

Report to the University of Hawaii at Manoa on the Hydrogen/Oxygen Explosion of March 16, 2016

Report 2: Recommendations for Improvements in UH Laboratory Safety Programs

Prepared by the UC Center for Laboratory Safety, June 29, 2016

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Executive Summary: Report 2

This is an investigative report of the March 16, 2016 hydrogen/oxygen explosion at the University of Hawaii at Manoa campus (UH), in which a postdoctoral researcher lost her arm and sustained burns to her face and temporary loss of hearing. The postdoctoral researcher was working in a laboratory at the Hawaii Natural Energy Institute in the Pacific Ocean Science and Technology (POST) building.

This investigation was performed by the University of California Center for Laboratory Safety at the request of UH. The University of California Center for Laboratory Safety, in its capacity as an independent third party review team, was contracted to investigate the circumstances that led to this laboratory accident. The investigation included multiple visits to the site of the explosion as well as other UH research laboratories, examination of physical evidence and documents, testing of equipment remaining after the incident, testing of identical equipment, and interviews with UH staff and administrators, Environmental, Health and Safety Office (EHSO) staff, research faculty, graduate students and postdoctoral researchers. The report is separated into two sections. The first report presents conclusions regarding the technical details of the explosion as well as presenting an analysis of its immediate cause. This report also provides an in-depth review of the documentation, physical evidence recovered from the incident scene, a detailed analysis of possible causes and a summary of the forensic testing performed on the equipment involved in the accident. The second report contains recommendations for improvement of the UH research safety operations.

This second report contains recommendations for improvement of the UH research safety operations, while Report 1 presents the Investigative Team's conclusions regarding the technical details of the explosion and its immediate cause. These recommendations were developed by reviewing documents provided by UH, visiting several research laboratories, and conducting interviews with administrators, EH&S staff, research faculty, graduate students and postdoctoral researchers.

While it could be argued that the experimental circumstances in the POST 30 lab were unique, the Investigative Team concludes that serious deficiencies in the institution's approach to laboratory safety contributed to a lapse in proper risk assessment and lack of a culture of safety that ultimately led to the accident. The Investigative Team noted systemic problems pointing to an overall lack of effective safety oversight at the UH campus, including insufficient training in hazard recognition and risk mitigation, poor gas cylinder safety, a deficient laboratory inspection program, a dated and ineffective chemical hygiene plan, and inadequate standard operating procedures (SOPs). Of particular significance for this accident was an absence of formal risk assessment protocols in place for processes involving highly hazardous chemicals such as explosive gases. Some of the recommendations to UH specifically aim to mitigate underlying problems that contributed to the accident and include researcher training in hazard recognition and risk analysis, handling of fuel-oxidizer mixtures, reporting and handling of near miss events, and preparation of effective Standard Operation Procedures. Furthermore, this report contains general recommendations for the campus laboratory safety program, research community and leadership.

This report was written to serve as a direct call to action for researchers, administrators and EHSO staff not only at the UH, but at all institutions of higher education that conduct research. The recommendations and lessons learned contained herein should be understood and addressed at all universities in order to help prevent laboratory accidents.

Introduction and Goals of Investigation

The goal of this investigation was to establish the cause and underlying conditions leading to the explosion that occurred on March 16, 2016 in the Pacific Ocean Science and Technology (POST) building on the University of Hawaii at Manoa (UH) campus. Based on the investigation, the Investigative Team formulated recommendations to prevent accidents of this nature from occurring in the future. Identifying institutional root causes of this accident can ideally lead to improvements in the overall institutional commitment to and success of safety programs that aim to prevent future laboratory accidents. The recommendations presented in this report focus on academic research institutions, however, it is our hope that stakeholders in industrial settings that use explosive gases to advance current technology can also benefit from the findings in this report.

Weaknesses in UH Laboratory Safety Program

Examples of lapses in laboratory safety as observed by the Investigative Team are provided here to support the conclusions and recommendations for improving the university's laboratory safety program. It must be noted, however, that these are only illustrative examples and do not represent of all research laboratories on campus, nor was the investigative team able to perform a comprehensive review of all the safety practices that could be improved.

Laboratory Safety Inspections

Laboratory safety inspections by EHSO can be a critical component of an institution's safety program. Knowledgeable and critical inspectors can bring a wealth of knowledge and insight to individual research laboratories. Researchers in turn can inform inspectors of hazardous materials and processes and discuss safe methods for experimentation. That collaboration also ensures that inspections are focused on correcting deficiencies and implementing additional safeguards to ensure safe research rather than being punitive in nature. This collaborative aspect of safety inspections seems to be missing at UH. Researchers reported that inspectors sometimes even inspected labs when no researchers were present.

The last inspection conducted of the PI's laboratory in January 2016 only noted documentation issues. At that time the gas storage tank was already in place in the lab. If the EHSO inspector had taken the opportunity to engage in a discussion with the research staff, it might have become apparent that oxidizing and fuel gases were combined in a storage tank within the laboratory.

Another key aspect of safety inspections is follow-through. The UH EHSO safety inspectors send laboratory inspection reports to the PIs and request a response indicating that corrections were completed. However, the inspectors do not conduct follow-up inspections to confirm that corrections were made and that all issues were thoroughly addressed. Furthermore, best practice for inspection reports suggests that inspector feedback differentiate between general safety issues (e.g., updating a chemical inventory) that should be addressed within a few weeks and hazardous safety issues (e.g., unsafe chemical storage) that should be addressed within a few days or even immediately. The UH "Lab safety Inspection Checklist" does not indicate any prioritization of inspection items.

Furthermore, the UH “Lab safety Inspection Checklist” is not comprehensive. The Investigative Team recommends a more in-depth checklist that also includes a section specific to compressed gases. The current checklist only includes two questions relating to gas cylinder storage. There are no questions about safe use of gas cylinders.

Storage of items around shower/eyewash stations that blocked clear access was observed in some laboratories. This suggested that researchers were not following best safety practices in between laboratory inspections, that inspectors had not been sufficiently rigorous in their observations, and/or had not taken the time to educate researchers regarding the need to maintain clear access to emergency equipment.

Chemical Hygiene Plan

A Chemical Hygiene Plan (CHP) can be a working resource for laboratory safety as many universities incorporate it within an overall Laboratory Safety Manual, but often it is merely a collection of compliance documents. A CHP is an OSHA required document for research laboratories. As per OSHA regulations the “employer shall review and evaluate the effectiveness of the Chemical Hygiene Plan at least annually and update it as necessary.”¹ The UH CHP is largely comprised of a collection of compliance documents.² A revision was made to the UH CHP in 2013, but much of the material is still significantly dated. The main enforcer of the CHP as written is the Workplace Safety Committee, which apparently has not met in years. This duty was supposedly taken over by the Campus Safety Committee which has too broad a mandate as its oversight responsibilities include sidewalks and lighting and is not focused on safety in research laboratories.³

Many sections of the revised UH CHP are one-sided and/or incomplete. A 24-page section on numerical Permissible Exposure for air contaminants is probably not helpful to researchers. Overall, information on laboratory safety was fairly minimal. A section on recommendations for using hazardous chemicals in laboratories was prominently labeled “NON-MANDATORY”. There are sections on chemical spills under Lab Safety and Hazardous Material Management, but both are identical and are not sufficiently informative.

A companion to the UH CHP is the UH “Departmental Health and Safety Guide”.⁴ Some institutions have developed this type of document into a helpful “Laboratory Safety Manual” for researchers, but the UH document is fairly brief, lacks detail, and may leave researchers unsure of how best to approach safety regulations and practices. For example under “Principal Investigator Responsibilities” the Guide states:

“All Principal Investigators and supervisors are responsible for compliance with this policy as it relates to operations under their control. Specific areas of responsibility include employee safety training, identification and elimination of hazardous conditions and recordkeeping.”

Clear guidance from UH EHSO should be provided to researchers on updates to the CHP and how it should be accessed and used by researchers. The postdoctoral researchers in the lab where the

¹ 29 CFR 1910.1450(e)(4)

² Reference <http://www.hawaii.edu/ehso/lab/CHP.pdf> accessed 6/1/2016

³ Reference EHSO Interviews

⁴ Reference <http://www.hawaii.edu/ehso/industrial/HSG.pdf> accessed 6/1/2016

accident occurred presumably had electronic access to the latest campus CHP, but the printed lab copy was dated 2003 and did not show evidence of updates.

Hazardous Waste

The UH Hazardous Waste Program was revamped in recent years to meet a diverse range of needs.⁵ All researchers receive effective training and updated protocols are regularly emailed to everyone in the training database, so the program is exemplary. However, at the laboratory level there could be improvements in how researchers handle chemical waste. The Investigative Team observed examples of less than ideal waste management such as very old containers with the contents not clearly marked. Ideally, these would be addressed during laboratory safety inspections.

