III.5 Demonstration of Full-Scale Glass Fiber Composite Pressure Vessels for Inexpensive Delivery of Cold Hydrogen

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Project End Date: September 30, 2012

Fiscal Year (FY) 2011 Objectives

- Optimize hydrogen delivery by tube trailer.
- Demonstrate strength improvements of glass fiber pressure vessels at low temperature.
- Develop materials and manufacturing for low temperature hydrogen delivery.
- Quantify performance and economics of developed pressure vessels.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Delivery (3.2) section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(F) Gaseous Hydrogen Storage and Tube Trailer Delivery Cost

(G) Storage Tank Materials and Costs

Technical Targets

All capital cost projections are detailed to the component level for composite pressure vessels (CPVs) including manufacturing capital, labor, materials, and disposal. Costs of other trailer components, however, are much less detailed (plumbing, CPV mounting, and integration). These non-vessel costs have been estimated based on compressed natural gas trailers as 43% of the total 1,100 kg H_2 trailer cost and 33% of the 2,350 kg H_2 trailer cost.

TABLE 1. Progress towards Meeting Technical Targets for Hydrogen Delivery

Characteristic	2005 value (Table 3.2.2)	DOE Targets FY2012/2017	LLNL+SCC 2011 status
Delivery Capacity (kg of H_2)	280	700/1,100	1,100
Operating Pressure (psi)	2640	<10,000	<10,000
Purchased Capital Cost ($)	$165,000	<$300,000	<$291,000

Notes: LLNL has also designed a 2,350 kg delivery capacity cold glass CPV trailer option that uses the entire International Organization for Standardization (ISO) 20 ft. long container volume, with same operating pressures and temperatures, and a projected cost of under $477,000. This option cuts delivered cost estimates from $1.01/kg-delivered to $0.82/kg-delivered (not including forecourt storage, compression, or dispensing).

Delivery costs are based on H2A models for labor and cab, while operating pressure has been optimized (for minimum $/kg-delivered) at 7,500 psi. We calculated refrigeration costs assuming 33% exergetic efficiency to worst case 140 K. The estimated cost of refrigeration ($0.24/kg-delivered) is conservative based on refrigeration costs calculated by Argonne National Laboratory [1] at the gas terminal scale.

FY 2011 Accomplishments

- Designed and built multiple full-scale pressure vessels to implement trailer design capable of delivering hydrogen (over 100-mile round trip) for less than $1/kg-delivered.
- Qualified vessel design and manufacturing processes for pressures (0 to 22,500 psi) and temperature (ambient to -100°C) required to support cold delivery mission.
- Successfully burst tested first full-scale pressure vessel (with water at ambient temperature) as the first and most significant step in the technical proof of concept.

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Introduction

This project has been funded to develop the key missing component necessary for LLNL's "cold glass" delivery approach: trailer-scale pressure vessels. Other technologies can build low-temperature-capable pressure vessels, but their vessels are either much too costly or too heavy for delivery trailers. Only CPVs are light enough to carry compressed hydrogen in sufficient quantity to achieve LLNL's optimized delivery costs within the volume and mass limitations of a trailer. Meeting the capital cost requirements of a trailer payload is not enough. Our target (below $1/kg-delivered, not including forecourt storage, compression, or dispensing) must pay for the energy and capital required for refrigeration, plus the operating and capital costs of the trailer cab (including labor to drive and load/unload). The CPV technology LLNL is developing with partner Spencer Composites Corporation (SCC) has the potential to meet this economic target for hydrogen delivery.

When first proposed in 2007, the CPV development effort was expected to advance the manufacturing readiness level (MRL) for this technology from 4 to 8 [2]. This translates to moving the technology from proven manufacturing feasibility to manufacturing processes that operate at target cost, quality, and CPV performance. Over the course of development, it was realized that this characterization was incorrect and the development effort has been re-defined as progressing the technology from MRL 3 (manufacturing process identified) to MRL 7 (proven manufacturing processes). The change required significant pre-production materials testing, and the development process is currently on track with the first proof of CPV performance from a full-scale vessel.

