Title: **A New Perspective on the Hazards of Liquid Oxygen**

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The National Fire Academy (NFA) recently launched an exciting new course, *Management and Safety in Response to Hazardous Materials/WMD Incidents.* I was fortunate enough to be a part of the course development team. In the process of building out scenarios for the class, I suggested using a Liquid Oxygen (LOx) spill on a freeway with the standard precautions that would follow this type of release. Discussing lessons learned when dealing with LOx, we identified the "standard" precautions necessary to ensure responder safety: 1) do not step on the frozen asphalt, it could explode, 2) do not drive over the frozen asphalt, the pressure could detonate under the weight of the vehicle, 3) do not allow LOx to come into contact with combustible materials, such as dried grass in the median, or hydrocarbons, such as diesel fuel, because it will spontaneously ignite resulting in a fast and intense fire and, 4) wait 30 minutes after the last frost is gone before stepping on the asphalt.

These precautions were based on traditional guidance and commonly accepted as accurate. We had all taught these precautions over the years as experienced hazmat instructors. Those of us with hazmat chemistry backgrounds were skeptical. None of us had really asked ourselves if these precautions had ever been scientifically tested and verified. Understanding that oxygen is a powerful oxidizer, would it really "ignite" hydrocarbons by simply coming into contact with them? Would the activation energy be sufficient to initiate combustion? I asked myself if it could really happen. Without testing theories, we were guessing and passing on our best guess as hazmat training. I decided it was time to test the "standard" precautions related to LOx response. We passed on using a LOx scenario for the new class.

Being at the NFA, I had the National Emergency Training Center Library as a tremendous resource to find the answer to my question. I spent hours researching the books, articles, and research papers in any way related to LOx. The sum of the precautions and "facts" I found regarding LOx were unsubstantiated and not independently verifiable. Most of the research was anecdotal and similar to Martel's *Chemical Risk Analysis*, "George Claude was seriously injured in 1903 after inserting a candle into liquid oxygen" (2000, pg. 242), or from the National Fire Protection Association (NFPA) 53, Annex D, which lists many types of LOx incidents but with the caveat, "NFPA cannot guarantee the accuracy of the reports" (NFPA 53, D.1.3). None of the 63 "incidents" in NFPA 53 Annex D were corroborated. Several vendors have produced Safety Data Sheets that state vague cautions such as LOx will violently oxidize organic material. The Compressed Gas Association pamphlet 2.7 on the handling and use of LOx systems in healthcare facilities states, "Stepping on or rolling equipment across a liquid oxygen spill can result in explosive ignition of combustibles." (CGA, 4.1.2.7).

I asked the students in my class at the NFA and members of the NFPA 470 Technical Committee if they had ever heard of any "explosions" when coming into contact with LOx. In my conversations, there were no experiences with ignition caused by pressure or any witnessed hypergolic reactions with LOx and combustibles. In my research efforts, I could not find a verifiable incident in the nation. Regardless, our testing at Utah Valley University (UVU) showed that when LOx saturates a combustible material *and then an ignition source is introduced* – violent and vigorous combustion occurs with increased burn rates, light, and heat. My review of the literature in fire service publications indicates that LOx spills have proven dangerous *in the presence of an ignition source*. Without an ignition source or when ignition sources were controlled, LOx did not pose a significant hazard beyond those associated with cryogenic liquids.

Our goal at UVU was to conduct field trials in a practical application to verify the aforementioned “dangers” of LOx. We conditioned several asphalt samples roughly 3 ½” square and 3” thick under LOx for a period of 30 minutes. We then subjected the frozen asphalt samples to a series of impact tests by raising the object to a specified height and dropping it onto the sample. The first two were a step and a stomp in a weighted rubber fire boot. We then struck samples with a 10 lb. sledgehammer, dropped a halligan (blunt headfirst), pipe wrench (headfirst), pike pole (point first), screwdriver (point first), and drove a fire engine over a larger conditioned asphalt surface and liquid pool of LOx. Forces were determined by subjecting a force plate device to these objects and digitally measuring the results of the force and calculating the height, pressure, and energy of the drop (see Table 1). None of the sources of mechanical impact or pressure caused any reaction in the asphalt after a minimum of five tests.