Safety Training

Safety education is a critical component of teaching researchers best safety practices and ensuring that the institution has a robust overall safety program. The UH campus has initial and refresher, in-class “Lab Safety Training” courses that cover general safety principles, but those should only be the starting point for researchers in an educational institution. Lab-specific safety education in the individual research laboratories is critical to ensure that researchers know the hazards and hazard mitigation plans of specialized techniques specific to their own research. The Investigative Team concluded that UH did not have policies and procedures in place to ensure that such training occurred for all researchers on a regular basis. Formal documentation for lab-specific training on specific hazards or hazardous processes was not observed.

Standard Operating Procedures

Given the generalized approach to campus-wide safety training, lab-specific safety training should be a mandatory requirement for all UH researchers. Beyond this requirement, Standard Operating Procedures (SOPs) should also play a critical role in ensuring that safe practices are followed in a laboratory when hazardous materials are handled or hazardous operations are performed. SOPs also play a vital role in training new researchers. The Investigative Team observed that the SOPs in some labs were inadequate, incomplete, or absent entirely. They did not present preventative barriers or emergency procedures. A sample SOP on the use of hydrogen gas merely stated:

“Hydrogen from cylinder is used to prepare gas mixture in gas tight containers. The gas is introduced into containers through PE tubing. Hydrogen gas must be released into fume hood via tubing or operated in fume hood. No flame is allowed in the room during the operation.”

UH researchers need better guidance from EHSO on how to write SOPs. Topics of this training should include: designing SOP content, promoting the routine use of SOPs, training researchers to use SOPs effectively, as well as documenting the use of SOPs within individual laboratories.

⁵ Reference EHSO Interviews

Personal Protective Equipment

Hazard controls are designed to provide a layered approach to control or prevent workplace hazards. While lower in the hierarchy of hazard controls than engineering or administrative controls, Personal Protective Equipment (PPE) plays a key role in employee protection when working with hazardous materials and equipment. The Investigative Team observed researchers not wearing appropriate PPE. It was also reported that the researchers did not consistently wear appropriate PPE in the laboratory where the accident occurred.⁶ Furthermore, despite using a highly flammable gas and pure oxygen, wearing flame resistant laboratory coats was not the norm. It should be noted that the postdoctoral researcher inquired whether a flame resistant lab coat was advisable in notes sent to the PI. The PPE section of the campus Chemical Hygiene Plan does not discuss a requirement for researchers to wear lab coats and does not mention flame resistant protective wear.

The Investigative Team wishes to point out that in many research laboratories, it is common for researchers to underestimate or not fully understand the chemical, biological and physical hazards present and hence underestimate their PPE needs. However, proper PPE designed to reduce exposure to the specific hazards present in the laboratory is vital to maintaining a safe work environment for UH staff and researchers.

Gas Cylinder Use

Since gas use was integral to the UH accident and since compressed gas cylinders present serious safety issues, several specific examples of improper gas and gas cylinder usage are detailed here.

1. Cylinders in the laboratories adjacent to POST 30 as well as in several laboratories located in different buildings, contained Teflon tape on the CGA connection threads to the cylinder valve outlet (Figures 1 and 2). This is a common safety problem noted at many user locations.⁷ Users mistakenly believe Teflon tape is required to seal the threads, which are straight rather than tapered, but it actually provides no advantage and might make the connection leak. Rather, Teflon tape serves as a lubricant to provide a better fit. Teflon tape should never be used for straight threaded connections such as CGA.

⁶ Reference PI and PD interviews

⁷ Appendix B



Figures 1 and 2: Gas cylinders with inappropriate use of Teflon tape.

2. A gas cylinder in POST 37 was improperly secured as shown in Figure 3. Instead of being firmly attached to the wall or an immovable object, it was secured to an adjustable shelf in a bookcase. Other examples of substandard cylinder restraint were observed in various labs.



Figure 3: Gas cylinder attached to an adjustable shelf in a bookcase.

3. A cluster of cylinders in the Post 30 lab showed two other common examples of improper gas cylinder restraint and storage. First, ten cylinders were grouped together and held by two cloth straps as seen in Figure 4. The typical gas cylinder clamp with cloth strap is only designed to support a single cylinder. Thus, a cluster of ten cylinders should be in a dedicated gas rack. Second, only cylinders of similar size should be secured together. Securing large and small cylinders together results in one cylinder size being secured at the wrong height.



Figure 4: Cluster of ten gas cylinders with shared restraint.

4. Another gas cylinder storage issue observed in several laboratories was storing cylinders without the valve protection cap in place or storing unused cylinders with regulators attached. These are not uncommon problems, but require vigilance by the laboratory safety inspectors and education of the researchers.
5. Problems with use of gas cylinders that were observed in several laboratories included inadequate gas tubing, unsupported, unlabeled gas lines (Figure 5), and leaking, aged regulators.
6. Use of plastic tubing such as polyethylene (PE) is not safe for hydrogen gas as it can diffuse through the wall. In addition, PE is a material that demonstrates poor compatibility in oxygen as it exhibits a low spontaneous ignition temperature and a high heat release when burning. Therefore it ignites easily as compared to other more compatible materials and exhibits a high ignition consequence. ASTM G04 recommends that non-metallic materials for oxygen systems be chosen that exhibit a compatibility opposite to PE (high spontaneous ignition temperature and low heat of combustion) and that ignition energy exposure for all non-metallic materials be minimized.⁸

⁸ ASTM International Committee G04 on Compatibility and Sensitivity of Materials in Oxygen Enriched Atmospheres

7. The gas storage tank contained an O₂ enriched mixture and was not properly cleaned as combustible oil was found on the threaded fittings. OSHA defines O₂ enriched to be concentrations greater than 23.5%.



Figure 5: Polyethylene tubing hung from the drop ceiling and only marked with colored tape.

General Recommendation: Use of clamps with cloth straps should not be used for restraint of gas cylinders for the following reasons:

1. The ability of the clamp to hold the weight of the cylinder will depend on how tightly the clamp is applied and to what it is attached.
2. Older style clamps only have a single screw thus providing only limited support.
3. The cloth strap can burn and thus provide no support in a laboratory fire.
4. Researchers will often secure multiple cylinders with a single clamp with strap, but it is only designed to support a single cylinder.

Therefore, gas cylinders should be restrained by chains secured to a wall with Unistrut steel bars. In earthquake areas there should be two chains placed at $\frac{1}{3}$ and $\frac{2}{3}$ height on the cylinder.

Recommendations for Safe Research

Training in Hazard Recognition and Risk Assessment

Research involving highly hazardous substances and processes requires the researchers to be trained in knowing the specific characteristics of the hazards and formally assessing the risk they take when working with the hazard. Hazard recognition raises awareness about the hazard and the activity that involves it and risk assessment mitigates safety challenges associated with the hazard. The American Chemical Society (ACS) has published guidelines on *Identifying and Evaluating Hazards in Research Laboratories*⁹, which are helpful for developing training on and implementation of hazard recognition and risk assessment in academic institutions. The guidelines also provide examples for hazard recognition, and illustrates how risk assessment can be integrated into a SOP.

Elements of hazard recognition include:

- Type of activity involving the hazard
- Researcher experience level
- Hazard type
- Potentially hazardous derivatives
- Potentially hazardous reactions
- Incompatibility with other chemicals
- Contributing factors (i.e., temperature, pressure)
- Appropriate storage conditions
- Waste management
- Potential equipment failure
- Recognition of changes to the experimental protocol
- Type and routes of exposure
- Knowledge of exposure limits
- Recognition of exposure symptoms

Elements of risk assessment include:

- Knowledge of the hazard's characteristics
- Sufficient hazard-specific training
- Detailed Standard Operating Procedure
- Concentration or amount of hazard used
- Knowledge of the hazard's worst case reaction
- Identification of the correct work environment
- Identification of protective barriers and PPE
- Identification of residual risk after implementing controls
- Response plan in case of an unexpected event
- Response plan in case of a near miss
- Emergency procedure

⁹ Identifying and Evaluating Hazards in Research Laboratories, American Chemical Society, 2015, <https://www.acs.org/content/dam/acsorg/about/governance/committees/chemicalsafety/publications/identifying-and-evaluating-hazards-in-research-laboratories.pdf>

- Emergency reporting structure
- Evaluation of changes to the experimental protocol
- Implementation of regulatory requirements
- Supervisory approval
- Safety committee approval

Facility

Work with highly hazardous substances or processes should be conducted only in facilities and with equipment that are designed to provide a sufficient protective barrier between the hazard and the researcher. Depending on the type of research, some operations involving hydrogen must be performed in explosion proof facilities located away from research buildings.¹⁰ This is often not a practical solution for many institutions; it is therefore critical to perform a well documented and reviewed risk assessment prior to engaging in research containing explosive gases. Unlike other explosive gases, hydrogen is very light. Thus, accidentally leaked hydrogen will accumulate at the ceiling where it may reach explosive concentrations. It is important that any lab housing compressed gas cylinders be properly ventilated with strategically located exhaust air pickup and makeup air points to prevent dead spots where pocketing can occur. Electronic hydrogen detectors are very sensitive devices and can be set to sound an alarm when a leak is detected. These devices could be installed at the ceiling above the gas cylinders, above the use point, and at the exhaust ventilation duct.