Approach

The cold glass strength effect needed for the glass-fiber composite material to potentially meet cost, delivered mass, and trailer payload mass targets was demonstrated in 2007 and later through proprietary glass fiber characterization carried out by a major fiber producer. A requirement of 3,650 temperature cycles between ambient and 100 K can routinely be met by commercially available fiber, but not by economical composite matrix and CPV liner materials. A new system of plastic materials is being developed that can perform over these thermal cycles and enable the LLNL CPV design.

Full regulatory approval of CPVs sufficient to carry hydrogen on U.S. highways requires a sequence of 16 full-scale tests. Such a test project is clearly beyond the resources available for this development effort. Therefore all key technical risks of failing any of those tests are being addressed by an affordable plan of burst, cycling, and permeation tests. No regulatory approval process has yet been formulated by Department of Transportation (DOT), ISO, or American Society of Mechanical Engineers (ASME) standards organizations for low temperature CPV service, mobile or stationary, so low temperature operation risks are being addressed with subscale test articles. Testing of the articles and of small-scale tensile coupons also allows risk associated with materials process development to be reduced. However, the processes needed to manufacture composites and liners do not scale from one size to another without posing significant risk to vessel performance and cost, and therefore testing of full-scale diameter (23") vessels is required once the technology has been shown to be acceptable prior to process scale up. However, to reduce materials process development risk, testing was first performed on small-scale tensile coupons and 3" diameter subscale vessels.

Results

The first successful burst test of a full-scale (23" diameter, length over 50" that can satisfy ASME Code X certification requirements for all greater lengths) is illustrated in Figure 1. This test was performed with pressurized water to meet permit requirements at SCC's facility in Sacramento, CA. Testing CPVs filled with compressed hydrogen over a period of weeks is planned to prove that full-scale CPVs do not permeate at maximum operating pressure.

Before conducting this successful burst test in FY 2011, we had built three full-scale vessels from 'proven' components in early 2010 that failed 'prematurely' at varying pressures of several hundred psi. These failures were all slight leaks through cracks in their liners. The form and location of those cracks was similar to cracks found and overcome in 3" subscale CPV testing. Scale up from the 3" vessels to the first 23" vessels involved the costly construction of large tooling, and was only undertaken after 3" vessel manufacture had been adjusted to avoid those earliest CPV cracks at burst pressures above 22,500 psi (the maximum anticipated burst pressure required by LLNL's proposed trailer delivery integration design). Therefore the premature failures encountered in the three full-scale 2010 burst tests came as a very unpleasant surprise.

The persistence of significant technical risks was not unexpected because of two previous kinds of failure experienced by this development project. Before the final of the three failed 2010 full-scale CPVs was built, the first attempt to cast its liner went awry in a very illuminating fashion. After succeeding in building a 51" long liner, the same materials, tooling, and process sequence was used to build a 114" long vessel, but the liner molding tool produced a horrid 200 pound lump of darkened plastic! This unexpected scale up failure came from tripling of resin mass put into the tool before it was employed for the fourth time to cast the longest liner. This problem was overcome with successive resin pours to prevent the thermoset plastic's exothermic solidification reaction from thermal runaway. The catalysis reaction that solidifies our chosen, low-temperature-stable liner plastic was well known, but its dynamics in the molding tool was the first warning that thermal control during liner casting could be tricky.

The other development problem of 2009 was overcome entirely in the 3" subscale process development effort, and was apparently fixed by resin formulation changes. Since the liner cracks that caused problems in the 3" effort looked almost identical and appeared to originate in almost the same end dome location as the cracks that failed the 2010 full-scale test CPVs, it made sense to reopen the diagnosis of those cracks. Such debugging is simply not affordable at full-scale, so no more full-scale vessels were built until the

