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NEXT GENERATION HYDROGEN TANKAGE

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Abstract

Efforts to continue research on advanced hydrogen vehicular tank technologies have been focused on a strategy that allows an affordable return to frontier experimentation, can sort out the mechanism responsible for premature failure in the record-setting tanks built in 2000, has a plausible path to adoption by industry, enables new classes of small hydrogen powered vehicles, supplies examples for regulatory reform initiatives, and demonstrates the effectiveness of innovations expected to reduce hydrogen vehicular tank cost (in mass production) by roughly a factor of two over the current state of the art.

Beside the overall strategy, two subtasks are detailed and some of the related efforts performed by LLNL's tankage research team are described briefly. Monitoring technical progress on DOE's ongoing contract with Quantum, learning from Sandia's destructive test program, and attempting to troubleshoot the multiple-organization vehicle integration efforts on two demonstration programs (the FutureTruck Competition and the Nevada Bus Project) are discussed briefly as sources of learning and opportunities to assist related efforts. The rationales for initiatives that LLNL has pursued in advocating technical reforms to current hydrogen tank safety regulations are also dissected.

Strategic Crossroads

The team at LLNL that set the percent-by-weight-hydrogen record in the year 2000 has to solve the inevitable strategic problem – what to do next.

This central problem had several disparate subproblems. Understanding of what happened at the limits of manufacturable tank weight performance was incomplete. A mysterious failure mechanism remains unidentified, and resources were clearly inadequate to return to the same experimental conditions. Many sorts of high leverage tankage innovations have come to light that were simply not affordable to investigate. Nearly commercial spinoffs of LLNL tankage innovations proven across the past three years were already heading for vehicle integrations demonstration projects, in which the LLNL team had a coordinating role. The expertise required to contribute to those demonstrations would soak up most of the DOE-funded staff hours at LLNL in FY01. The lessons learned from the contract and demonstration roles turned out to be relevant for the bigger strategic problem.

Related Activities

Arduous participation in demonstration vehicle projects will be sketched in a section (Demonstration Projects) below. That participation may appear tangential to the research conclusions that form the backbone of this Annual Report. In two different ways, those efforts resulted in learning that come in early enough to determine strategy. A relevant failure mode was observed in prequalification testing conducted by IMPCO (now Quantum), the winning bidder now under contract with DOE to develop lightweight hydrogen tanks. LLNL team members acting as technical monitors on that contract were able to debrief IMPCO on results that would otherwise have escaped notice. Another relevant failure mode was encountered several months later at Sandia in extreme penetration testing.

These failures that LLNL learned of and inquired further about came to LLNL's attention because participation in DOE demonstration and development projects paid for large (>$100K) human interface costs. These failures were relevant because their shrapnel morphology appeared similar to the mysterious failure mechanism that cost LLNL's record-setting tanks a consistent 7% in weight performance.

The other connection or spinoff of LLNL tankage 'diplomacy' came through LLNL's assumed responsibility to contribute expertise into the tankage regulatory process. It had become clear to LLNL tankage innovation advocates over the past ~3 years that safety regulations derived from the NGV2 standards for compressed natural gas tanks were seriously flawed. LLNL's first recommendations were contributed in haste to the ISO regulatory process in 1999. Another round of recommendations had accumulated from LLNL's participation in the IMPCO development contract over year 2000. Now year 2001 has delivered some lessons vital to new recommendations that counter deeper conceptual flaws in proposed regulations. Besides penalizing innovation and testing the wrong objectives, draft regulations now before the ISO are already posing barriers to adoption of hydrogen fueled vehicles by robbing obvious safety innovations of the ability to be certified safe.