In 1970, the Apollo 1 capsule fire killed astronauts Gus Grissom, Ed White, and Roger Chaffe. They died in a near 100% oxygen enhanced atmosphere when a fire broke out and consumed them before NASA could affect rescue. NASA became keenly aware of the dangers of LOx. To better understand liquid and gaseous oxygen environments, field testing of LOx-soaked asphalt and mechanical impact was designed and conducted by NASA in 1973 on runway materials. To everyone’s surprise, mechanical impact on LOx-soaked asphalt detonated and blew the apparatus they designed 30 meters into the air and created a debris field 50 meters in diameter (Moyers, Bryan, & Lockhart, 1973, p.11).

At UVU, we wanted to replicate and verify NASA’s 1973 test using a scientific method. We were successful in replicating the NASA test, and so could endorse and validate their results.

Because we were able to replicate energetic reactions using our apparatus, the results of the UVU tests would also have validity. In 2017, the American Society of Testing and Materials (ASTM) created the *Standard Test Method for Determining Ignition Sensitivity of Materials to Mechanical Impact in Ambient Liquid Oxygen and Pressurized Liquid and Gaseous Oxygen Environments* (G86-17). ASTM codified the configuration of drop mechanisms used to test the sensitivity of materials to mechanical impact pressure. The apparatus designed and built at UVU was designed in compliance with the ASTM impact testing configuration (see Figure 1).

ASTM G86-17 states that any one reaction in 20 drops of the mechanism, (5%), indicates the tested material is “reactive.” We experienced five reactions in 20 drops of the plummet, (25%), and were able to duplicate those reactions again 60 days later (see Figure 2). The tested strata were composed of crumbled asphalt, on which an aluminum block was placed, then covered by additional crumbled asphalt before being immersed in LOx (see Figure 3). It was this configuration that exploded during the NASA test in 1973.

Dan DeMille and Brian Patchett at UVU captured the reactions using three high speed cameras (RED® Epic Dragon, GoPro® Hero 3, and a Phantom® VEO 1310L). A Sony® NX5U was used to capture real-time video and an additional high speed infrared thermal camera, courtesy of Teledyne FLIR®, was used to detect any thermal changes. These provided outstanding resolution and captured what the naked eye couldn’t see due to the speed of the reaction. In real time, we knew that a reaction had occurred when we heard what sounded like a gunshot. These audible reactions were heard by the research team and captured on video however, sound level data was not captured using audio measuring devices.

From these tests we concluded that mechanical impact could occur with the NASA configuration, however, after testing several control configurations, we found that a reaction would only occur using that unique strata. Our highways do not consist of crumbled asphalt covered with a one-inch-thick plate of aluminum which is then covered with more crumbled asphalt. These reactions should be viewed with that important context. No reaction occurred with solid asphalt blocks and LOx, crumbled asphalt and LOx, LOx alone, or an aluminum block and LOx. The aluminum was the surface to which the microscopic bubbles in the LOx were compressed by the 20 lb. plummet falling 43.3” when struck by the ½” diameter stainless steel striking pin.

Chemistry and physics faculty at UVU, Dr. Merrill Halling and Brian Patchett, in consultation with Eugene Ngai, a compressed gas expert, explained to me the likely ignition source. The reaction occurred as the plummet compressed the micro-bubbles in the LOx, almost instantaneously increasing the pressure and thus the temperature of the oxygen gas inside the bubble, then releasing that energy as adiabatic heat. Adiabatic heat differs from isothermal heat in that it cannot be dissipated. The pressure and heat serve as the ignition source for the hydrocarbons in the asphalt and the surrounding super-charged oxygen environment. The adiabatic heat principle is similar to what occurs in the cylinder of a diesel engine due to compression.