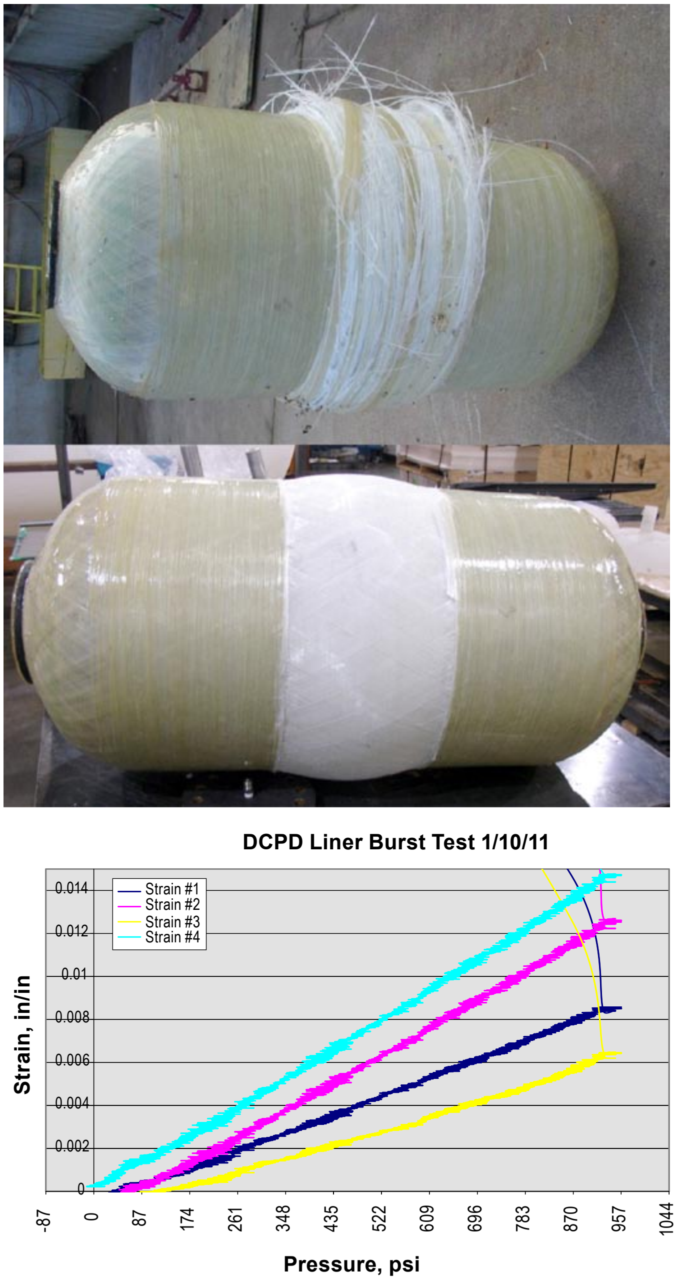

FIGURE 1. Successful Burst Test of Trailer-Scale CPV – Figure 1 shows a 23” diameter glass fiber composite pressure vessel that was burst tested with compressed water at ambient temperature. The photograph above shows the CPV after burst was declared, with its composite overwrap layer shredded. The vessel did not actually rupture, but lost most of its pressure and no fluid escaped. This is a very unusual outcome, due to the unprecedented toughness of SCC’s liner material. The middle photograph shows the bulge that formed in the unruptured liner, which accounts for an internal volume increase of roughly 3%, and is enough to explain the depressurization due to the relative incompressibility of water. The bottom figure illustrates four strain gage traces during this test, which prove this CPV’s manufacturing is adequate for designs that ‘burst’ at any pressure within the capabilities of plumbing seals.

problem was fixed in subscale articles without the earlier formulation changes. The same material that was cracking at low pressure in both early 3” and 2010 23” burst tests continues to stretch 18% in tensile tests, but something else had to be going on in particular end dome locations of liner castings for that material to crack at much lower strain. Figure 2 shows the variety of different hypotheses our team collected to explain these cracks, and the diagnosis we arrived at through skillful use of the scanning electron microscope (SEM) just in time to show dozens of SEM photographs at the 2010 annual merit review.

The internal features of our failing liners were responsible for the repeatable location of crack initiation. Defects had been built into the liner material during its casting process that were not built into the flat plaque tensile test specimens. Those defects were not visible to the naked eye, nor to an optical microscope, nor in unbroken liners – but they were visible in the SEM on the surfaces of cracks in the vicinity of crack initiation. When the liner cracking problem was first ‘fixed’ by resin reformulation, it appeared that the trouble was transient rather than built-in because almost all of the crack surface was shiny like the fracture surfaces on broken glass, indicating brittle failure. Resin additives that increased liner toughness and stretchiness (maximum elongation at tensile failure) appeared to fix it, until the problem returned at full scale.