Standard Operating Procedures

Work with highly hazardous chemicals requires clear established procedures that are uniformly implemented by all individuals throughout the entire organization who are working with the same hazard. These procedures should take into account the severity of the hazard and aim to minimize the risk of an incident. They should include the following:

- Standard operating procedures with a step-by-step breakdown of the experiment including a hazard analysis dependent on the hazard concentration, a description of the amount, concentration, and circumstances in which the chemical is known to create a hazardous event (e.g., toxicity, explosion, fire, etc.), the equipment to be used with a justification for safety selection, appropriate safety barriers and other worker protection (PPE), and emergency procedures in case of an unforeseen event. SOPs involving highly hazardous chemicals or processes should be reviewed by a committee that includes experts in the field.
- Researchers should be trained and demonstrate proficiency in performing the SOP.
- A Management of Change Amendment for highly hazardous materials or processes is defined as a written amendment describing any planned change to the SOP. The management of change pertains to scaling-up, changes in physical properties such as temperature or pressure, change of

¹⁰ NFPA 55: Compressed Gases and Cryogenic Fluids Code

equipment, and/or change of personnel. The amendment should be reviewed by a committee that includes experts in the field.

- A regular unannounced walk through should be done by a safety committee member to emphasize the importance of safety and to gain a realistic impression of ongoing operations. The walk through could target one lab group per month.
- Stop work protocols require the researcher or PI to cease all work involving a highly hazardous chemical or process in the event of a near miss or otherwise observed highly unsafe situation. Anybody directly or indirectly involved or observing the Near Miss event should be empowered to call for a stop work protocol; this extends from an undergraduate student to the PI. Emergency protocols should be in place to mitigate unsafe situations immediately. Stop work may extend beyond the lab to the entire facility with similar operations. An immediate critical review of a near miss event is important to discover underlying problems. The near miss review should be initiated by the laboratory involved and reported to their campus safety program including the appropriate safety committee for further discussion. It is important to publicize near miss events involving highly hazardous materials and processes as learning opportunities for other laboratories.

Near Miss Events in Research Laboratories

A *near miss event* is an unplanned and unexpected event that does not result in any injury, illness or property damage, however could have had the potential to do so. In the near miss event that occurred just prior to the more serious explosion in POST 30, the force of the explosion was contained within the pressure vessel. The postdoctoral researcher was not protected in any way had the explosion not been contained; there was no safety barrier in place and the postdoctoral researcher was not wearing any face and eye protection nor was she wearing a lab coat. It was reported that as a general practice, “Eye protection was used occasionally.”¹¹ The PI recommended wearing gloves at all times to prevent static charge transfer, but this was not followed regularly.¹² Even though it was clear that an explosion had occurred, none of the researchers related this near miss event to the similar hazards posed by other ongoing experiments involving even larger quantities of the gas mixture. *A near miss event involving any type of highly hazardous chemicals or processes should have automatically triggered an immediate shutdown of all operations. It also should have triggered a thorough investigation of all procedures.* This did not happen.

Why did this near miss event fail to attract the serious attention it deserved? It seems that the answer to this question uncovers a deeper, wider reaching problem relating to how researchers in academic institutions generally perceive risks when identifying potential hazards within their experiments. Research has shown that if a hazard is voluntarily chosen, controllable, and perceived to be familiar it is considered to be less risky.¹³ Typically, researchers choose whether or not to work with explosives or other highly hazardous compounds, agents or processes. Once trained, the hazard often becomes a routine part of their experimentation and researchers perceive themselves to be experts in handling the hazard.

¹¹ Postdoctoral lab-colleague and PI interview

¹² Postdoctoral lab-colleague and PI interview

¹³ Risk Perception: Theories, Strategies, and the Next Steps; Campbell Institute, National Safety Council, <http://www.nsc.org/CampbellInstituteandAwardDocuments/WP-Risk%20Preception.pdf>, accessed 6/1/2016

Perceived familiarity can shift the awareness level from cautiousness to complacency. There are prominent examples of complacency when handling highly hazardous substances such as at the Centers for Disease Control and Prevention (CDC) where employees were accidentally exposed to ebola and anthrax, and a dangerous strain of influenza virus was accidentally shipped to another lab.¹⁴

Regular discussions about Near Miss and Lessons Learned events should be conducted to remind every researcher and administrator of the risk involved when working with highly hazardous substances or processes.

Use of Fuel-Oxidizer Mixtures

Mixing a flammable gas (hydrogen, methane, etc.) with an oxidizer gas (oxygen, chlorine) is an inherently unsafe activity. In the worst-case scenario it can result in a reaction leading to a detonation which can be fatal and cause significant damage. Even mixtures at 1 atmosphere pressure can cause severe damage. In 2011, an incident at the University of Missouri involved hydrogen and air concentrations in an anaerobic chamber that accidentally reached the flammable range. The explosion critically injured the researcher who was working with the chamber and did considerable damage to the laboratory.

The POST 30 incubators and bioreactors contained explosive gas mixtures at pressures of up to 117 psig. Even after the incubator or bioreactor pressure is vented a hazard still exists. When the researcher opens the incubator or bioreactor, the mixture could ignite due to electrostatic discharge (ESD) or metal friction. The explosion could burn the researcher or cause hearing loss. If the mixture is not vented to a safe location it can ignite and the flame velocity of a stoichiometric mixture of H₂ and O₂ can approach a speed of 11.75 m/sec.¹⁵ This speed exceeds the typical gas vent velocity and the flame front will propagate back into the incubator or bioreactor causing the mixture to explode. Ignition could also have occurred while filling the FEP gas sample bag since static electricity is a very common problem with plastic films.

If an explosive gas mixture is pressurized the danger increases. Depending on the concentration, an overpressure of up to 20 times the initial pressure can be created. O₂ rich mixtures are more energetic than a stoichiometric concentration. A stoichiometric concentration of H₂ and O₂ is estimated to have a TNT equivalency of 3.45 while in an abundance of O₂ it can be up to 30.9.¹⁶

Even gas mixtures that have flammable or oxidizer gas concentrations too low to propagate a reaction can be dangerous at some point if not prepared properly. For example, preparation of a 70% H₂ 30% air mixture in a container would be in the flammable region for a period of time if the air was placed in the

¹⁴ <http://www.usatoday.com/story/news/nation/2014/12/24/ebola-error-exposure-lab-atlanta/20878521/>

¹⁵ Deliverable D113 Initial Guidance for Using Hydrogen in Confined Spaces - Results from InsHyde, NCSRD and INERIS, Jan 30, 2009

¹⁶ Werley, Barry L., Hansel, James G., Buchter, William C., "TNT Equivalency Concepts", Spring 1998 ASTM G-4 Seminar, April 1998, Atlanta, GA

container first. The mixture would pass through the flammable region as the H₂ flows into the container. If the H₂ was added in the container first it would never pass through the flammable region.¹⁷

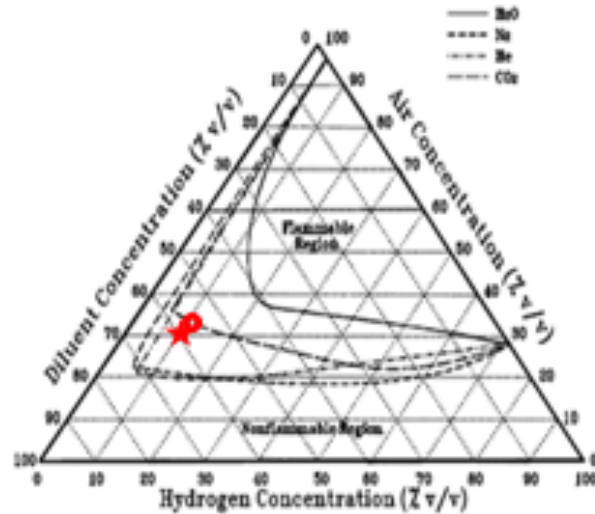


Figure A2.2
Effects of N₂, He, CO₂, and H₂O Diluents on Flammability Limits of Hydrogen in Air at 101.3 kPa (14.7 psia) (The effects of N₂, He, and CO₂ are at 298 K (77 °F) and H₂O is at 422 K (300 °F))

Figure 6: Diluent gas (N₂, He, CO₂ and H₂O) effects on flammability of hydrogen in air mixtures.¹⁸

The flammability diagram above shows the effect of N₂, He, CO₂ and H₂O as diluent gases in hydrogen and air mixtures. The effect of N₂ and He appear to be similar while CO₂ reduces the flammability range of the mixture. The star is located at 10% H₂, 30% air, 60% diluent gas. In N₂ and He the mixture is in the flammable range while with the same concentration of CO₂ it is not. The circle is located in the area when 10% H₂ becomes flammable in CO₂: 10% H₂, 35% air, 55% CO₂.