Strategic Choice

If the LLNL tankage team chooses the right direction for its investigations, all of these partially related problems can be tacked with research results. Instead of ‘diplomacy’ and exponentiating manpower costs that must be sunk into regulatory ‘outreach’ programs, new experiments with actual hydrogen tanks could directly alter future regulations and development possibilities. No arm twisting will be required to get manufacturers to adopt the new technology LLNL has selected. The routes to adoption available for previous generations of LLNL hydrogen tankage innovation were closing down as some of the fruits of LLNL labors in previous years approach commercialization. Thiokol, which made the bridge between state-of-the-art aerospace composite fabrication expertise and LLNL new technology initiatives in tankage, is effectively out of this business (due to management decisions and ownership changes). No strategy that threatens the market positions of current tankage manufacturers is likely to prosper. Therefore it makes sense to move LLNL’s tankage research focus 3-5 years into the future, away from its previous 1-2 year aims.

This strategic choice was well aligned with the suggestions of Sigmund Gronich, in charge of DOE’s Hydrogen Program. In a tankage research planning session (August 2000), he suggested moving LLNL’s focus from weight to economic performance. Economic performance was also an imperative to be able to afford any experiments that might return to conditions similar to the mysterious failure mode on the weight frontier. The Hydrogen Program insisted on economic analysis in every years reporting prior to this year, and the 500,000 cars/year quantities used as the basis for those required cost projections allowed for several next generations of tankage technology. What innovations would be advanced enough not to threaten current commercialization market positions but could still pay their own way and sell themselves by reducing the cost of hydrogen tankage?

Experimental Program Rationale

This strategy of pursuing the next generations of vehicular hydrogen tankage does more than supply a plausible path to market adoption. It would be worthless without an understanding of what techniques to investigate and why. Without models validated by testing actual hardware, economic performance projections based on technologies that may not work would be moot. When this fiscal year began, the burst failure mechanism that limited tank weight performance wasn’t understood, and appeared unlikely to be sorted out without an effort our industrial partners (Thiokol and IMPCO) call a “Science Experiment.” Why might it be worthwhile to conduct those experiments? Without the understanding that such experiments should bring, the proponents of advanced technology would be promoters, not experts. Economic performance and plausible adoption paths provide the why for selecting among innovations, as long as near-term economics can afford the experiments to prove the innovations will perform as advocated.

The LLNL tankage research strategy that has emerged is quite detailed. Test articles suitable for motorcycles, scooters, lawnmowers, wheelchairs, leaf blowers, etc. go a long way to solving the experiment affordability problem. End dome contours are currently being computationally designed by a LLNL subcontractor to complete the specifications for a liner mold. A reasonable fabrication price is likely to be bid that could deliver copies of an integrated tank test article for

<$500, using less than $15 of T700S (the most economic composite fiber type available for the next few years).

The economic performance projected for the next generation tanks that LLNL advocates is not the same as the economic affordability of research experiments. Those experiments are designed to understand the technical issues that separate the current state of the art from one that is projected to cost approximately half as much to do the same job. Performing research, not necessarily mass production, at a smaller tank scale has many other advantages besides affordability of experiments. It threatens no hydrogen tank commercialization efforts now underway, and postpones the prohibitively high cost of tooling up to manufacture tanks big enough for automobiles or trucks to ambitious firms, who can pay for it when the production volumes in a next generation industry can afford it.

Technologies Selected

Figure 1 shows LLNL's most recent cost projections as a function of the total quantity of automotive scale tanks produced. These projections are based on component and assembly costs of a 5,000 psi tank that holds 3.6 kilograms of hydrogen. These projections extend results that have already been confirmed by LLNL's collaborators in industry (for low volume, near-term commercial production) to later generations of mass production. They forecast a switch to next generation technologies advocated below at quantities that can afford to sink their significant development costs, somewhere between 20,000 and 1,000,000 units produced.