The correct diagnosis was based on SEM imaging of the entire crack surface from the failed 23” liners. The cracks forked, with forks not left on the failure surface being those that didn’t run faster than those that formed the surface. These ‘diving’ forks were later seen on examination with low power optical microscopy, saving considerable time in the SEM. The direction that the ‘tines’ of these forks pointed must be the crack propagation direction, so the crack initiation region was localized between a single pair of forks whose tines pointed away from each other. In that region, shiny surfaces gave way to slight localized frostiness; presumably before the crack propagation ramped up to high speed and could take advantage of orders of magnitude stress concentration at its crack tip. Those frosty regions are represented by the SEM sequence that appears in Figure 3, which focuses in on the “smoking gun” feature found on the complex surface of a diving fork.

That feature is a crater sticking up into a void, but not like craters seen in geology or astronomy. New materials have new failure modes, and this one occurred when the resin was a weak gel. Earlier SEM diagnosis had already determined that the forked cracks in the vicinity of crack initiation were not running in the maximum strain energy release direction (perpendicular to local tension), but went curling around with geometries that might be seen on the surface of puddings that had dried from neglect. The crater feature in question has sharp edges, but these could not have formed when ejecta blew into the void it sticks up in. Gas erupted through the surface of a weak gel into that void, then the gel shrank to form facets on the crater. Although density

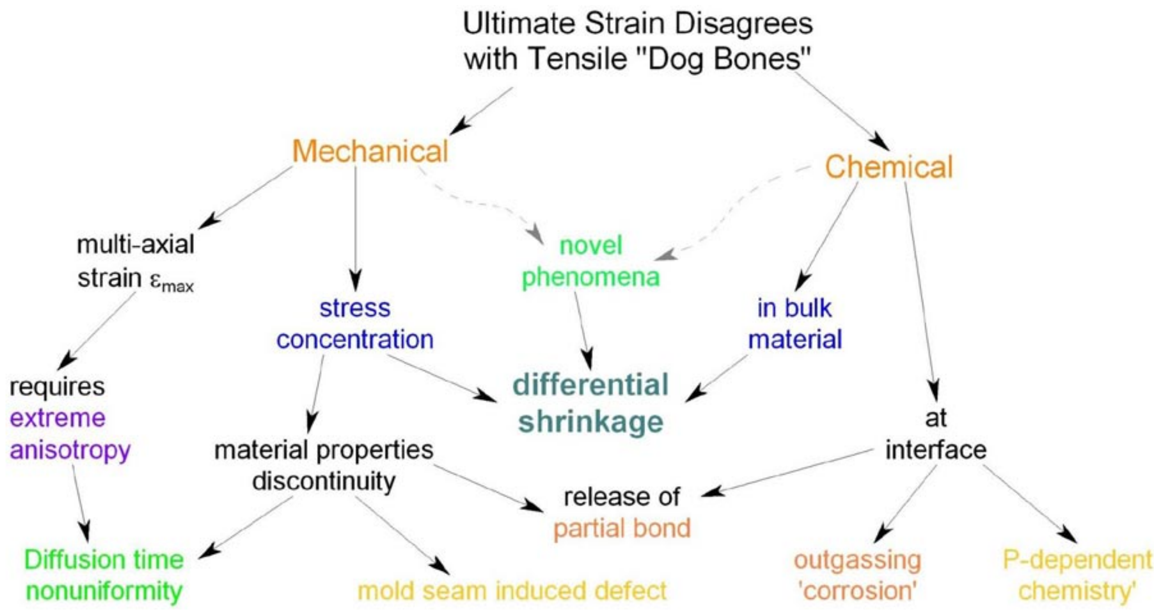

FIGURE 2. Tree Diagram of Hypotheses for Premature Liner Rupture - Figure 2 illustrates all the possibilities LLNL and SCC hypothesized to account for obscure failures observed in burst testing 3" and 21" diameter CPVs and unwrapped liners. For over two years experimental liner material formulations passed tensile testing at 8-9,000 psi ultimate stress and roughly 18% strain, yet failed when built into CPV liners at strains as low as 0.3%. These materials are not brittle, and most formulations were capable of toughness roughly 30-fold above epoxies. The materials failed as liners 'prematurely' despite passing every toughness test with an ASTM drop tower impact. Hypotheses in orange type were proven partially correct, yellow type were proven incorrect, and green type were verified. The odd conjecture shown in purple type was proven to be a result of the unprecedented solidification mechanisms of this material, while the hypothesis in teal type was found to be an unexpected part of that mechanism.

measurements have long shown a 6% densification of this resin upon solidification, how that shrinkage was distributed in space did not appear to matter. After LLNL's diagnosis, it was clear that the plastic was cracking itself just where it ran out of more liquid for a wave of catalysis to solidify.

