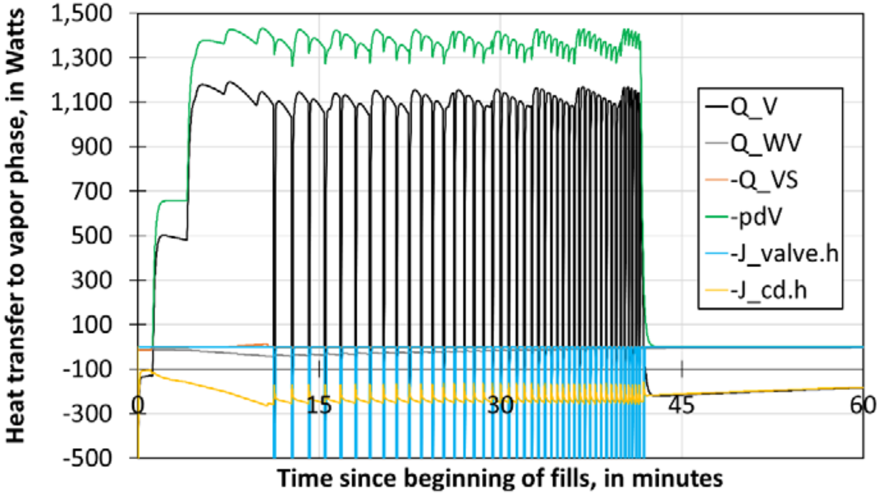


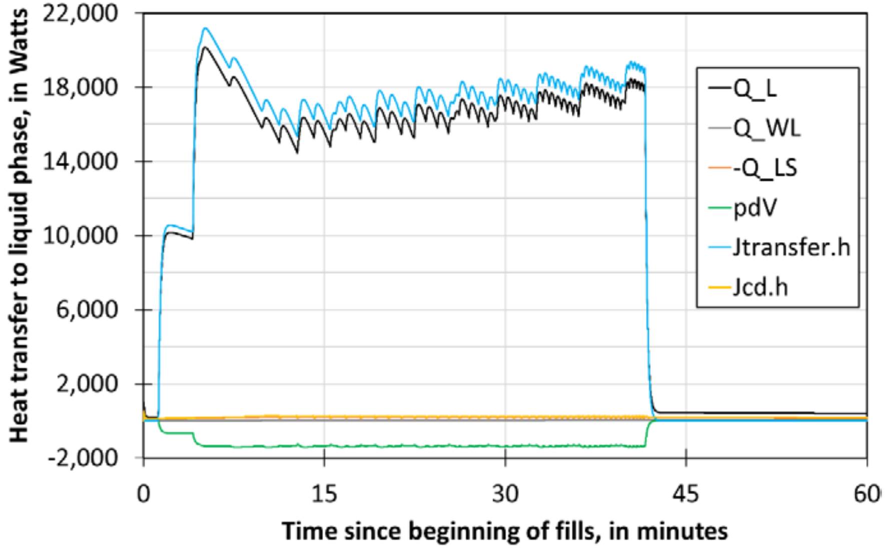


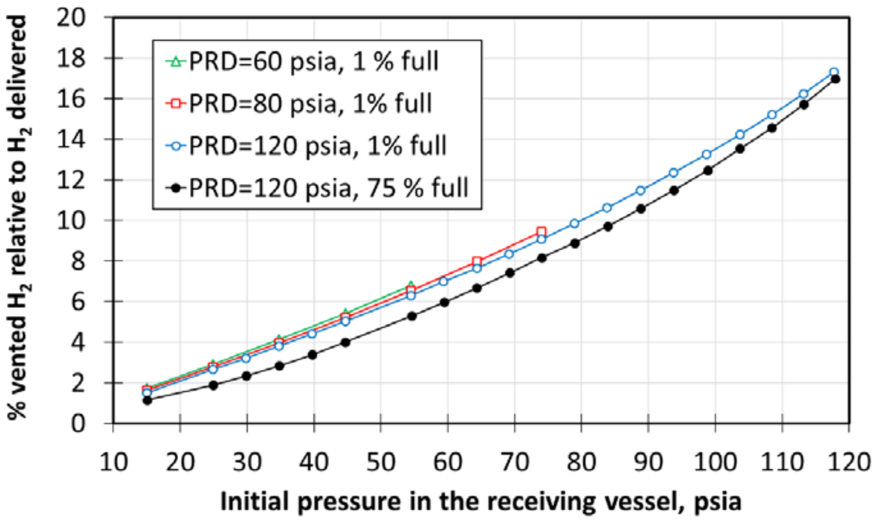


Model enables estimates of temperature and loss variations

Losses during transfer: bottom fill



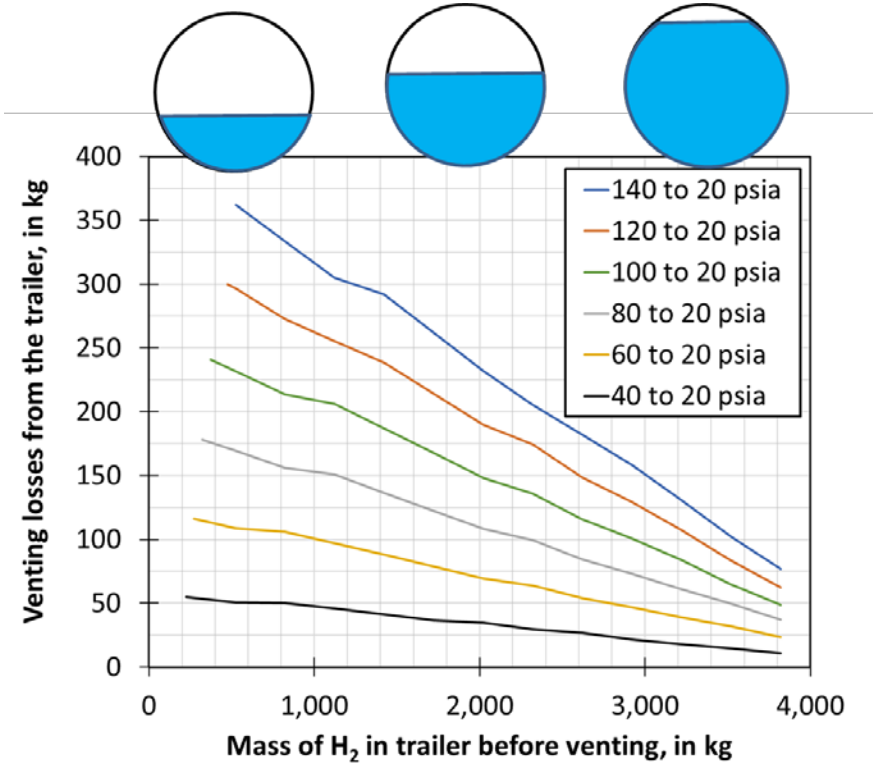




Transfer losses for bottom fill due to “pdV”.
Very sensitive to initial pressure in receiving vessel