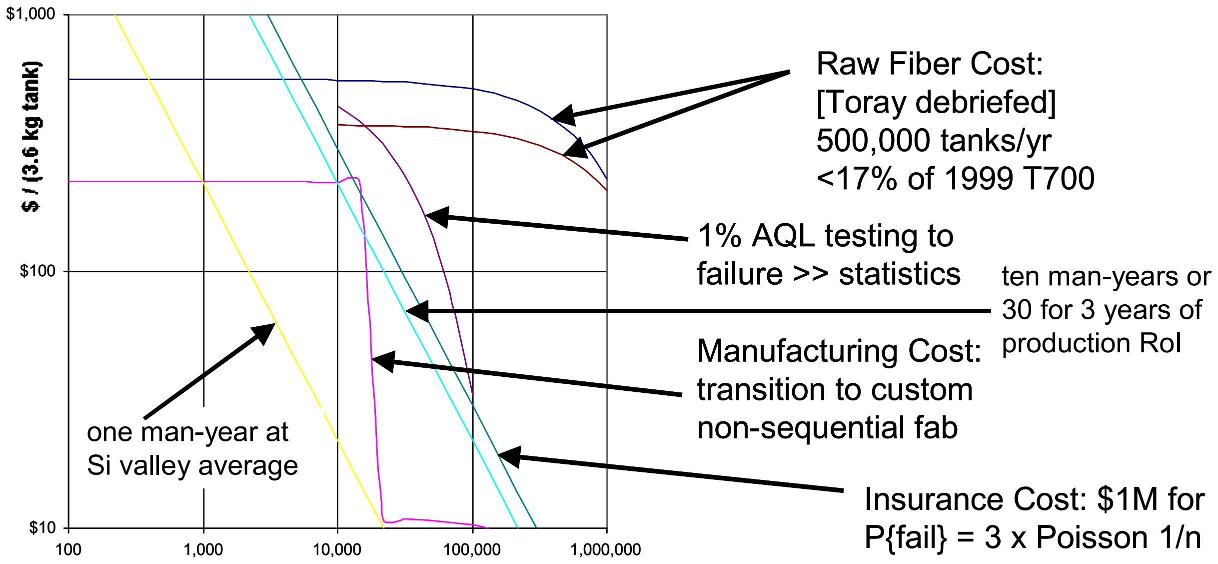

Figure 1 – Cost Projections vs. Quantity Manufactured

What advanced technologies can pay for their own development and still save costs in hydrogen tankage? A preliminary understanding of the design options and process parameters required to specify today's best hydrogen tanks was forming over the last two years as LLNL collaborated with Thiokol, ATL, and IMPCO to build record-setting tanks. That understanding was inadequate to chart the possible frontiers for innovation. Several experts were added to the LLNL team's roster of consultants, and a mini-forum was held between the entire LLNL team, its consultants, and likely subcontractors in Salt Lake City early in 2001. A very truncated list of innovations emerged from that meeting that combine to save a projected 50% in tank cost. These projections are based on detailed estimates of the improvements possible in the various component costs of the detailed production economics models that industry has already agreed with at low volumes, they rely on an understanding of how various innovations would change components of the tanks themselves, not on hand-waving. These projected savings depend on recognition by the regulatory consensus that difficult testing programs will allow manufacture of safer, lighter, more compact, as well as less expensive tanks.

For the purposes of proving that a tank technology is manufacturable and safe, statistical quantities of tanks must be tested to failure. Smaller research test articles make statistical testing affordable for LLNL tank research efforts, while sufficient production volumes of larger tanks can afford this cost by allocating ~0.5 to a few percent of each production run to a form of self-insurance. Most of tank cost in large scale production is proportional to composite materials mass. This cost component includes the expensive fiber, as well as machine time to process fibers into overwraps. If fiber material and production processes are unchanged, lighter tanks will be proportionally cheaper tanks. Roughly 35% of the LLNL projected tank cost savings of 50% comes from weight reduction. All of these analyses assume the same economical winner of the competition among composite materials for lowest cost per unit strength (Toray's T700S), but LLNL's analyses forecast the substitution of much higher production rate processes (fiber placement of performs in molds) for the conventional fiber winding process. Weight reduction that is correlated with cost reduction can be advantageously traded for higher density to simplify packing enough hydrogen to drive long ranges aboard more conventional vehicle designs, at the cost of about 17% for 10,000 psi operation than the current 5,000 psi technology.