Knowing what went wrong did not initially make it clear how to fix it. Another wave of dozens of 3" bottles became the front line for variations in the mold tool and resin pour sequence. Control was taken over where catalysis started, and care taken to never let the catalysis wave pass through liquid resin up against a solid wall, either of the mold or of previously solidified plastic. A technique was found to locate defective regions of castings without breaking them and to prepare the shards for SEM imaging, that is shown in Figure 4. But the next question was whether the project could afford to rebuild the 23" tool to incorporate these necessary improvements. The answer appeared to be no, before a real customer for such CPVs showed up in late summer of 2010. The customer could and did pay for a new tool which LLNL's liner mold fit into, but wanted CPVs built faster than SCC had any confidence they might pass ASME certification. This led to an extreme scramble to get LLNL development done on the tool the customer paid for, before the customer got its parts.

In January of 2011 the first good liner emerged from this tool to wind glass composite around, and then to burst test into the article shown in Figure 1. That burst test vindicated the improved liner molding process, because it ended in an unprecedented CPV failure mode, which might be called burst without rupture. Just because all the water remained inside after a loud noise and a big pressure drop does not mean this mode is really safer, since gaseous contents would not have dropped in pressure with just a little midriff bulge. But the survival of the liner in that bulge region does prove that the liner remained ductile under rapid straining to over 11% strain. Since design hydrogen delivery pressures only call for 3% liner strain, the liner component that has caused this project so much trouble has been proven to operate beyond its requirements at full scale.

Further surprises were in store when the happily undestroyed vessel in Figure 1 was cut into to see how well its liner's end dome was cast. If the vessel had burst in a more normal way, the region wherein more 'defects' were found might have been lost. Instead Figure 4 shows failure surfaces that have nothing to do with the performance of the CPVs LLNL and SCC are building, and everything to do with the nature of the new material we are developing. Composites built with this material as a matrix have all the right properties, including fiber 'translation' (material tensile strength divided by raw fiber strength) over 90% and no strength loss at 77 K. Castings built with it, however, can have localized frosty regions whereat catalysis ran out