Current Practices and DOT Regulations

Venting from LH2 trailer at end-of-fill



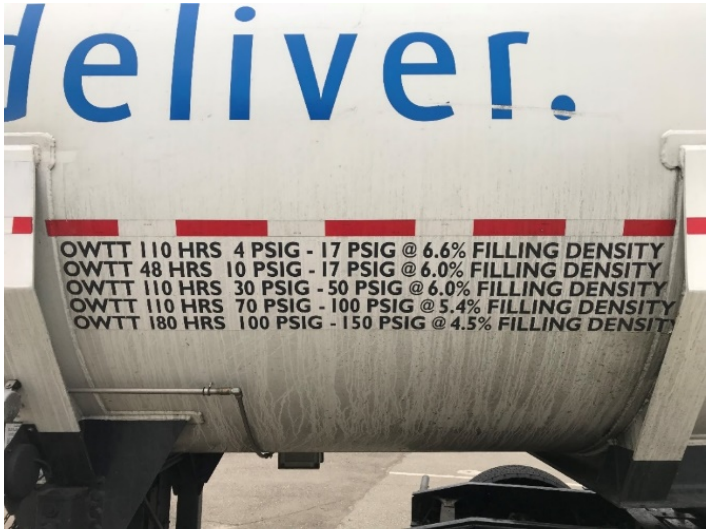
Results from model

Why is the trailer vented ?

What does the CFR say ?

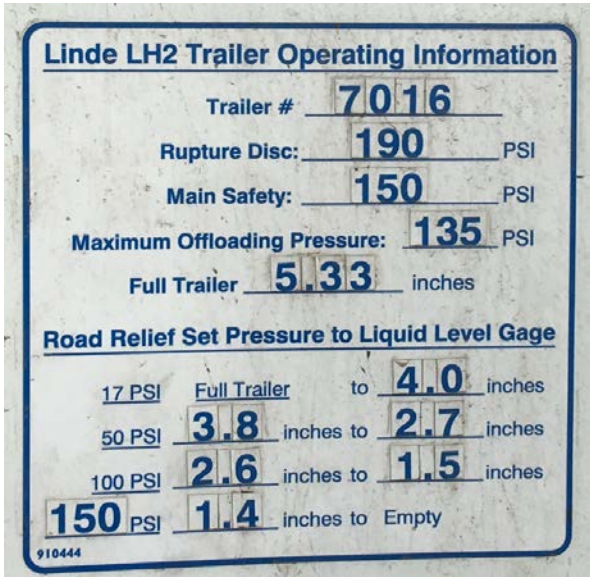
Title 49, Volume 2, Subtitle B, Chapter I, Subchapter A, part 177 stipulates that:

> *§177.840(i)* No person may transport a Division 2.1 (flammable gas) material that is a cryogenic liquid in a cargo tank motor vehicle unless the pressure of the lading is equal to or less than that used to determine the marked rated holding time (MRHT) and the one-way travel time (OWTT), marked on the cargo tank in conformance with §173.318(g) of this subchapter, is equal to or greater than the elapsed time between the start and termination of travel. This prohibition does not apply if, prior to expiration of the OWTT, the cargo tank is brought to full equilibration as specified in paragraph (j) of this section.



OWTT 110 HRS 4 PSIG - 17 PSIG @ 6.6% FILLING DENSITY
OWTT 48 HRS 10 PSIG - 17 PSIG @ 6.0% FILLING DENSITY
OWTT 110 HRS 30 PSIG - 50 PSIG @ 6.0% FILLING DENSITY
OWTT 110 HRS 70 PSIG - 100 PSIG @ 5.4% FILLING DENSITY
OWTT 180 HRS 100 PSIG - 150 PSIG @ 4.5% FILLING DENSIT

Pictures of Linde LH_2 trailer



Linde LH2 Trailer Operating Information

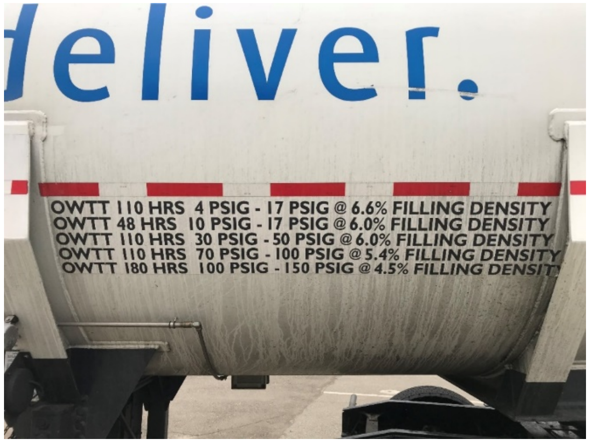
Trailer # 7016
Rupture Disc: 190 PSI
Main Safety: 150 PSI
Maximum Offloading Pressure: 135 PSI
Full Trailer 5.33 inches

Road Relief Set Pressure to Liquid Level Gage

17 PSI Full Trailer to 4.0 inches
50 PSI 3.8 inches to 2.7 inches
100 PSI 2.6 inches to 1.5 inches
150 PSI 1.4 inches to Empty

910444

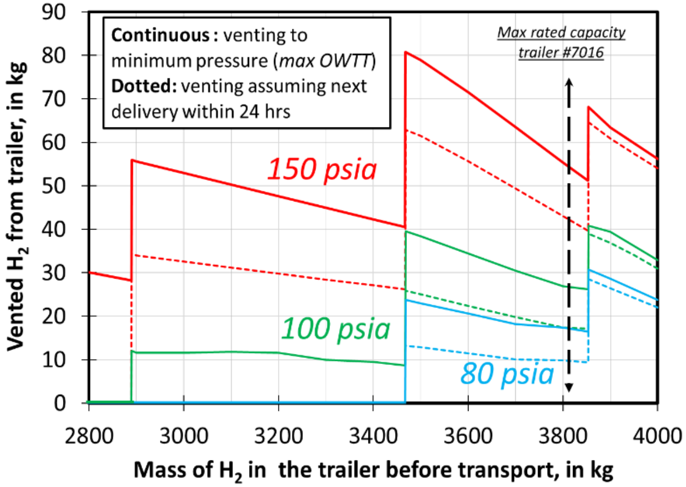
Analysis of Code of Federal Regulations shows that minimal to no venting from trailer is necessary.