Blow Molding

The rest of LLNL's projected cost savings come from lower component and manufacturing operations counts. The quasi-instantaneous (generally below 2 seconds per molding cycle) provides access to a much wider list of plastic liner materials than the state of the art rotational molding plastics that LLNL has explored exhaustively in previous years. This process is capable of producing the thinnest liners possible without etching (a costly process that is difficult to control, used in exotic aerospace aluminum and titanium tank liners). Thinner liners have a slight but significant effect on saving weight, increasing overall density, and reducing cost. Tooling for blow molding cost so much for an automotive scale tank that this process must wait for at least 10,000 units to be produced to be economically advantageous. For near-term experiments, a preliminary quotation (January 2001, from a contractor recommended via Kirtland AFB tank researchers) for tooling and 200 liners from the first mold run was $20,000 for a mold just 10" long and 5" across.

Blow molding provides a cost-effective substrate for several coating-in-the-round processes LLNL hopes to investigate in 2002. Although cost savings from the high-volume blow molding process are barely significant for the entire tank, the new liner materials this process can form into liners are very significant because they facilitate low-cost, high-throughput, and structure mass saving innovations. Blow molding can produce liners so thin that the best coatings can account for most of an advanced liner, so soluble that etching them out to manufacture 'linerless' designs could produce cheaper tanks by removing failure initiation sites on the liner-composite interface. Some blow-moldable liner materials are strong enough to allow prestressed coatings and very high winding tension to be applied onto pressurized liners before they are reinforced with cured composite overwrapping. Integrated tank leak/permeation testing will provide the first valid data on permeation aging and statistics. Thin liners combined with minimum weight composite overwrapping should also be ideal for recreating the mysterious failure mode whose elimination could save 7% in costly fiber mass.

Process Research

Burst testing of statistical quantities of small tanks can provide direct evidence that 33% of the 35% savings projected due to weight reduction is feasible. Dropping safety factors from 2.25 (burst pressure over maximum expected operating pressure) to the vicinity of 1.5 (where many aerospace systems are routinely engineered with great attention to performance variation) will depend on plenty of burst data statistics to recruit a consensus of safety 'experts.' One of the process variables that statistical process research should explore directly influences variability in burst pressures for at least one failure mode: bending in the transition region between end dome and cylindrical sections of a tank. This variable is also a design variable, and will be constrained by the shape of molded liners' end domes unless very advanced forms of composite fabrication (fiber placement that can preclude lateral tow slip and depart from geodesic fiber trajectories) are employed instead of winding. Ultimately those advanced processes may be economically justified at high volumes, but they will be difficult to include in near term variation of parameter studies. These sorts of studies are the staple of Silicon Valley semiconductor process research, and make sense to conduct whenever it is possible to gather enough statistics.

The other two process parameters that are affordable and important enough to investigate on a one-year timescale are wind tension and curing cycle temperature. The parameter list for manufacturing next generation composite tanks can get much longer, but twenty five produced and burst test articles barely suffice to begin exploring statistical performance. Five burst pressure measurements are required for reasonable confidence in estimating variance, so five tanks with identical manufacturing process parameters must be built to determine the performance and manufacture controllability of each point one might advocate exploring in process parameter space. Wind tension is the process parameter anecdotally known to greatly influence burst pressure. The mysterious failure mode of the record setting tanks was encountered on tanks that were wound with unusually low tension. Micro buckling of the wound composite before it was cured, or alteration of HDPE thin liners curing a cure just degrees below HDPE's flow temperature are two strong hypotheses that might explain consistent, measured 7% low strain at failure (compared to Thiokol's large data base of measurements on the same composite materials and TCR matrix impregnation and winding machines, but cured on sand mandrels).

Experimental Equipment

Experimental plans have been developed in even greater detail than the previous consideration of which process variables to vary might suggest. Two test sites have been considered, and are accessible for burst testing, while both manufacturers LLNL has worked with in the past (Thiokol and IMPCO) have an incentive to perform at least one or two burst tests to cross check their own burst testing procedures. Two related instrumentation systems, one at LLNL, another at a likely testing subcontractor, are being built up to allow safe burst testing in bunkers. Percent hydrogen by weight performance also relies on accurate measurements of tank volumes at elevated pressure, which can be made by at least three techniques. Both test rigs should be capable of making volume vs. pressure measurements by the most accurate technique, weighing the water that is pumped into the tank under test during a preliminary run up to proof pressure.