Interestingly, we subjected a used, soot-contaminated, leather firefighting glove and a brand-new glove with liners, both NFPA 1971 compliant, to the hammer test under LOx. The new leather glove had no reactions when struck six times. The contaminated glove had four reactions when struck eight times with the hammer, a 50% reactivity rate. Additionally, the contaminated leather was visibly damaged, and a loud report was heard with each of the positive reactions (see Figure 4). The new leather was completely intact after the tests.

To determine non-impact reactivity, we poured LOx directly onto an asphalt surface and dropped a road flare into the LOx pool. Other than some increased flare length and burning of the flare paper, no flaming combustion or explosion occurred. We poured LOx directly into 11 different hydrocarbon compounds commonly available and observed no reaction other than creating a frozen liquid. Saturated and unsaturated hydrocarbons, synthetic and natural compounds, alcohol-based products, various viscosities, and three liquids with flash points below 100° F did not react in contact with LOx. Likewise, combustible materials, such a cup of potato chips, oily and organic, did not react in contact with LOx. This having been said, when any of these combinations of hydrocarbon liquids or organic materials and LOx met with an ignition source, the combustion was rapid and intense. Combustion, influenced by LOx, is noticeably more rapid and vigorous than "normal" combustion occurring in our atmosphere of 21% oxygen.

The UVU tests also considered static electricity. We found a static spark to be an unreliable source of ignition. The spark was certainly hot enough (+1,800° F), however, the duration of the heat source, only milliseconds, may have been too brief to cause ignition. Arcing, caused by shorting out the positive and negative sides of a 12V battery, produced visible sparks and molten metal beads which immediately ignited any combustible fuel in LOx. Don't discount the arcing of a vehicle battery short circuit on the scene when controlling ignition sources.

Conclusions:

1. LOx soaked and frosted over asphalt will not react from the pressure associated with being stepped on, stomped on, driven over, or impacted by common response tools that are dropped on it, or the pressure from a direct sledgehammer strike.

2. LOx, spilled on asphalt, would be extremely difficult to ignite with common ignition sources found on the emergency scene. Heat sources added to LOx/asphalt combinations only increased the rate of vaporization of the LOx.
3. LOx will not react on contact with common combustibles, organic materials, flammable materials, flammable liquids, and other common hydrocarbons *unless an ignition source is introduced* – in which case the combustion will be violent and instantaneous.
4. The NASA explosion from the plummet test in 1973 was successfully replicated at UVU however, circumstances leading to the detonation of the LOx and asphalt configuration are unrealistic, i.e., the aluminum plate inserted in a crumbled asphalt stratum. Explosions could not be replicated using solid or crumbled asphalt and LOx alone, a much more likely configuration.
5. Practical testing of hazards associated with LOx should be expanded in the future.

Responders should take every precaution necessary when dealing with the primary hazards of LOx, namely embrittlement of surfaces in contact with the super-cooled liquid, high expansion ratios, and frost formations. Anytime LOx is mingled with combustible materials or flammable and combustible liquids, sources of ignition should be eliminated due to the possibility of extremely vigorous combustion. Any modifications to your agency's procedures should be evaluated carefully based on these conclusions.

Table 1. Drop testing data.

Test	Force (lbs.)	Pressure (psi)	Joules	Drop H (ft)	Area (in^2)
Hammer	434.6	983.3	36.88	2.52	.44
Stepping	187.4	6	47.05	1.5	31
Stomping	801.9	66.8	94.09	3	12
Halligan	356.2	158.3	45.7	3	2.25
Pipe Wrench	362.7	11,700*	13.14	4	.031
Screwdriver	14.9	765	2.09	7	.019
Pike Pole	455.4	14,970.9*	134.42	6	.03
Fire Engine	6,100	72.5*	13,774.8	n/a	84.15
NASA test	219.8	1,119.4	97.55	3.6	.196

* These pressures seem high, and the fire engine seems low due to the surface area contact in relationship to the weight of the object.

Figure 1. The UVU test apparatus replicating NASA and ASTM specifications.