Dynamic blending of the gases by using flow meters or mass flow controllers would eliminate this problem as the gas mixture never enters the flammable region. This type of gas mixing is commonly used in laboratories that include gases in their research projects. It was also used to supply mixed gases to a second bioreactor in the POST 30 lab.

Due to the danger of potentially creating an explosive gas mixture when preparing a low concentration fuel and oxidizer gas mixture (e.g. 1% Methane in Air), the compressed gas industry follows a strict protocol. The European Industrial Gas Association (EIGA) developed the standard, "Safe Preparation of Oxidant-Fuel Gas Mixtures" in February 2004, and it was adopted by the Compressed Gas Association (CGA) as CGA Standard P-58. These standards outline seven basic principles that must be adhered to

¹⁷ Cox, M, "Explosive Potential of Gas Mixtures Commonly Used in Anaerobic Chambers". Infectious Diseases 1997;25 (Suppl 2):S140, The University of Chicago.

¹⁸ Coward, H.F. and Jones, G.W. "Limits of Flammability of Gases and Vapors", Bureau of Mines, Bulletin 503, 1952, N70-74476, AD 701575

when making these types of mixtures.¹⁹ Preparation of these mixtures are also limited to approved gas facilities.

Recommendations for work with explosive gas mixtures:

1. Written instructions shall be provided
2. Equipment and facilities shall be properly designed
3. Written instructions shall be prepared by competent staff using recognized data
4. Personnel shall be trained
5. Intended cylinder content shall be identified before filling
6. Supply gases and cylinders shall be controlled
7. Facilities and procedures shall be audited

Despite these strict protocols mistakes periodically occur, sometimes with devastating results. As recently as October 2015 a cylinder suspected of containing an explosive gas mixture exploded and killed a chemist in the laboratory and injured 7 others in a Singapore gas facility.²⁰

There is a need for rigorous safety evaluations for research with explosive gas mixtures. Evaluations should address:

Potential Causes of Explosions:

- Electrical hazards (defective equipment, defective electrical installations)
- Equipment hazards (not rated for use with explosive gas)
- Electrostatic charges
- Rapid pressure changes or flow effects

Preventative Measures:

- Calculation of the potential explosive force to determine level of protection
- Detailed and thorough Standard Operating Procedures
- Specialized training on highly explosive materials
- Use of well-designed, hazard-rated equipment (intrinsically safe as a minimum rating)
- Grounding and bonding of equipment
- Blast barriers
- Engineering controls for highly explosive materials
- Administrative controls limiting access
- Outside review of procedures, equipment and engineering controls

¹⁹ CGA Standard P-58, "Safe Preparation of Compressed Oxidant-Fuel Gas Mixtures in Cylinders"

²⁰ <http://www.todayonline.com/singapore/one-dead-7-injured-fire-tanjong-kling-road?page=1>

Recommendations for the Campus Laboratory Safety Program

The UH Manoa campus has over 300 principal investigators with over 500 laboratory rooms. The laboratory safety program is housed within the Environmental Health and Safety Office that reports to the Vice Chancellor for Research. It is composed of the 22 individuals as shown on the organizational chart below (Figure 7). This reporting structure provides an excellent connection between research and safety programs. Some universities place their EH&S departments under a Vice Chancellor for Facilities which unfortunately can place a barrier between the research and safety enterprises. As detailed within this report, safety must be a process integrated into research practices and not treated as a collection of compliance regulations to be satisfied.

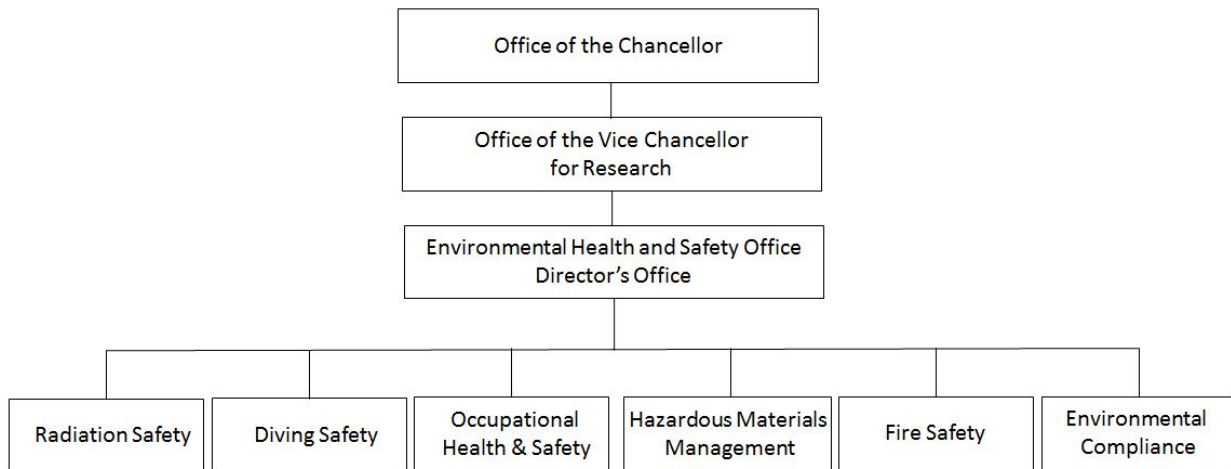


Figure 7: Organization Chart for UHM Environmental Health & Safety Office.

Although a complete review and audit of Environmental Health and Safety program was not conducted as part of this investigation, it was apparent that a number of improvements could be made to the EH&S program based upon the interactions and observations conducted during our visit. A number of recommendations for improvement are listed here.

1. ***UH should formulate a unified Research Safety Program.*** This would involve incorporating EHSO staff supporting research operations into a single operational unit of EHSO that focuses on Research Safety. This model has been successfully used at a number of universities across the nation in order to make the most efficient use of resources and to provide effective health and safety services to complex research environments.
 - a. The recommended programs that should be included or combined into a single program include the laboratory safety program, radiation safety program, biosafety program, and

elements of the Occupational Safety and Health program such as chemical exposure monitoring, carcinogen use and laboratory fume hood monitoring.

- b. Currently two individuals, the Chemical Hygiene Officer and Industrial Hygiene Technician within the UH EHSO directly support the research operations and provide safety training. Additional staff is needed to provide adequate oversight and support to the laboratories.
 - c. UH lacks a Learning Management System to integrate researcher training.
 - d. EHSO lacks IT support to upkeep their website with pertinent safety information.
2. ***UH should hire highly qualified individuals for EHSO positions within the Research Safety unit.*** It is advisable for individual with research experience in the domains for which they are responsible to inspect and provide consultation. Ideally individuals with board certifications such as Certified Industrial Hygienist or Certified Safety Professional should also be recruited.
 3. ***Laboratory inspections should be carried in the presence of laboratory researchers.*** The laboratory operations and inspections should always be conducted with members of the laboratory present. It is not enough to review the equipment and setup of the laboratory. Lack of interaction with the laboratory staff limits the effectiveness of conducting a laboratory safety inspection. It is also important to assess employee understanding of how to use this equipment safely and to recommend additional safeguards, protocols, and trainings that should be in place to ensure employee safety.
 4. ***Laboratory inspections by EHSO should be performed at a time when research is being actively conducted within the laboratory setting.*** Inspections can provide an educational experience for both researchers and inspectors when done collaboratively. Researchers can learn how to perform research in compliance with safety regulations and best practices. Inspectors can learn how hazardous materials are being used in the laboratory and make suggestions for safety improvements. One best practice to encourage active participation in safety inspections by researchers is for each research laboratory to have a designated Laboratory Safety Officer that acts as the contact for EHSO inspectors and can accompany inspectors on inspections of their laboratory operations.
 5. ***Laboratory inspections by EHSO should be more rigorous and thorough.*** It is recommended that the UH "Lab Safety Inspection Checklist" be revised with greater detail for each inspection category and that items be grouped so that serious hazards are addressed within a shorter time frame. Furthermore, there should be follow-up to ensure that complete corrective actions have been taken and PIs need to be held accountable if there is a lack of compliance. Finally, attention should be paid to how hazardous materials are used in research processes in addition to how they are stored. This requires knowledgeable and inquisitive EHSO staff.