Picture of Linde LH_2 trailer (side)

CFR title 49 §177.840(i) stipulates that maximum <u>required</u> on-road pressure is a function of time until next delivery, which depends on vapor pressure and LH_2 level.

Therefore, if travel time is short enough *or* pressure is low enough *or* LH_2 level is low enough, **NO** venting is necessary.



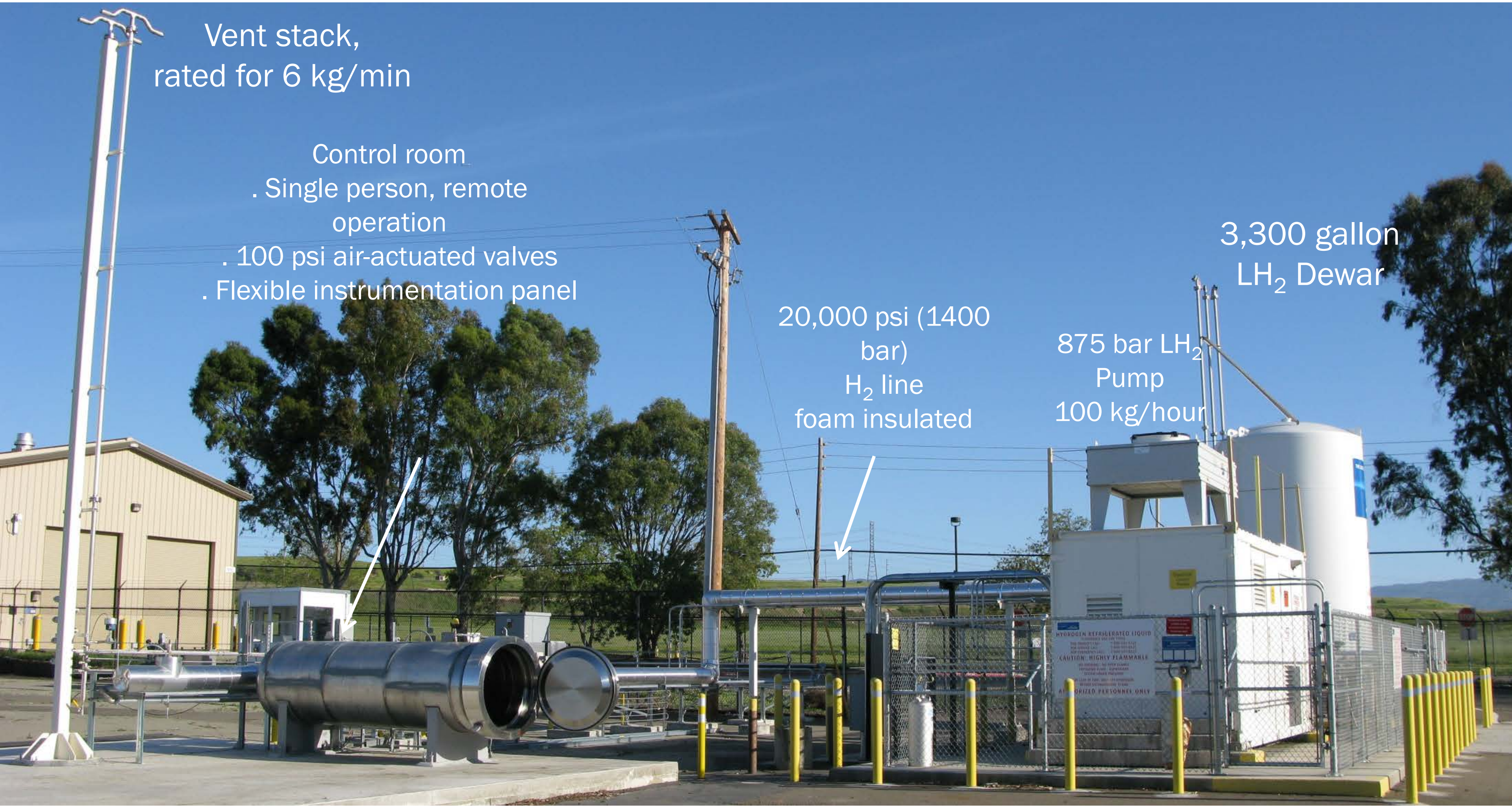
For a system operating at up 80 psia (typically, LH_2 pump), no venting is required most of the time, per code

For a system operating at larger pressure (typically, compressors), a maximum of 10 kg venting may be needed if trailer delivers a small load when full.