The LLNL field test rig has been designed for subsequent augmentation to allow it to take data at video rates. This feature will allow trials of non-imaging sensors (e.g. fiber proximity sensors, laser beam occlusion, piezo accelerometers) with sufficient bandwidth to resolve the mechanism responsible for “turn to dust” failures. This new failure mechanism has likely been observed in three related series of tank-destroying tests, including LLNL’s mysterious discrepancy between 12% design and 11.3% tested-to-failure percent-by-weight-hydrogen result. It has anecdotally been observed many times in impacting testing of military composite subassemblies like missile casings, but not reported because subsequent design modifications ‘fixed’ it.

Benign Failure Possibility

The ability to observe “turn to dust” failures as they happen has pure scientific value as well as potentially vital safety benefits for compressed hydrogen storage. The lack of large shrapnel (except for the end domes in Sandia’s experiments, which were shielded from the failure onset site by massive clamping straps) in the ~7 related failures suggests that the lightest tank technologies could be designed to burst with unprecedented safety, producing shrapnel but not shrapnel hazards. Expertise at Thiokol familiar with very many failure analyses has argued persuasively that the lack of large shrapnel precludes these failures being localized. If one part of a tank fails first, it always kicks portions of the opposite side away intact.

The conclusion that this failure mode is not localized, plus the speed of the tanks self-destruction recorded on fast-framing cameras by Thiokol and Sandia (which proved this phenomena happens in less than 250 microseconds) endorse the most likely hypothesis: this is a new class of instability. This unproven mechanisms is analogous to turbulence in fluids, where orderly motions becomes disorderly, except that it results in fracture on a characteristic small scale. Similar to snow avalanches, which discharge gravitational potential energy already stored in a medium, this hypothetical mechanism would discharge stored strain energy. Unlike avalanches, or detonation waves which release available chemical energy already stored in their media, this mechanism partakes of fundamentally tensor mechanics due to stress waves in partially ordered, anisotropic, two phase media. No mathematical models capable of handling this hypothesis have yet been found in the literature of physical instabilities.

Fiber dust shrapnel is potentially benign shrapnel. A bit of sheet metal is sufficient to stop a five micron rod of fiber from puncturing people, or even nearby equipment. The creation of this shrapnel should soak up a lot of free energy creating fresh surfaces, like the Velcro tape detachment 'ripcords' now providing dissipation in safety harnesses. The energetics of free surface creation energies in composites also appears to be a neglected topic in the literature of composite materials testing or modeling. Sharpie impact testing (which measures toughness by measuring energy lost in propagating a crack through a bar) might be followed by SEM-based estimates of free surface are creation to estimate the amount of energy shrapnel creation might be consuming. Such quantitative estimates might agree with the 1-2 megajoules of stored strain energy LLNL has calculated were present at burst in the record setting tanks. Combined with another safety initiative (that takes advantage of hydrogen flame speed to vent the ~ half gigajoule of chemical energy stored in a Smart Tank), the development of benign shrapnel would render next generation compressed hydrogen tanks much safer than any other chemical energy storage system.

Safety Considerations

Rather than attempt to dissect the demonstration projects that the LLNL tankage team was involved in from the research plans sketched above, their inherent cross fertilization can be seen if the order of exposition follows regulatory issues into the demonstration projects with their wealth of vehicle+infrastructure integration requirements. LLNL entered the hydrogen tankage regulatory arena in order to enable the adoption of thin, rotationally molded plastic tank liners (whose performance was a key to weight minimization). Metal lined tanks continue to lose the weight and cost performance competition with plastic liners, whenever the competition is performed on a level playing field. Yet the about-to-be-adopted hydrogen vehicle tankage safety regulations contain many leftovers from the era of metal tanks' impermeability, as well as a few bad assumptions from the natural gas tank safety (NGV2) regulations.