Recommended Checklist Sections for Laboratory Inspections:

- Documentation
- Training
- Hazard Communication
- Emergency Information
- General Safety
- Fire Safety
- Personal Protective Equipment
- Housekeeping
- Chemical Safety
- Gas Safety
- Electrical Safety
- Mechanical Safety
- Fume Hoods and Biosafety Cabinets
- Hazardous Waste

6. ***UH should complete a thorough revision of the Chemical Hygiene Plan and the Health and Safety Guide.***²¹ A Chemical Hygiene Plan (CHP) along with a Health and Safety Guide or Campus Laboratory Safety Manual are important safety resources for laboratory researchers. They not only present compliance regulations, but also present best practices for working with hazardous materials and equipment. They should aim to move the campus from a culture of compliance towards a more comprehensive culture of safety wherein safety is an integral part of conducting research. It is recommended that these UH documents should be revised by a joint team of EHSO and research faculty to achieve these goals.
7. ***EHSO should work with researchers to identify hazardous operations and develop effective SOPs.*** It is recommended that UH ESHO revise all aspects of SOPs. Researchers need better guidance and assistance to identify what processes need SOPs, what information should be presented within an SOP, how SOPs should be developed, how new researchers should be trained on SOPs, how experimental changes should be managed within an SOP, and how SOP understanding and use should be documented.
8. ***EHSO should develop a mechanism to address risk assessments.*** The root cause of this incident was a failure to recognize the extreme hazards presented by a gas tank filled with an explosive gas mixture. It is recommended that UH EHSO develop a researcher specific training that covers the following topics: hazard identification, hazard analysis, risk assessment, and risk mitigation. UH EHSO should provide researchers with technical assistance for development of and implementation of risk assessments. This is a very challenging, but critical, task that can have a significant impact on laboratory safety. For research that carries a high degree of risk, a Research Safety Committee approval should be required before such experiments can be conducted.

²¹ This was also a recommendation of the CSB to following the incident at Texas Tech University.

Recommendations for Campus Research Faculty and PIs

The Investigative Team has several recommendations directed towards faculty and PIs at UH. Several of these arose as a result on interviews with both researchers and EHSO staff during the site visit.

1. **Take an active role in changing safety practices at UH.** Faculty expressed trepidations that the University would impose broad requirements on faculty and research groups as a result of the incident that do not directly impact actual laboratory safety. The best way to avoid that outcome is for faculty to be engaged with both the campus administration and EHSO to guide changes. For example, faculty should lead a Chemical and Physical Safety Committee that can set campus policies, guidelines and training requirements regarding safety as well as direct guidance to EHSO. This committee should include representation from EHSO (e.g., the Chemical Safety Officer) to ensure a collaborative process between researchers and safety experts; but the committee composition should primarily consist of faculty. As another example, faculty could be involved in revisions of the Chemical Hygiene Plan and Laboratory Safety Manual to make them effective safety tools for research students rather than a collection of out-dated or uninformative regulations.
2. **Demand that the campus administration provide the resources to build a strong and effective laboratory safety inspection program.** Faculty are experts in their areas of research, but are often intimidated and confused by the myriad of safety regulations, codes, jargon, and trainings that apply to their research. Researchers need access to knowledgeable safety professionals to give them advice on improving the safety of their experiments. Finally, cursory laboratory inspections can bypass true hazards, and furthermore, fail to establish a collaborative relationship between EHSO and the research community. To address issues such as these, highly trained, and effective people must be hired.
3. **Support faculty, and new faculty in particular, not only with general lab safety training, but with tools for integrating a culture of safety in their research.** If established faculty are challenged by the demands of a rigorous laboratory safety program, then new faculty find it even more daunting on top of everything else they are doing to establish their careers. Just recently, as a consequence of the accident, the HNEI created a document, “HNEI Lab Safety Walkthrough” for faculty. The purpose of the guide is:

“... to assist principal investigators, supervisors, employees, students and all other lab personnel to identify and comply with the available safety resources, required training, and documentation required for safe operation of HNEI on-campus and off-campus laboratories and facilities.”

This excellent resource should be used by EHSO to support faculty in laboratory safety across the UH campus.

4. **Campus administration, EHSO, and researchers should work toward a robust Culture of Safety wherein safe practices are integrated into daily work practices.** Safe laboratories are the result of concerted efforts at every institutional level which looks well beyond mere compliance with safety regulations. A Culture of Safety allows free communication between researchers, PIs and institutional leadership sharing the same expectations of safety outcomes

and experimental results. The institution's leadership should openly display a keen interest in keeping researchers safe.

Ideally, regulatory compliance is not the end goal of a safety program, but rather the outcome of a strong culture of safety in the workplace.

One example of a best practice that was observed by the Investigative Team in this instance was inclusion of safety performance in the selection and recruitment process for the postdoctoral researcher by the PI. It was noted that the concept of evaluating a candidate's qualifications in safety as part of the screening process was a good, but uncommon, practice.

Recommendations for Campus Leadership

There are several recommendations to Senior Campus Leadership. It is reassuring to note that at the time of this report, the University of Hawaii at Manoa has already begun implementation of initial recommendations made by the Investigative Team during their onsite visit.

1. **Statements should be issued from the highest level within the University reinforcing the importance of conducting all research safely.** Chancellor Robert Bley-Vroman issued such a statement on April 4, 2016 in a letter to the UH community. In it he stated that is *"it important that we as a community reaffirm our commitment to a culture of safety in each and every research and teaching laboratory on our campus. Toward that end, I want to reemphasize the importance of ensuring that laboratory safety protocols and training are up-to-date, including ensuring that all equipment is suitable and meets relevant requirements and that emergency access to all laboratories is readily available."*
2. **Campus administrative and EHSO leaders should review the U.S. Chemical Safety and Hazard Investigation Board report on the 2010 Texas Tech University laboratory explosion²².** The explosions in Texas and Hawaii were remarkably similar in the institutional issues involved. Thus, the key problems summarized in the CSB report are directly applicable at UH:
 - Laboratory safety management for physical hazards
 - Hazard evaluation of experimental work in research laboratories
 - Organizational accountability and oversight of safety
3. **Campus administrative and EHSO leaders should review and determine how the Association of Public and Land-Grant Universities (APLU) report *"Guide for Implementing a Safety Culture in Our Universities"*²³ could be utilized to improve the research safety**

²² <http://www.csb.gov/texas-tech-university-chemistry-lab-explosion/>

²³ <http://www.aplu.org/library/safety-culture/file>

programs at UH. The Guide has resources specifically designed to assist research universities in strengthening laboratory safety:

- Call to Action
- Core Values of Safety
- Recommendations to Strengthen and Promote a Culture of Safety
- Analysis of Recommendations with Key Resources
- Toolbox for Implementing a Culture of Safety
- Actions that Support a Culture of Safety

4. It is strongly recommended that a faculty-led safety committee be formed to address safety needs relating to chemical and physical hazards.

As of the writing of this report, the University of Hawaii has established such a committee. This committee should be charged with developing the criteria used to identify high-hazard experiments and those experiments should be brought forward to this committee for their review and oversight. Specifically included in this list of high-hazard experiments should be work with explosive gas mixtures. It is unlikely that this accident would have occurred if other members of the Hawaii Natural Energy Institute had reviewed the experimental protocol. It is the Investigative Team's belief that other researchers would have raised concerns about the experimental setup and, more importantly, correctly assessed the degree of risk inherent in the creation and storage of hydrogen/oxygen.

This committee could help UH and its researchers make risk-based decisions regarding controls needed to safely conduct high-hazard research. The committee would be able to provide guidance on special training needed by graduate students and postdoctoral researchers working in such research areas.

The committee could help establish a campus PPE policy, guide the EHSO on ways to ensure that laboratory researchers are wearing appropriate PPE, and advise the campus administration on possible funding needs to provide PPE.

The committee could be involved in revision of the campus Chemical Hygiene Plan to make it an effective tool for both researchers and EHSO to create and maintain safe research laboratories.

- 5. It is recommended that UH develop a process by which near-misses are promptly reported to EHSO and/or a safety committee that can investigate and propose changes in protocol or other ways to mitigate hazards for a research experiment²⁴.** We believe that an effective incident investigation program should cover all incidents including those that don't result in injuries or damage. Identifying and correcting these hazards will improve the culture of safety and could prevent more significant accidents like the one that took place this March. In order to be effective, near miss reporting must not result in punitive actions.

²⁴ This was also a recommendation of the CSB to following the incident at Texas Tech University.

Conclusions

As discussed in Report 1, an in-depth inspection of the accident scene, interviews with witnesses and emergency response personnel, as well as outside testing of the equipment used in the experiment, enabled the Investigative Team to conclude that the most likely immediate cause of the accident was an electrostatic discharge between the postdoctoral researcher and the gas storage tank which led to this laboratory explosion. However, the overall underlying cause of the accident was failure to recognize and control the hazards of an explosive gas mixture of hydrogen and oxygen. Given the low energy required for ignition of the gas mixture and the variety of scenarios that could provide that ignition energy, a detonation of the explosive gas mixture was bound to occur.

The safety program at UH was not designed to assist researchers in identifying hazards, making risk assessments, and controlling laboratory hazards. An effective laboratory safety program needs to be thorough, consistent and sustained within the research institution. Firm guidance and support must be provided by campus leadership. It must be embraced at every level of the institution from the Chancellor down to beginning students or newly hired staff. Most importantly, an effective laboratory safety program must be integrated into the research process rather than being an annual housekeeping exercise conducted days before an anticipated annual laboratory inspection. The tragic accident at UH on March 16, 2016 should engender dramatic improvements across the UH safety program in order to prevent another major accident.