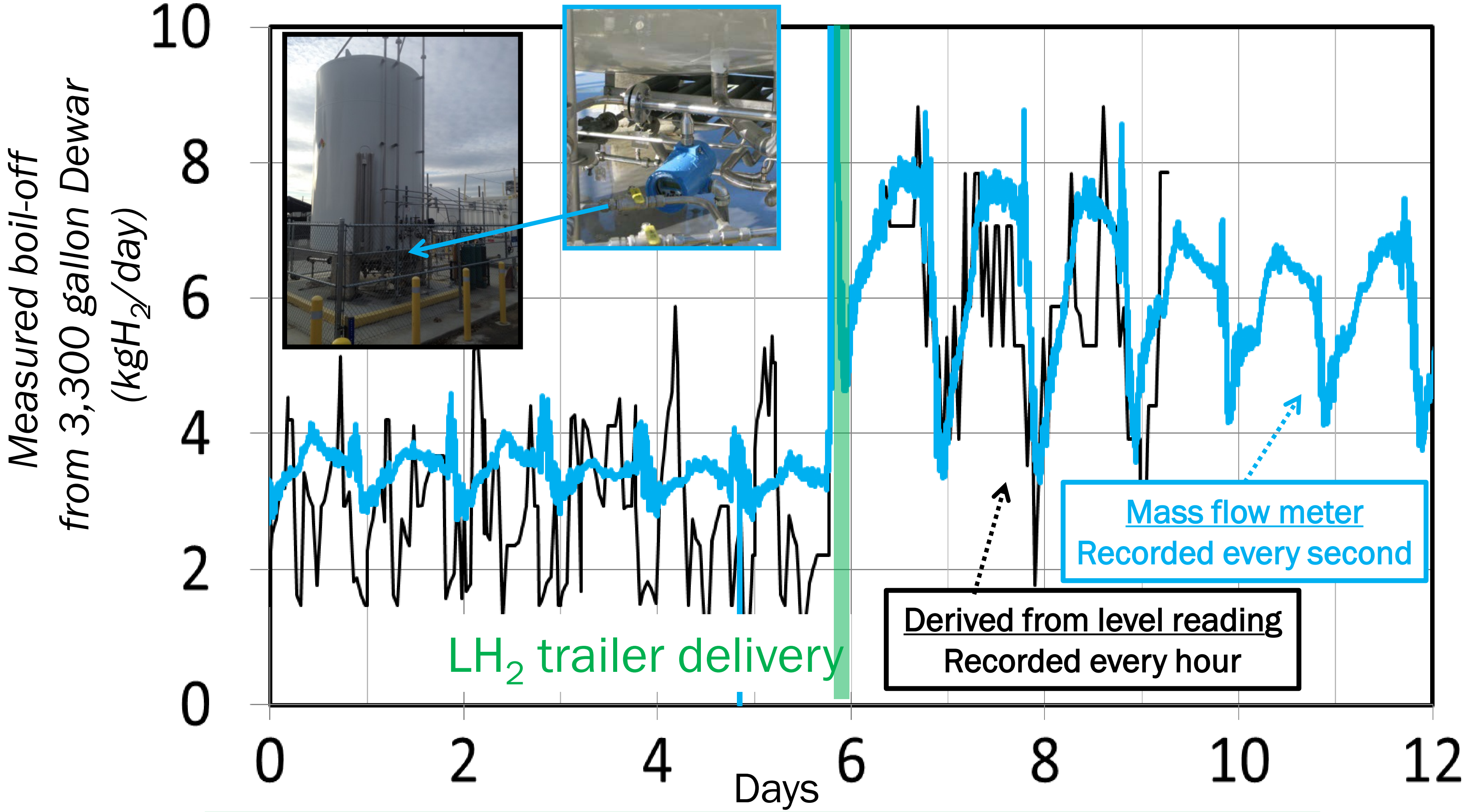
If <24 hours between 2 LH_2 deliveries, and > 350 kg is delivered at up to 80 psia, NO venting necessary

Data Collection at LLNL to Inform Early-stage R&D in Boil-off Mitigation

LLNL owns a test facility for rapid cryogenic H_2 cycling within 3 m^3, 65 bar containment using 875 bar LH_2 pump

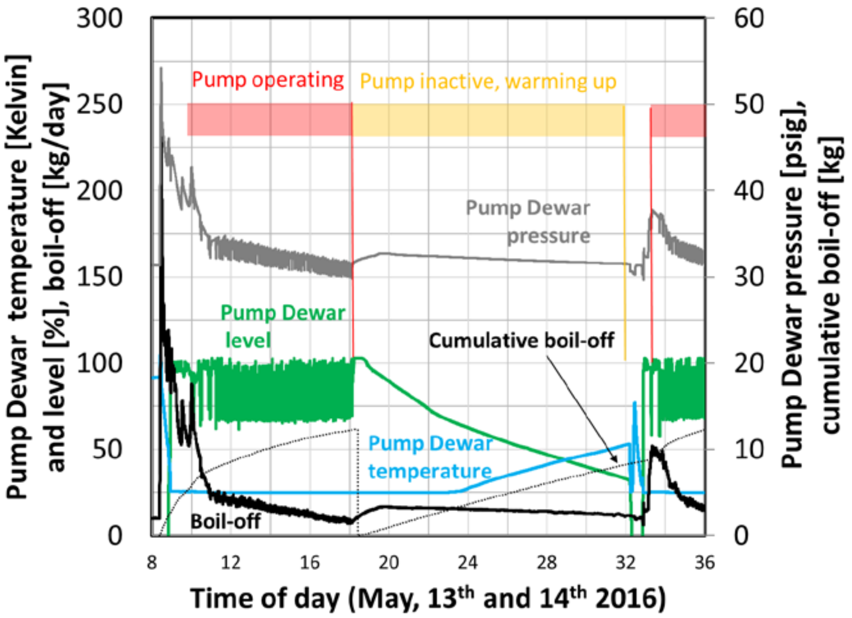


Boil-off flow meter installed on 3,300 gallon Dewar

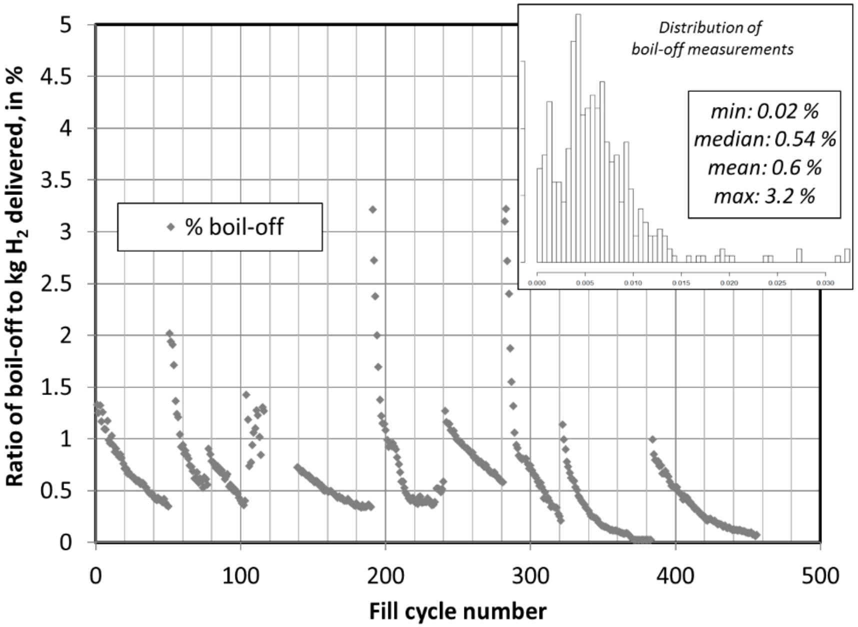


Directly measuring evaporation is more accurate than inferred evaporation from LH_2 level changes

Measurements of boil-off losses of ENTIRE system (Dewar + pump) during pump utilization