Unless the allowable permeation specifications are rewritten, the only plastic-lined hydrogen pressure vessels (Type IV tanks) that will be considered safe have liners almost as thick as their composite overwraps. Fortunately, analyses being performed to contribute to new building codes are bearing out the excessive, 1-2 orders of magnitude in excessive conservatism grandfathered into the ISO TC197 (hydrogen vehicular tanks safety standard), which the LLNL tankage team discovered was based on assumption errors in 1999.

Thin liners enable relatively lightweight tanks, but their relatively insignificant cost savings (2-4% in LLNL projections) are almost irrelevant compared to the benefits likely to accrue from their ~5-fold larger range of available materials. The testing of permeation phenomena for a variety of new liner materials pointed out the advantages of integrated pressure vessel permeation testing compared to single material coupon testing. Thiokol and IMPCO found a factor of two independently in pre-NGV2 qualification test programs that consistently measured vessel permeation below what the coupon permeation tests predicted. This in not good news, since nobody has studied cyclic and environmental degradation of permeation resistance. By testing permeation at beginning of life (even when the required test sequence makes end of life test articles available), excess liner thickness is being required to preserve an untested, ad hoc safety factor that even meager statistical test could drastically reduce while actual safety would be improved by knowledge of how permeability degrades.

Consideration of the safety implications of hydrogen permeation leads to the conclusion that key current regulations are based on flawed assumptions. Catalytic safety components inside a tank's envelope aren't rewarded, since hydrogen leaving the tank interior is circumscribed instead of hydrogen escaping to the tank exterior where it could contribute to flammable gas mixtures. Since advanced tanks require "shoulder pads" to pass the currently required drop test, components exterior to the pressure containment envelope are clearly part of the item being safety certified. The only harm done by regulations that ignore the possibility of turning permeated hydrogen into water vapor is that thin liner innovations are erroneously assumed to be unsafe.

Smart Tanks

Other safety recommendations appear in Table 1. LLNL staff still has the expertise to contribute constructively to the strife that advocating these recommendations would entail, but not the support sufficient to see that strife through to victory. Several of the highest leverage suggestions derived from Sigmund Gronich's suggestion that LLNL follow up on the Smart Tank efforts funded by DOE some years ago. Like the diplomacy required to advocate regulatory initiatives, debriefing of the now reassigned experts in industry who performed the Smart Tank work was abandoned for lack of resources. But Before Task 1 of LLNL AOP for tankage in FY01 was concluded, it turned out that Bluetooth (a trademark held by a consortium) Wireless technology is destined to make earlier work obsolete. At <$10 per chip, with a proven wireless range of 15 feet, this technology already has a manufacturer base, a customer base in luggage and hospital equipment and truck tires, a software community, dozens of venture funded new applications, and production volumes growing rapidly somewhere beyond 2 million chips per year.

Table 1- Recommendations for Regulatory Improvements

Redefine permeation to allow water from catalytic vent devices
Set permeation specification 1,000X too conservative, not 10,000X Worst-case garage ventilation rates and statistics are known, stay < LEL
Test permeation at end of cycle life (test article already in NGV2) Current test at beginning of life fails to screen for barriers that degrade Current tests may give false optimism to some barrier technologies Counterproductive waste of safety margin on permeation for degradation
Measure worst-case temperature rise allowable for fast fill rates Filling stations need to know what inlet temperatures are safe for liners
Allow orderly migration to advanced standards as quantities rise Standard practice in Electrical Engineering standards (e.g. ethernet) Advances 'unsafe' without such provisions for revision every few years
Wireless "Smart Tank" features phased in to avoid filling mistakes Earliest software prevents tanks from being used beyond tested cycle life Later prevent tanks from being re-used after mishandling and accidents
Allow statistical qualification to trade cost and mass for more testing
Allow nondestructive testing to trade cost and mass for more testing
Collect real crash data to establish crash-worthiness of mountings
Reward tougher designs by requiring adequate self-insurance plans

A vehicle or portable appliance with a Smart Tank can be a lot safer. Fire risks can be mitigated by remote control. DTI claimed (in a phone conversation) that 5% of auto accidents include fire. Firefighters can easily communicate with Bluetooth enabled ‘smarts’ to specify when and how hydrogen that is still in the fire hazard vicinity can be safely vented. Certainly dropped tanks, filling to excessive pressure levels, tanks resold after collisions, and tanks sold beyond their cycle life can all be prevented by ‘smarts’ that implement a fuel ‘level’ sensor. This avenue of innovation may not need government sponsorship, but its insertion into the contentious safety regulatory arena will consume lots of “people skills” that industry has little incentive invest until ‘smarts’ are deemed safe.