The Investigative Team would like to thank the leadership of UH for their assistance, openness, and responsiveness during this investigation. In particular, we would especially like to recognize Dr. Michael Bruno, Vice Chancellor for Research, and Dr. Brian Taylor, Dean of the School of Ocean and Earth Science and Technology, for their outstanding leadership after the incident. There were many helpful staff who assisted in the investigation, but Hans Nielsen, EHSO Training Coordinator, should be commended for his remarkable responsiveness and professionalism.

Recommended Reading

Texas Tech University Laboratory Explosion, Case study by the Chemical Safety Board, 2010, http://www.csb.gov/assets/1/19/csb_study_ttu_.pdf

Guide to Implementing a Safety Culture in Our Universities, APLU Task Force on Laboratory Safety, 2016, <http://www.aplu.org/projects-and-initiatives/research-science-and-technology/task-force-laboratory-safety/about-lab-safety-tf.html>

Safe Science: Promoting a Culture of Safety in Academic Chemical Research, Board on Chemical Sciences and Technology, 2014, <http://dels.nas.edu/Report/Safe-Science-Promoting-Culture/18706>

Identifying and Evaluating Hazards in Research Laboratories, American Chemical Society, 2015, <https://www.acs.org/content/dam/acsorg/about/governance/committees/chemicalsafety/publications/identifying-and-evaluating-hazards-in-research-laboratories.pdf>

NFPA 45: Standard on Fire Protection for Laboratories Using Chemicals, 2015 Edition

http://catalog.nfpa.org/NFPA-45-Standard-on-Fire-Protection-for-Laboratories-Using-Chemicals-2015-Edition-P1177.aspx?order_src=C900&gclid=CjwKEAjwtLO7BRDax4-I4_6G71USJAA6FjN1CmByQUmqG2c3WkxhhRFWVuUV-fHa1gdCEOAUbXLxQxoCGyHw_wcB

APPENDICES

Appendix A: Initialisms and Acronyms

AIT	Autoignition temperature
APLU	Association of Public and Land-Grant Universities
ASME	American Society of Mechanical Engineers; ASME certification assures that a the design, fabrication, assembly, and inspection of boiler and pressure vessel components are done according to ASME specifications. The ASME stamp symbolizes quality control assures reliable allowable pressures.
ASTM	American Society for Testing and Materials
CDC	Centers for Disease Control and Prevention
CHP	Chemical Hygiene Plan
CGA	Compressed Gas Association
CSB	Chemical Safety Board
DOT	Department of Transportation
EHSO	Environmental Health & Safety Office
FEP	fluorinated ethylene propylene
GC	gas chromatography
GHS	Global Harmonized System
HFD	Honolulu Fire Department
HIOSH	Hawaii Occupational Safety and Health
HNEI	Hawaii Natural Energy Institute
ICF	International Fire Code
Investigative Team	The four investigators representing UCCLS for the investigation
MAWP	Maximum Allowable Working Pressure
mJ	Millijoules

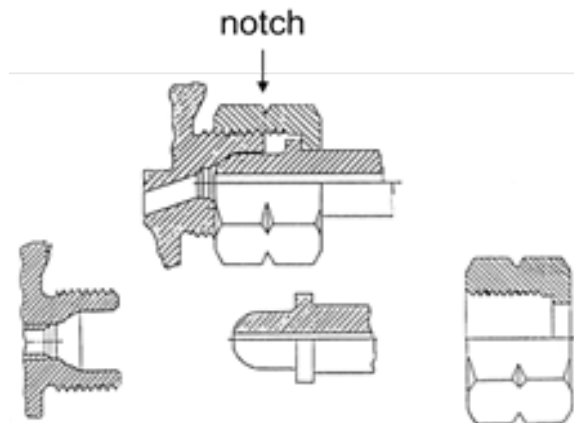
NEC	National Electric Code
NFPA	National Fire Protection Association
NIST	National Institute of Standards and Technology
NPT	National Pipe Thread
PE	Polyethylene
PHA	polyhydroxyalkanoate
PI	Principal Investigator
POST	Pacific Ocean Science and Technology building
POST 30	basement laboratory room 30 in Pacific Ocean Science and Technology building
PPE	Personal Protective Equipment
PRD	Pressure Relief Device
psia	Pounds per square inch absolute is the pressure is relative to a vacuum rather than the ambient atmospheric pressure. Psia = 0 is a vacuum. Atmospheric pressure at sea level is about 14.7 psi and this is added to any pressure reading made in air at sea level. The mixture calculations by the researchers to be accurate were based on psia.
psig	Pounds per square inch gauge, indicating that the pressure is relative to atmospheric pressure which is about 14.7 psi. Psig = 0 is no pressure above atmospheric pressure. The digital pressure gauges from Ashcroft all read in psig.
SCC	Stress Corrosion Cracking
SOP	Standard Operating Procedure
UCCLS	University of California Center for Laboratory Safety
UH	University of Hawaii at Manoa

Appendix B: Compressed Gas Safety Guidelines

Compressed Gases

Besides their respective chemical and physical hazards, many of the compressed gases comprise a pressure hazard. The more common gases such as nitrogen, hydrogen or helium are filled in high pressure cylinders to pressures exceeding 2,000 psig. In some specialty applications such hydrogen fueling systems the pressures can exceed 10,000 psig. Systems that handle these gases must be designed to handle any foreseeable pressure due to temperature or mechanical failure. For most applications a pressure regulator is used to reduce the pressures to a safer level. Pressure relief devices are also required to protect the systems from overpressure.

Cylinder valve outlet connections are selected based on the gas characteristics. A variety of valve outlet connections are used to prevent incompatible gases from being connected together. Hydrogen for example has a CGA 350 connection which is a nipple seal with a nut that is a left handed thread. Oxygen is a CGA 540 which is also a nipple seal but the same size nut is a right handed thread. The universal rule worldwide is to have a notch on the nut to indicate that it is left handed. A CGA 350 connection is shown in the following figure.



Schematic of CGA 350 connection for hydrogen gas.

Selection of outlets is based on CGA Standard V-1 Compressed Gas Cylinder Valve Outlet and Inlet Connections. Regulators should be ordered with the appropriate CGA connection attached. Adapters shall never be used to adapt to a regulator used for another gas.

Pure oxygen gas presents a serious combustion hazard, so oxygen regulators in particular must be clean and free of all contaminants. Since oils and grease become highly combustible in the presence of oxygen, never use oil, grease, or any other petroleum-based or flammable substance on or around oxygen equipment. Further, DO NOT change regulators from one gas service to another by changing the CGA connections. Changing a different gas regulator into an oxygen regulator can result in fire or explosion due to contaminants in the regulator.

Users should be aware of some basic safety rules for the following compressed gases groupings: Note that these are not comprehensive guidelines, the user should consult the supplier technical data sheets or Safety Data Sheets.

1. **Extremely flammable gases:** Hydrogen and Acetylene are extremely flammable because of their low ignition energies, wide flammable ranges and high reaction speeds. They are also lighter than air and have unique chemical properties. Therefore, there are special safety considerations:
 - Proper grounding and bonding of the system is required.
 - Intrinsically safe electrical devices are required.
 - Equipment components that are in contact with hydrogen should be inspected regularly since hydrogen embrittlement can occur with low alloy steels at operating pressures approaching their tensile strength.
 - Non metal tubing is unsafe because hydrogen will permeate to the exterior surface. Increasing temperatures increase the rate.
 - High pressure releases of hydrogen almost always ignite.
 - Hydrogen burns without a visible flame.
2. **Oxygen:** High pressure oxygen is extremely reactive. Even low pressure oxygen can be extremely reactive as shown by the Apollo 1 fire in 1967 which killed the 3 astronauts. After that incident, NASA conducted numerous studies on oxygen safety.

Equipment for use with oxygen must be properly designed and maintained:

- Systems must be oxygen cleaned using the methods described in CGA Pamphlet G-4.1(see below)
- Valves must be opened slowly to avoid adiabatic compression heat.
- Systems must be made with compatible materials. Aluminum or carbon steel will react at very low pressures.
- Flammable tubing such as polyethylene (PE) are not safe to use. They can readily ignite and burn with high energy output. With few exceptions, materials become more flammable in oxygen as pressures increase. This includes metals, plastics, elastomers, lubricants, and contaminants. In fact, nearly all polymer materials are flammable in 100 percent oxygen at atmospheric pressure. Guidance is found in: Rosales, K. R., Shoffstall M. S., Stoltzfus J. M. "Guide for Oxygen Compatibility Assessments on Oxygen Components and Systems" NASA/TM-2007-213740, March 2007
- Systems must be marked and dedicated for oxygen service:
 - Oxygen fires have been caused as a result of surface contaminants in the system interior such as machine oil or metal particle impact. Metals such as aluminum or titanium should not be used in high pressure oxygen service. Aluminum can ignite at pressures as low as 25 psig (Alloy 6061) while 304 stainless steel does not ignite until 725 psig. I.
 - Accidents have occurred when users needing an oxygen regulator replaced the CGA connection from a regulator used in another service with a CGA 540 connection and attached it to the oxygen cylinder. When the cylinder valve was opened, the adiabatic compression heat reached the autoignition temperature of the contaminant in pure oxygen.