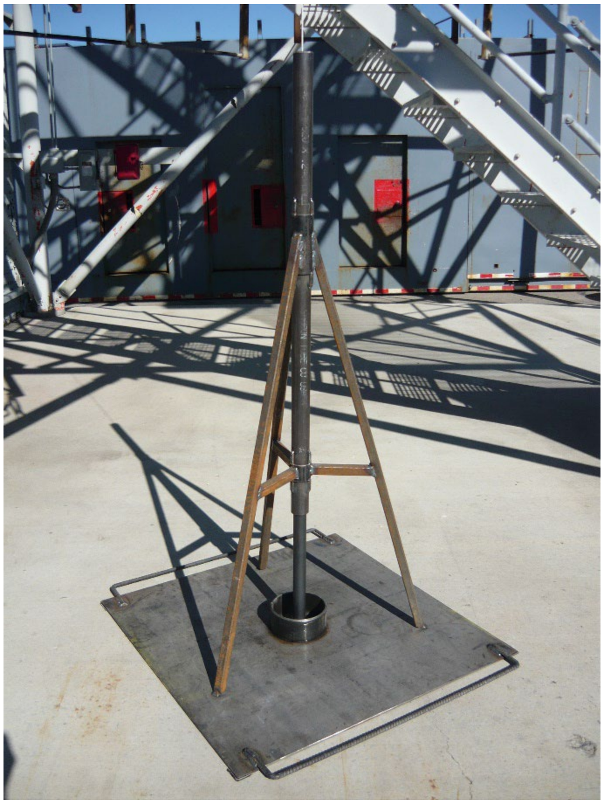


Photo credit: Eugene Ngai

Figure 2. October 21, 2021 UVU test #16 reaction.

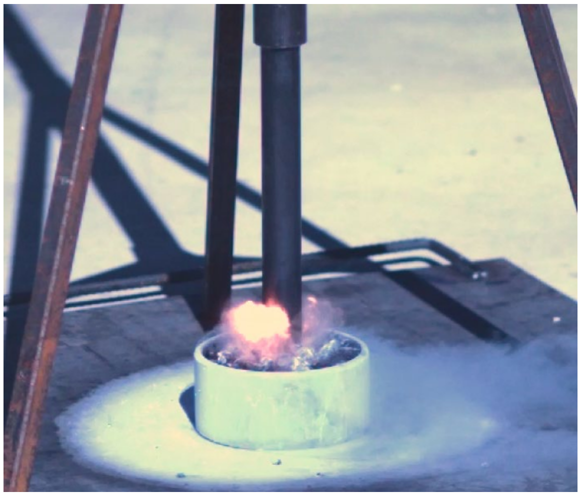
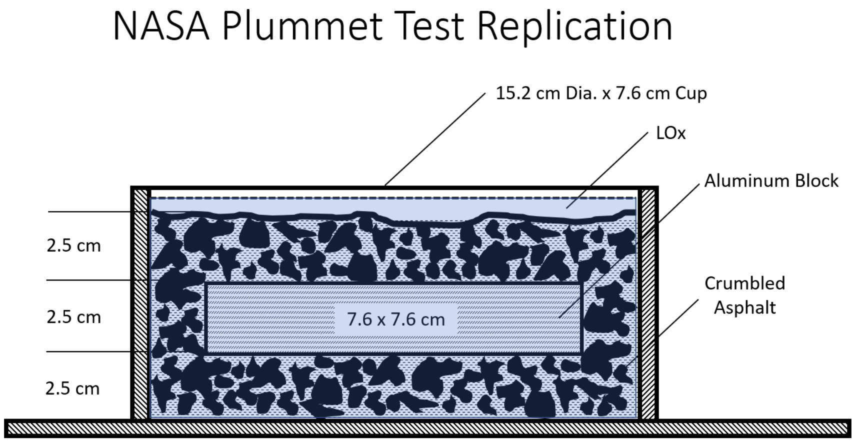


Photo credit: Brian Patchett

Figure 3. NASA configuration of the asphalt and aluminum strata.



Source: Author

Figure 4. The contaminated glove and the hammer test device.

Photo credit: Oscar DeMille

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