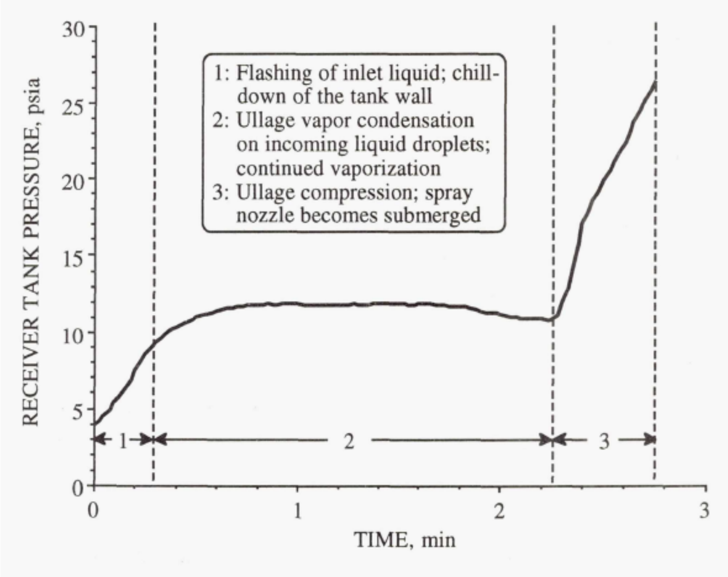
Pump warming up overnight
(~8 kg lost over 16 hours)



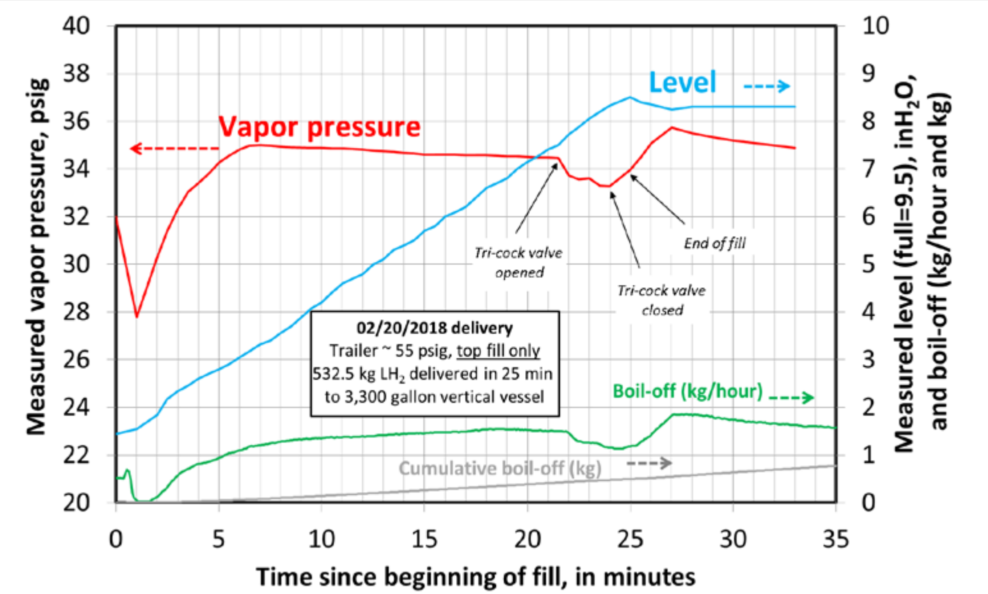
Dispensing to 700 bar at ~100 kg/hour
(peak: 3 kg/hr, average: 0.6 kg/hr)

Boil-off losses during pump utilization can be precisely measured

Top filling a LH2 vessel enables minimal boil-off losses from receiving vessel during transfer



Results from NASA LRC (Ohio), Moran and Chato



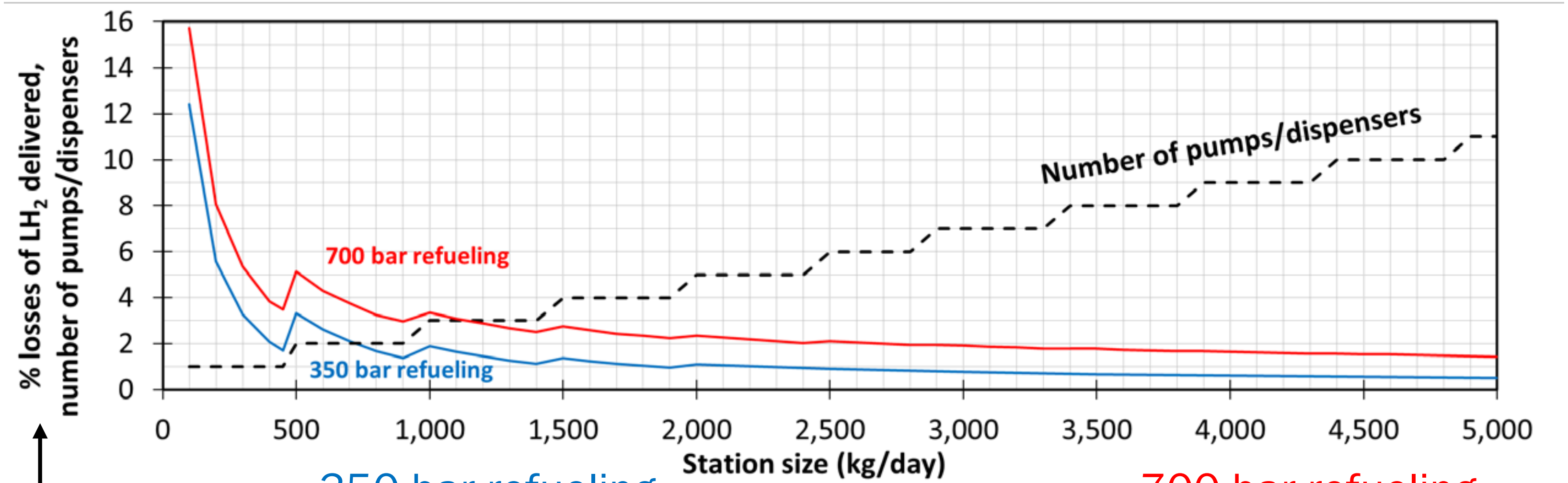
02/20/2018 delivery
Trailer ~ 55 psig, top fill only
532.5 kg LH_2 delivered in 25 min
to 3,300 gallon vertical vessel