Regulator used for another gas service was adapted for oxygen use and exploded when the cylinder valve was opened.

- Air Products Safetygram 1 Oxygen states: “Systems used in oxygen service must meet stringent cleaning requirements to eliminate any incompatible contaminants.”
- CGA Pamphlet G-4.1, “Cleaning Equipment for Oxygen Service,” describes cleaning methods for equipment used in oxygen service.
- CGA Pamphlet O2-DIR, “Directory of Cleaning Agents for Oxygen Service,” provides comparative information on cleaning agents used to clean oxygen equipment

These incompatible contaminants—many of which are very difficult to detect—can be the initial fuel for a promoted ignition event. (Luxfer Cylinders Inc.)

- Machining oils (including residual oil film)
- Hydrocarbon-based grease and lubricants (including compressor oil)
- Some soaps, detergents, solvents and cleaning solutions, especially those that contain organic compounds
- Skin lotions and emollients and cosmetics
- Sun-tanning oils and lotions
- Human skin oil and bodily fluids
- Insects and insect body parts
- Paint, wax, and marking crayons
- Carbon dust from filtration systems
- Metal fines, filings, scale and burrs
- Chrome chips (usually from valves and other chrome-plated parts)
- Rust particles and dust
- Metallic oxides in general
- Airborne soot and dust
- Pipe thread sealants
- Residue from soapy water and leak-detection fluids used to check for leaks
- Lint from cloths used in cleaning

- Any other material containing organic compounds and hydrocarbons

Once these are cleaned from the system, it must be protected to prevent recontamination when the system is not being used.

NASA recommends a formal oxygen compatibility assessment process that may be used as either design guide or as an approval process for components and systems. The required oxygen compatibility assessment procedure is:

- Determine the worst-case operating conditions
- Assess the flammability of system materials
- Evaluate the presence and probability of ignition mechanisms
- Determine the kindling chain, which is the potential for a fire to breach the system
- Analyze the reaction effect, which is the potential loss of life, mission, and system functionality as the result of a fire
- Identify the history of use
- Report the results of the analysis

3. **Highly toxic gases:** DOT as well as the Fire Codes require additional safeguards for highly toxic gases such as arsine, phosphine or diborane

- 49 CFR 173.40: Performance tested cylinder valve protection caps. These are marked and should not be exchanged with other cylinder caps.
- 49 CFR 173.40: Cylinder valve outlets must have a gas tight outlet seal. When loosening this, proper PPE and safety procedures must be followed.
- 49 CFR 173.40: Requires a metal diaphragm valve, the only exception is the use of a packed valve with a gas tight stem cap (phosgene, cyanogen chloride, fluorine).
- Most of the highly toxic gases have an olfactory threshold well above the danger levels. Electronic leak detection must be used to test for leaks.
- Arsine in any quantity requires a CFATS level 1 security plan.

General Guidelines for Compressed Gas Safety

OVERALL GUIDELINES

1. Cylinders shall not be stored or used if the contents are not properly identified. Never use color as the identifier.
2. Labels and markings on the cylinder shall not be covered, defaced or removed.
3. All compressed gases shall be in approved cylinders made to recognized government (Department of Transportation, United Nations, Korea Specialty Gas Corporation, etc) specifications.
4. Compressed gas cylinders shall be used and stored only in designated locations in the facility.
5. Proper PPE shall be worn at all times.
6. Compressed gases shall be used only by trained and qualified personnel.
7. Compressed gas cylinders shall be transported only by trained and qualified personnel.

8. Valve outlet connections used for compressed gas cylinders shall conform to nationally or regionally recognized standards in the US the Compressed Gas Association (CGA), Japan the Japanese Industrial Standard (JIS), Germany the Deutsches Institut für Normung e.V (DIN)
9. Liquefied gas cylinders shall be used, transported and stored with the vapor space in communication with the pressure relief device. (Exceptions include forklift propane cylinders that are designed to be horizontal.)
10. Gas cylinders should have a status tag to indicate status.

HANDLING AND TRANSPORTATION WITHIN THE FACILITY

1. Cylinders are to be moved using approved cylinder handcarts. Approved handcarts are designed for transporting cylinders, for physical stability they have outrigger wheels. Dragging, rolling or lifting by the cylinder cap is not approved. They shall not be dropped or struck against each other or other surfaces.
2. Cylinder rolling is authorized only for short distances between the cylinder cart and the final use or storage point (less than 5 feet).
3. Properly designed cylinder carts shall only be used for a maximum of 2 cylinders.
4. All approved cylinder carts shall have a restraining device such as a chain to prevent a cylinder from falling out.
5. All cylinders shall be transported with the cylinder valve protection cap on.
6. All cylinders shall be leak tested prior to removal from storage or use area.
7. Cylinders are not to be left unattended during transportation.
8. Transport only at approved times in the facility.
9. Transport only through approved routes.
10. Large cylinders can be a significant physical hazard when handling. If one should tip, do not try to catch it! Let it fall.
11. Lifting magnets, cylinder caps or slings shall not be used to move cylinders using a crane or hoist. Cylinders shall only be lifted using specially designed cages or cradles.
12. Forklift movement shall only be in skids/cradles designed for cylinders.
13. With the exception of lecture bottles, cylinders shall be moved standing upright.

STORAGE

1. Cylinders shall be stored in dedicated areas conforming to local/national regulations.
2. Storage areas shall have adequate natural or mechanical ventilation.
3. The area shall be protected from the weather.
4. The area shall be free of standing water.
5. Cylinders shall be secured using straps or chains at the midsection of the cylinder. In earthquake areas they shall be secured at 2 points.
6. Cylinders shall be grouped into compatible groups based on their primary hazard class.
7. Incompatible groups shall be separated by a fire partition a minimum of ½ hr fire rating or a distance of 20 feet.
8. Segregate full and “empty” cylinders.
9. Storage areas shall be adequately marked.
10. Storage areas shall be secured from unauthorized entry.
11. Storage areas shall have adequate lighting.

12. Cylinders should not be stored for extended periods of time. In general 3 years is the maximum.
13. Cylinders of hydrogen fluoride and hydrogen bromide should be returned to the supplier within 2 years.

USE SAFETY

1. All cylinders are to be placed into the final use area/cabinet and immediately restrained using cylinder straps or chains, prior to removal of the cylinder cap.
2. Cylinders are not be subjected to temperatures outside of the following range: -20 °F (-29 °C) to 125 °F (52 °C).
3. Only properly designed heating systems are to be used. For safety a second independent temperature controller shall be used to alarm and shut off the heating system.
4. Valve outlet adapters to change the valve outlet connection to match the gas cabinet pigtail are prohibited.
5. Teflon tape or pipe thread sealant shall not be used on any cylinder CGA outlet connection threads.
6. Connection to the valve outlet shall be smooth and not forced.
7. Tools such as wrenches shall not be used to open or close valves unless they are designed for wrench operation, in this case a short wrench 6" (15 cm) shall be used.
8. Tools or other objects shall not be inserted into the cylinder cap vent hole help remove it.
9. Gas systems set up for one gas service shall not be used for other services unless formally reviewed and approved.
10. All compressed gas cylinders in use, except low vapor pressure gases such as boron trichloride, shall have a pressure regulator to lower the pressure.
11. "Buddy System" when changing highly toxic or pyrophoric gas cylinders.
12. Highly toxic or high-pressure pyrophoric cylinder valves shall have a RFO (Restrictive Flow Orifice) installed sized for the size of the abatement system.
13. Only systems designed and cleaned for oxygen service shall be used for oxygen and other oxidizer gases.
14. Strong fluorine gases (ClF₃, F₂, NF₃, etc) shall only be used in systems that have been oxygen cleaned and fluorine passivated.
15. Fluoride gases that hydrolyze in air (ClF₃, F₂, SiF₄, BF₃, AsF₅) create a HF exposure hazard when released.

SYSTEM DESIGN RULES

1. Whenever a cryogenic liquid or a liquefied gas can be trapped between two valves install a pressure relief valve to relieve the liquid expansion.
2. Dedicated high pressure purge gas cylinders shall be used for compatible groupings of highly toxic or pyrophoric gases.
3. Purge gas cylinders shall only be shared between compatible gases.
4. Piping/tubing through a wall shall be sleeved to physically protect them.
5. Piping/tubing hidden behind walls, ceiling or floor shall be welded, there should be no hidden mechanical connections.

Guidelines for Cylinder/Pressure Vessel Filling Safety

Under the ASME regulations any container larger than 1 gallon (3.8 liter), with a diameter larger than 6" and a pressure higher than 15 psig must be designed as a pressure vessel under ASME (American Society of Mechanical Engineers) regulations or as a cylinder under the DOT (Department of Transportation) Regulations²⁵.