Demonstration Projects

The demonstration projects LLNL participated in were very instructive, as well as sources of intense frustration for their remaining participants. DOE solicited advanced weight performance tanks based on LLNL’s research in FY98 and FY99 from industry in March of 2000. LLNL tankage research team members acted as technical monitors assisting the DOE Golden contracting office/officer to write the solicitation and keep the winning bidder on track toward likely success in the upcoming vehicle demonstrations. What to deliver has changed twice in the course of this contract. Two sorts of demonstration vehicles are to receive tanks supplied by this contract. Figure 2 presents a quick sample of the LLNL’s teams’ original design for the first of these two projects, the FutureTruck SUV competition.

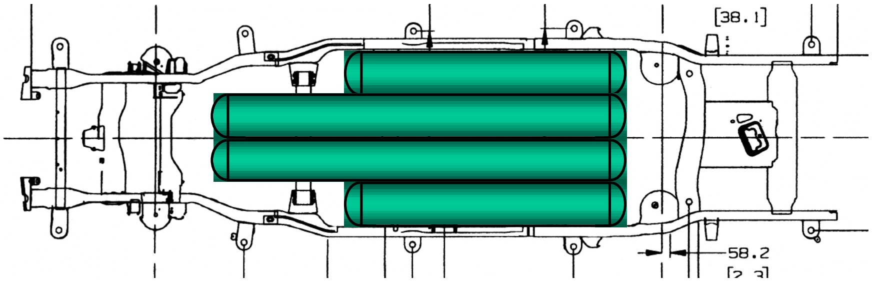

Figure 2 – Original tank layout fit in frame of GM Suburban SUV

The Nevada Bus project presented a plethora of issues (“who’ll do what?”) that needed resolution before solicitations could be written for vehicle integration contractors who would install DOE-supplied tanks, modify the bus, train its operators, etc. Many staff hours were spent at LLNL figuring out what needed to be installed or tested, who was capable of doing it, and who would be responsible for what. Ultimately LLNL’s planning effort for this project was captured in a 24-page suggestion document delivered to the OE Contracts office in Golden, Colorado, which is currently overseeing the ongoing tank development contract. Although LLNL learned how to build and safety certify compressed hydrogen filling facilities, it seems best to clone and employ the costly implementation currently deemed safe in Palm Desert, California.

In advocating a division of labor for the Nevada Bus project, LLNL investigated how to develop a fueling infrastructure and what is needed to modify a vehicle for crashworthy roof-mounted tanks. Oral and written reports of these lessons learned helped convince DOE Hydrogen Program management to let industry "carry the ball" on hydrogen vehicle demonstrations from now on. Liability considerations provided a major justification for this decision. This decision made sense to the LLNL team, but it also effectively severed LLNL participation in the FutureTruck competition (two university teams, Texas Tech and Virginia Tech, are installing DOE supplied tanks on GM SUV's as this report is being written), as well as in the Nevada efforts. Safety arrangements on these projects are likely to be made by GM in Michigan and Air Products in Nevada. These arrangements will doubtless contribute to the several proprietary fueling implementations that are currently deemed safe in the absence of applicable regulations and even in the absence of disinterested qualification testing.

Acknowledgments

Management of LLNL's internally-funded EyeGlass LDRD Strategic Initiative has allowed the author to pursue tankage research at some cost to their project's own probability of success. Other projects at LLNL (sponsored by DARPA, NASA, AFRL, and internal funding) have contributed sufficient support to related research on this leading edge of Joules-per-kilogram.

References

Technical report (not referenced in text above, but prepared at DOE request)

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