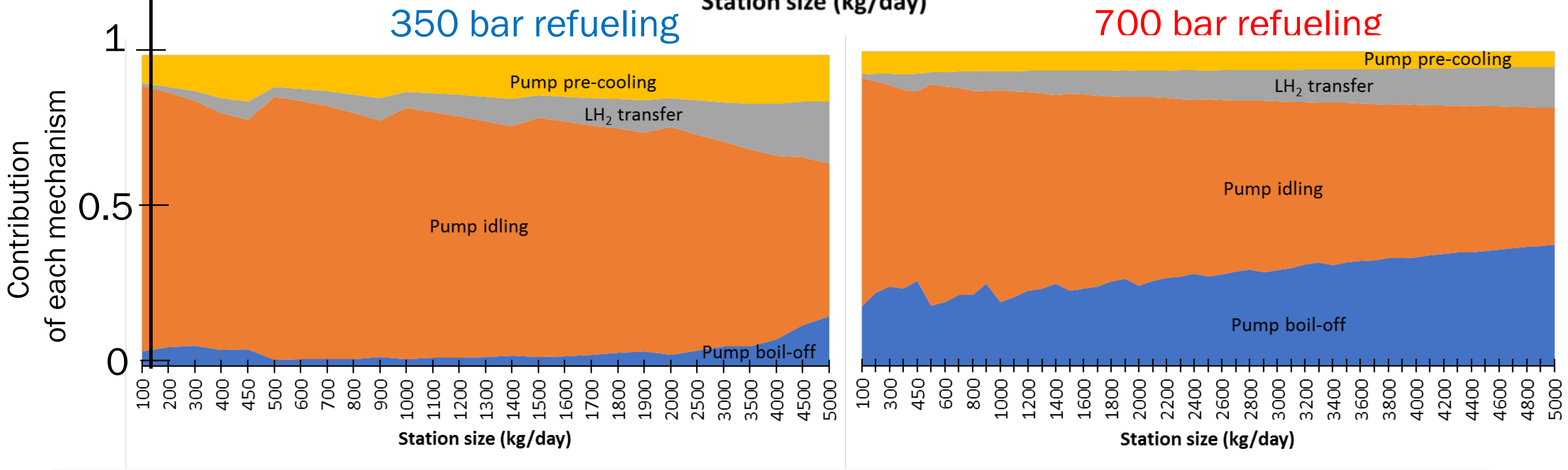
Experimental measurements from LLNL

Using top fill only, less than 1 kg of boil-off for a 532 kg LH_2 delivery over 25 minutes was measured (2 kg/hr peak boil-off flow)

Prediction of boil-off at a station

Boil-off loss budget for LH2 Operations

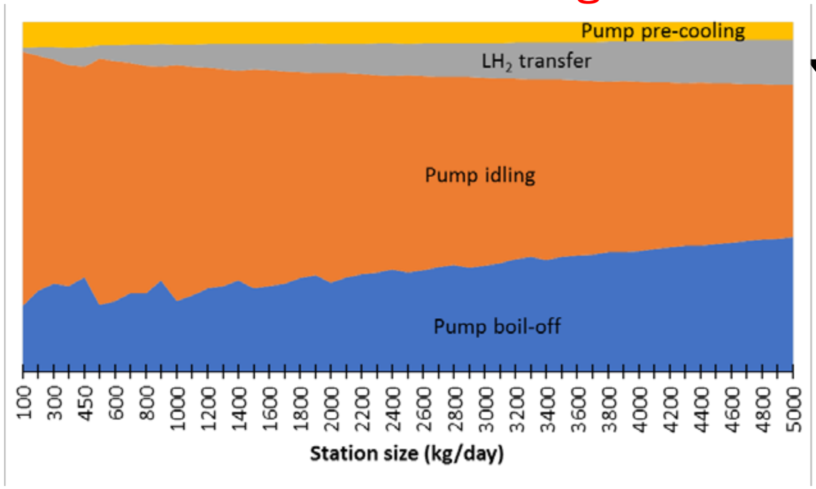




Less than **2%** boil-off losses
for {>2,500 kg/day, 700 bar} and {>1,000 kg/day, 350 bar} HRS

Mitigation & boil-off recovery approaches

700 bar refueling



Peak: 0.8 kg/hr, **Mean:** 0.5 kg/hr

Peak: 3 kg/hr, **Mean:** 0.6 kg/hr

Peak: 2 kg/hr, **Mean:** 0.5 kg/hr

Peak: 2 kg/hr, **Mean:** 1 kg/hr

- Better cryogenic design would certainly help reducing first 3 boil-off mechanisms. For example, LH_2 pump is located about 10 meters from main vessel at LLNL
- Better models may help understanding the influence of initial conditions on top fill performance, ultimately reducing LH_2 transfer losses
- If losses can not be further reduced, boil-off recovery solutions may be needed

2-3 kg/hr *peak* venting flow rate needs to be captured for routine LH_2 operations, based on measurements at sub-optimal LLNL setup

Considerations for boil-off recovery approaches…

- Various technologies can be used to recover boil-off losses:

Compressors	**Cryo-coolers**	**Fuel Cell**	**Flaring ?**
(mechanical, electro-chemical, metal hydride)	(Stirling, Gifford-McMahon, pulse-tube)	(net metering, local power provider)	(catalytic burner, …)

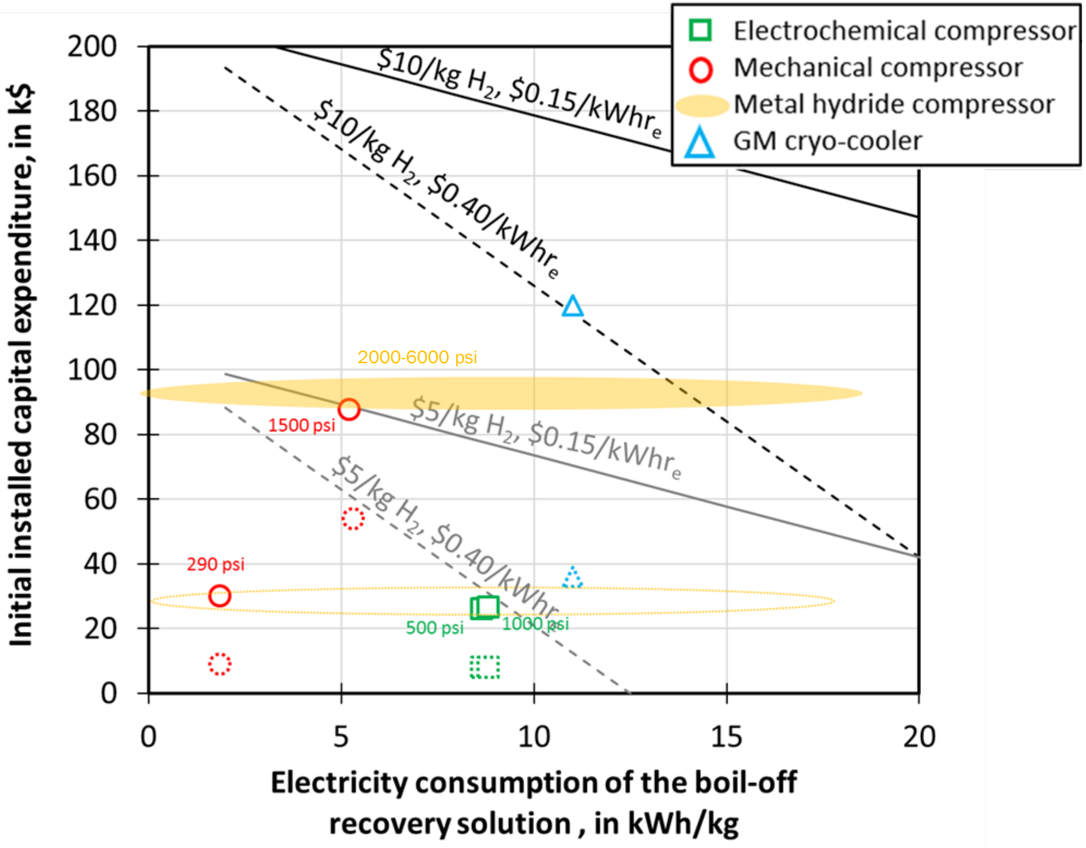
- To make sure all boil-off is captured, the solution should be sized for peak flow (2-3 kg/hr), even if it would operate at a lower nominal value (0.6 kg/hr) most of the time…