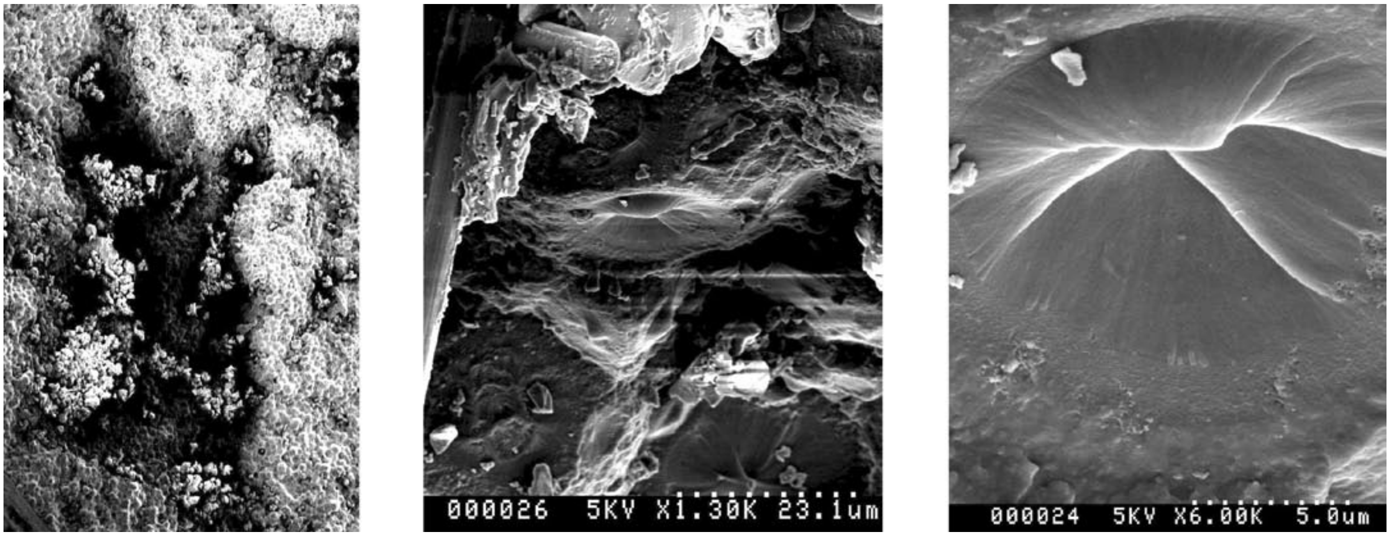

FIGURE 3. SEM Photographs of Liner Crack Surface – Figure 3 shows the "smoking gun" sequence of SEM photographs of a particular portion of the surface whereat a full scale (21" diameter) liner cracked inside of an early-2010 burst CPV. None of these features are visible in an optical microscope, and the sequence of photographs taken at the same point on the failed specimen increase in magnification from left to right. This particular spot was close to the origin of the crack that ruined this liner, causing the test CPV to leak below 800 psi and 0.7% nominal axial strain. The detective work that found the crack origin vicinity is based on forks in the cracked surface, whereat branches of the crack that did not succeed in forming part of the final separation surface dive beneath the surface on view. The origin of the crack must be somewhere between the two forks whose branches point away from that region. Looking into a fork of the crack, in the middle photograph shards of 2.7 micron glass fiber are visible which have been blown into a diving fork branch. On the wall inside that branch the odd "flying saucer" that appears centered in the micrograph at right initially resisted interpretation (since SEM views do not have darkness reflecting tilt angles as optical views do), but many attempts to view it at different angles convinced SEM operators this is a crater with sharp radial ridges.

of resin. This generation of 23' liners just happens to have one of those regions in a ring on its outer mold line (OML, casting terminology for exterior molded surface). The 3" liners that were cracking had several such regions on their inner mold line (IML, interior surface), and that surface goes into tension when the liner inflates, whereas the OML region on the 23" liners goes into compression.

The defective regions were actually visible to the naked eye, with the aid of a flashlight, when looked at through the polished edge of the burst success liner end dome cut out segment. They appear as a tenuous frostiness, which LLNL has come to term 'nanocracking', since any frosty region on a cast surface has the kind of frosty surface shown in Figure 3 when examined in the SEM. Once cast into the part, the penetrant dye that visualizes these regions in Figure 4 cannot get in to detect them, but when bar shaped specimens cut with this region in the middle were broken, the dye can be used to decorate the cracks. A forked crack is visible in the left micrograph of Figure 4, which was broken in tension at extreme elongation. A much more complex swirl appears in the right hand micrograph which failed at a few percent strain in torsion.

Although stress and strain have tensor rotation properties, it turns out that failure stress and strain do not rotate like a proper 2-tensor in these materials! Material so anisotropic that shear and longitudinal failure properties are decoupled is the consequence of its rapid solidification by Grubbs catalysis. It does not matter if shear stress is identical to tensile stresses exactly twice as large when the coordinate system is rotated by 45 degrees, because the molecular structure in nanocracked regions has almost no bonds to carry force in that direction. So an adequate solution for a 23" CPV liner is not the only fruit of these investigations: an informed strategy to design liners without bending stresses that put tension on the IML, and to design mold tooling that drives catalysis waves from IML to OML, enables progress (at customer expense) to be defect tolerant. The ability to detect defective regions before building CPVs around them, plus the advancing mass production of 3" CPVs with this technology improve the odds that reliable cold strength and inconsequential liner OML surface nanocracking can be proven before this project ends.

Conclusions and Future Directions

- First significant risk reduction test at full-scale passed with benign failure mode.
- More full-scale vessels under construction for cycling and permeation tests.
- Permeation test rig for dangerous compressed hydrogen filled, multi-week duration permeation tests under construction.
- Further quantitative proof of cold strength effect at various reduced temperatures anticipated with subscale (3") glass fiber pressure vessels tested in expendable dewar.