- What to do with recovered H_2 ?

Feed cascade, if cascade is present…
10 to 60 kg of boil-off may be recovered every day. 1 typical industrial gas bottle holds 0.5 kg H_2

- Recovery makes economic sense only if the associated costs (CAPEX+OPEX) are lower than the cost of the recovered H_2…
- The value of recovery may also lie in easing station permitting

Economics analysis of boil-off recovery options



Continuous symbols: 2 kg/hr, Dashed: 0.6 kg/hr

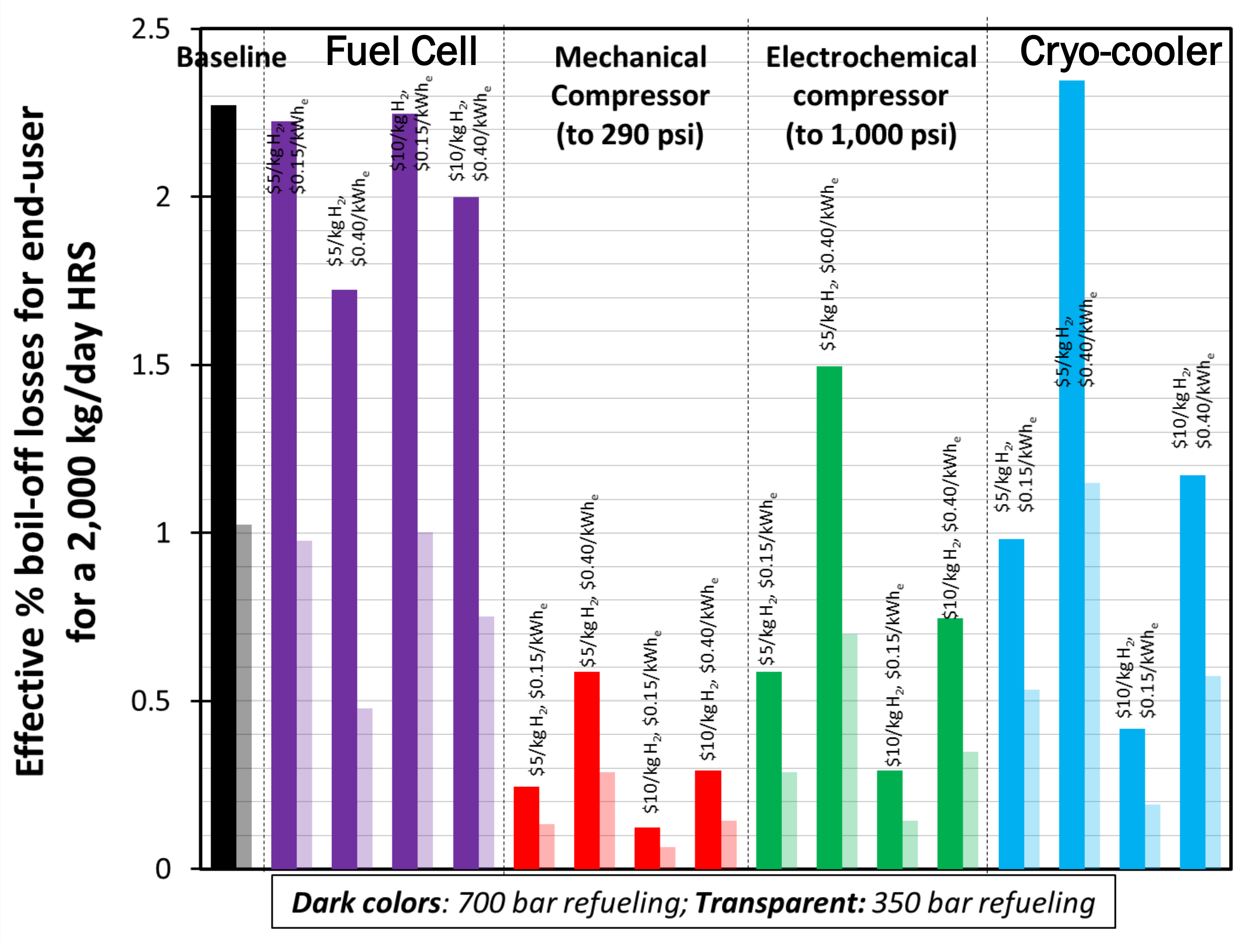
Assumes 5 year pay-back

- All solutions assume recovered H_2 is ultimately sold, at $5 or $10/kg.
- For compressors, H_2 could be stored to cascade, in trailer or gas bottles (cost not included in calculations)
- For GM cryo-cooler, vapor H_2 is re-condensed
- Metal-hydride compressors do not use electricity but heat. Also, not well developed for application (more R&D needed to refine costs)

Note: “value” of boil-off recovery solution should be analyzed on a case-per-case basis. Other factors include: footprint, permitting, outlet for gas resale, noise, vibrations, connection to grid…

Mechanical and electrochemical compressors seem to make most economical sense, although other factors should be considered

Boil-off recovery options would enable lower effective boil-off



<u>Assumptions:</u>

- Only expenses: electricity & maintenance (5% CAPEX/yr)
- Effective boil-off assumes all H_2 is captured and sold (except for FC)
- Additional expenses are expressed on a kgH_2 basis

Note: “value” of boil-off recovery solution should be analyzed on a case-per-case basis. Other factors include: footprint, permitting, outlet for gas resale, noise, vibrations, connection to grid…

Boil-off recovery solutions may reduce extra cost to end-user, from **2.2%** to less than **1%** (at 700 bar)

Collaborations with Industry Leaders

- **Linde:** Very cooperative, sharing detailed information, interpreting and sharing data from multiple pumps, and on LH_2 deliveries.

Special acknowledgements to Martin Bruecklmeier, Wilfried Reese, Kyle McKeown, Erik Tudbury.

- **Praxair:** Sharing data on LH_2 plant operation. Visit of Ontario (CA) plant.

Special acknowledgement to Al Burgunder.

Risks/Challenges for FY18 milestones, Future work

- *Challenge: need adequate simulation tool for top fill*
  - **Challenge**: our 0D thermodynamic simulation framework can not capture the underlying physics of sprays (boiling heat transfer, droplets interaction...
  - **Solutions** : In the future (beyond scope), a full CFD code should be used, similar to the work performed by Yanzhong Li and Lei Wang from the Xi'an Jiaotong University (Xi'an, China) and the State Key Laboratory of Technologies in Space Cryogenic Propellants (Beijing, China)
- *Future work up to end of FY18*
  - Publish reports and articles at IJHE
  - Already published:

5 page memo on how DOT regulations apply to trailer venting: https://www.osti.gov/biblio/1424618

2 codes released as open-source: https://github.com/LLNL/LH2Transfer, https://github.com/LLNL/cryoH2vehicle

Concluding remarks on minimizing boil-off

- *On-road boil-off from LH_2 trailer is negligible*
- *Follow CFR requirements applicable to venting at LH_2 station*

  In most, if not all, scenarios for H_2 as a fuel: >350 kg-H_2 will be delivered during first fill of full load, < 24 hrs between 2 deliveries, and <110 psia head pressure

- *Use top fill when delivering from trailer to station storage*

  This may be limited by the required minimum pressure for compressor/pump

- *Make sure station design matches actual demand*

  System idling may cause significant losses, although latest designs exhibit much lower sensitivity to idling

- *"Intrinsic" boil-off may be mitigated using compressors, FC, or cooler*

  The value of a such a solution will depend on cost, access to local gas merchant market, footprint/setback distance requirements.

LLNL has developed models to simulate boil-off losses from plant to car for LH2 pathway, quantified their magnitude & proposed mitigation solutions

Relevance	LH_2 has great benefits for large scale(s) hydrogen deployment (cost, logistics, safety…) Better understanding of losses is necessary
Approach	Simulate losses mechanisms along the LH2 pathway using real gas EOS and 2 phases, data collection at LH2 facility
Progress	Quantified losses along ENTIRE pathway, including from CcH2 vehicle (<2% up to dispensing for large stations, 0 to 5% for 99% of drivers, 0.25% of hydrogen consumed is boiled away through driving) Identified potential to reduce/eliminate losses from trailer Identified main contributors to losses (high P in Dewar, pump) Analyzed techno-economics of boil-off recovery technologies
Future work	Publish 1 report (60+ pages) and 2 papers (IJHE) Develop CFD capabilities for modeling top-fill (beyond scope of the project)

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Question and Answer

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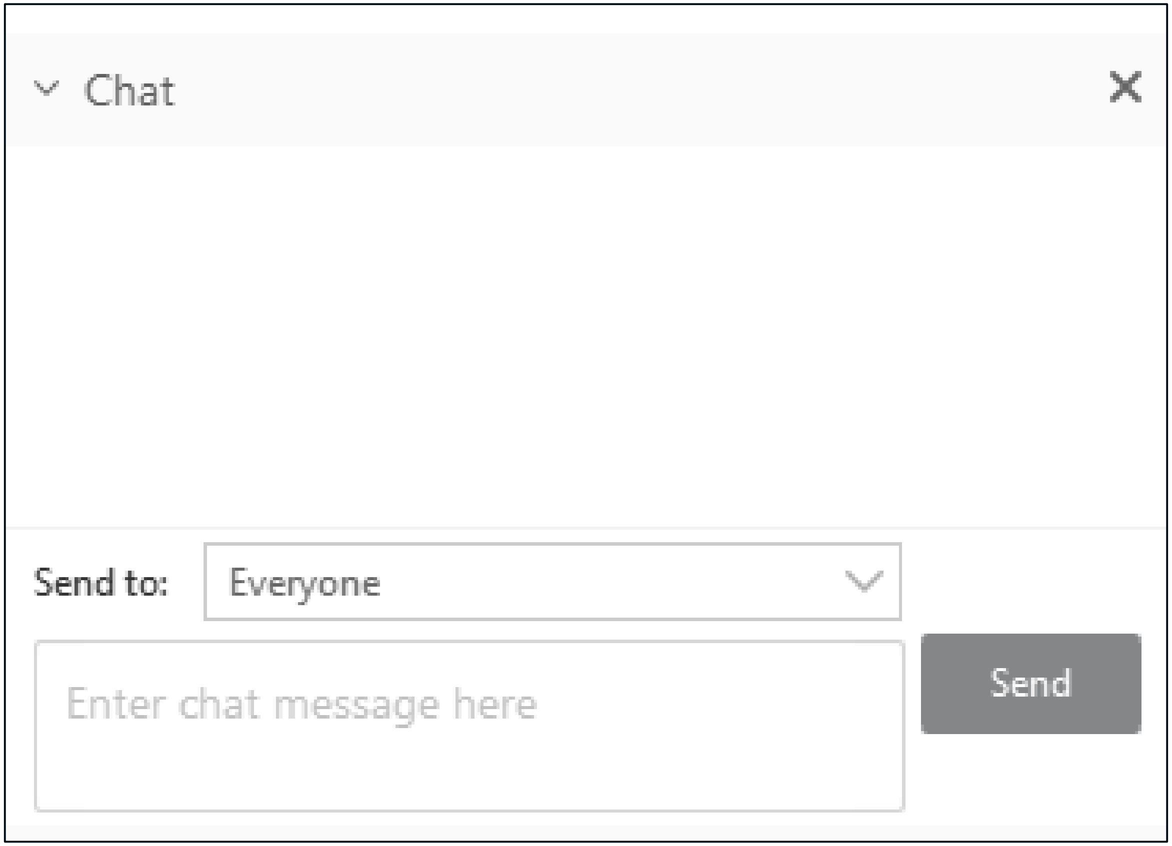

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Thank you

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