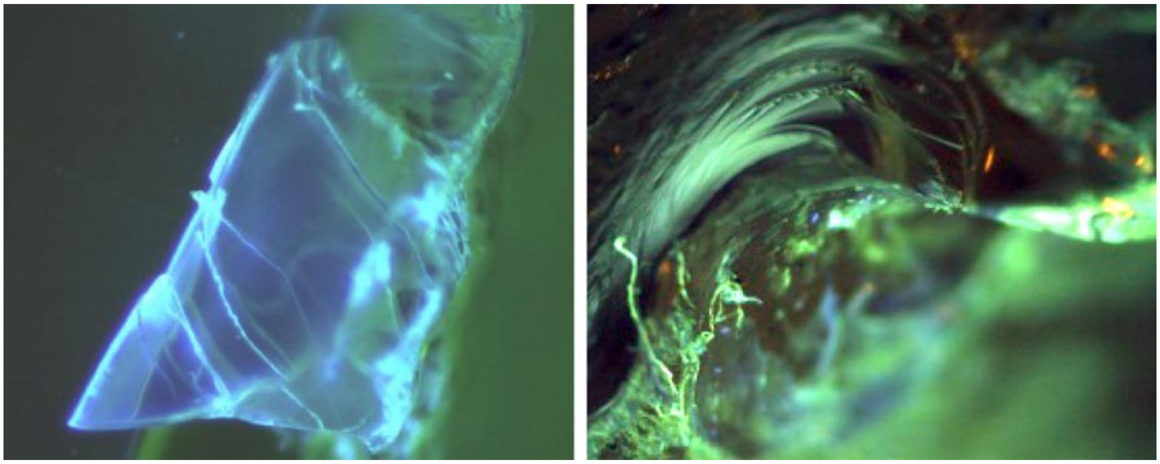

FIGURE 4. Observed Cracks in Specimens of Successful Liner – Figure 4 shows the splendid images resulting from two crude strength tests performed in a vise. These photographs are taken at low magnification with an optical microscope (commonly called a macroscope), in a combination of ultraviolet and visible illumination. SCC developed a diagnostic technique to make defective liner casting regions visible without a SEM, using a penetrating fluorescent dye. While the SEM cannot image regions likely to initiate cracks buried within cast parts, this technique cannot image defects directly on surfaces. Since the successful liner had not broken during burst testing, it made a fine vehicle to see whether defective regions could be found before they triggered cracks. This 'experiment' was conducted in January of 2011 by plunging an industrial vibratory cutter into the dome region of the unruptured yet burst CPV, then taking the wedge cut from the dome through a band saw to cut test specimens. The specimen at left was pulled with a vise grip pliers, and failed at over 100% strain, while the one at right was twisted and failed at several percent strain. They both failed in the millimeter-thick circumferential region where cloudy fuzziness is visible when polished edges of the wedge were illuminated by flashlight, on which the band saw cuts were centered to produce test specimens 3" long by roughly 0.3" square.

- ASME regulatory approval test program of nearly identical CPVs based on a batch of 20 full-scale (23" vessels) paid for by a private SCC customer anticipated in 2012.
- Joint DOE/DOT demonstration project possibility likely under discussion by early FY 2012 with hydrogen proponent DOT managers who currently have responsibility for certifying highway-rated pressurized containers.

FY 2011 Publications/Presentations

1. High-Density Automotive Hydrogen Storage with Cryogenic Capable Pressure Vessels, Salvador M. Aceves, Francisco Espinosa-Loza, Elias Ledesma-Orozco, Timothy O. Ross, Andrew H. Weisberg, Tobias C. Brunner, Oliver Kircher, International Journal of Hydrogen Energy, Vol. 35, pp. 1219-1226, 2010.

References

1. Mintz, M., and Elgowainy, A., "Hydrogen Delivery Infrastructure Analysis," Proceedings of the DOE Annual Merit Report, Washington, DC, 2010.

2. Manufacturing Readiness Level chart (and accompanying 72 page category descriptions) provided by DoD web site www.dtic.mil/whs/directives/corres/pdf/500002p.pdf.