General

1. Prior to executing any new procedure to fill cylinders in the laboratory, there must be a detailed hazard review done and documented by people and companies familiar with the materials and hazards.
2. Cylinder must be an approved ASME or DOT Pressure Vessel with a design pressure equal to or less than the intended operating pressure. MAWP must never be exceeded.
3. Cylinder owned by others may not be filled without their consent.
4. Cylinder must be labeled with contents as per GHS.
5. Cylinder must be marked with the maximum allowable fill pressure/amount.
6. Cylinders for filling of liquefied gases must have the tare weight based on the as used condition, e.g cylinder cap off.
7. Cylinder must have pressure relief device as defined by CGA S1.1 "Cylinder Pressure Relief Devices" or ASME Unfired Pressure Vessel Requirements typically MAWP or less.
8. Cylinder can only be filled by someone trained on the procedure.

Fill Amount

To insure that dangerous amounts of gas are not put into a cylinder, care must be taken to calculate the allowable amount:

1. Scales used to weigh cylinders must be routinely calibrated. Check weights are used to test the scale prior to use.
1. Pressure in the cylinder may not exceed the design pressure under any temperature that the cylinder will be exposed.
2. Only cylinders constructed of aluminum or stainless steel may be exposed to temperatures less than -30°F (-34.4°C).
3. In the US cylinder fill densities have been determined based on a maximum temperature of 130°F (54.4°C) as defined in the transportation regulations.
4. They must be immediately reweighed after filling and the cylinder has been disconnected to verify content.
5. Some gases such as BF₃ or SiH₄ have high thermal expansion ratios that must be taken into account.

Visual Inspection Before Fill

A prefill inspection must be done prior to each fill. This must be recorded

²⁵ Title 49 Federal Code of Regulations

1. Prior to filling, cylinders must be visually inspected for physical damage, gouges, cuts, dents, pits, corrosion as per CGA C-6.
2. Cylinders showing any evidence of exposure to fire or welding cannot be refilled until requalified.
3. Cylinders that have been modified by drilling or welding additional piping cannot be refilled until requalified.
4. Cylinders must be weighed to determine if they contain any residue.

Things that can compromise cylinders

1. Gases that can cause embrittlement of carbon steel cylinders include:
 - a. Ammonia
 - b. Carbon Monoxide
 - c. Carbon Dioxide
 - d. Hydrogen
 - e. Hydrogen Sulfide
 - f. Hydrogen Chloride

Review material of construction before proceeding

1. Oxygen systems must be properly designed and cleaned. These must be marked and dedicated for oxygen use. Aluminum systems cannot be used for oxygen. Aluminum cylinders are authorized.
2. Fluorine and other strong fluorine gas (ClF_3 , BrF_3) systems must be constructed of approved materials, oxygen cleaned and fluorine passivated
3. Aluminum cylinders cannot be used for the halogen acid gases (Cl_2 , HBr , HCl) unless they are gas mixtures at low ppm concentrations.

Mixing Gases

Incompatible gases in the same cylinder can be dangerous.

1. Gases that are reactive with each other shall not be mixed in cylinders
 - a. Flammable and Oxidizer gases
 - b. Acid and Alkaline gases
2. If a fuel and oxidizer gas are to be mixed together, the precautions in CGA P-58, "Safe Preparation of Compressed Oxidant-Fuel Gas Mixtures in Cylinders" must be followed.

Some gases are unstable and require stabilizers.

Some gases are unstable and can auto-decompose or polymerize in a self sustaining exothermic reaction. The byproducts and heat can violently rupture the cylinder.

1. Acetylene must never be filled to a pressure above 15 psig. Pressures higher than this must be in special cylinder filled with specially designed solid and solvent. Copper must never be used with acetylene.
2. Gases that require a stabilizer:

- a. Tetrafluoroethylene
 - b. Tetrafluorohydrazine
 - c. Cyanogen Chloride
3. Gases such as Diborane are limited in the maximum fill amount since the full decomposition can create 3 times the amount in H₂.
 4. Germane fill density assumes the instantaneous decomposition and heat.
 5. To minimize adiabatic compression heat from initiating a reaction, Nitric Oxide fill is limited to 500 psig and Nitrogen Trifluoride to 1450 psig.

Miscellaneous

1. Valve Outlet Connections shall follow CGA V-9.
2. Cylinders must be tested and inspected as required.
3. When a cylinder valve is opened and no gas comes out, the safety rule is to determine if the valve is plugged or inoperable by pressurizing the valve outlet to see if gas enters the cylinder.
4. A cylinder is never considered empty until it has been purged of its contents.

Appendix C: Biographies

Dr. Craig Merlic

Professor Merlic obtained his B.S. degree in chemistry from the University of California, Davis and his Ph.D. in organic chemistry from the University of Wisconsin, Madison. After a postdoctoral position at Princeton University he joined the faculty in the UCLA Department of Chemistry and Biochemistry in 1989. Professor Merlic's research focuses on applications of transition metal organometallic chemistry to organic synthesis and extends from catalysis to synthesis of new chemotherapeutic agents. He teaches courses on introductory organic chemistry, advanced organic synthesis, organometallic chemistry, scientific ethics, and safety in chemical and biochemical research. He has received awards for his teaching, educational projects, and scientific research. His research has been supported by the National Science Foundation, the National Institutes of Health, the Petroleum Research Fund and various corporate sponsors.

Professor Merlic has been active promoting chemical safety at UCLA and the University of California system. He serves as chair of the Department Safety Committee, the campus-wide Chemical and Physical Safety Committee, and the UCLA Safety Oversight Committee. At the University of California system-wide level, he is the Executive Director of the UC Center for Laboratory Safety (<http://cls.ucla.edu>) that has ongoing projects to improve laboratory safety policies, procedures, and training based on scientific studies. He works with an information technology group located at UC Davis creating safety software tools for use at all ten university campuses. He serves as a Board Member for University of California Risk & Safety Solutions.

Mr. Eugene Ngai

Eugene Ngai holds a Bachelor of Science in Chemical Engineering and a Master in Environmental Engineering. He has over 40 years of Specialty Gas experience in production, laboratory, R&D, engineering, safety and executive management positions. He retired from Air Products in 2009 and formed Chemically Speaking LLC a compressed gas safety and emergency response training and consulting corporation. Chemically Speaking LLC currently has numerous multi-year agreements to advise manufacturers, suppliers and users of specialty compressed gases, primarily in the semiconductor, LCD or photovoltaic industries.

He is active in a number of worldwide industry association working groups including CGA G-13 (Silane), NFPA 55 (Industrial and Medical Gases), NFPA 400 (Hazardous Materials), NFPA 318 (Semiconductor), SEMI EHS, SESA and UN TC58 SC2 WG7 (Gas Toxicity, Flammability, Oxidizer). He coordinated silane release testing in 2011 and 2012 to gather data for revision of the CGA G-13 standard on silane, a pyrophoric gas that has been involved in over 16 fatal accidents.

He has made over 200 presentations worldwide on Emergency Response, Product Safety, Gas Technology and Environment and has campaigned extensively on silane safety. He chaired twelve one day silane safety seminars, in Taiwan, Korea, Singapore, US and Europe starting in 2006. He conducts compressed gas safety and emergency response classes throughout the

world. He teaches courses on compressed gas safety and emergency response and has trained over 10,000 users from government agencies, universities, gas manufacturers and semiconductor fabrication facilities. He has also taught at Fire Academies worldwide, including New York, Honolulu, San Jose, Camden County and Singapore and as well as HazMat Conferences. Over 4,500 firefighters have been trained. In 1988 he designed the sold the 5501 and 5502 ERCV's which can be used to isolate high pressure leaking gas cylinders to safely transport them to a remediation site. These have become the industry standard, known as the Solkatronic. He has five patents on gas safety devices.

Dr. Imke Schroeder

Dr. Imke Schroeder is the Research project manager at the UC Center for Laboratory Safety (<http://cls.ucla.edu>). She is also an Adjunct Associate Professor in the Department of Microbiology, Immunology and Molecular Genetics (MIMG) at UCLA. Dr. Schroeder received her Ph.D. in Microbiology from the University of Marburg, Germany, and performed her postdoctoral training at UCLA. After a year as senior researcher at the Veterans Administration Medical Center in San Francisco, she joined the Department of MIMG in 2001, where she has worked on virulence determinants of the select agent *Burkholderia pseudomallei*. She has extensive experience in diverse areas of microbiology including research on extremophiles and select agents. She has technical expertise in various bacterial cell culture methods including anaerobic and microaerophilic technics, and bioreactor fermentation with H₂ and O₂. She has cultured the hyperthermophilic bacterium *Aquifex pyrophilus* with H₂ and O₂ at elevated temperatures on a 80 L scale for protein purification purposes. She has also performed mammalian cell cultures, protein purifications, various gene manipulations, RNA-sequencing and high throughput screening methods. She is an expert in the risk assessment associated with each agent and process.

Her current academic activities include research on laboratory safety, safety culture survey design and analysis, accident analysis, identification of leading factors for accidents and unsafe behaviors, and laboratory safety training. Furthermore, she manages subject matter experts for the Safety Training Consortium (<http://safety-consortium.org>) and co-organizes workshops on laboratory safety.

Mr. Kenneth Smith

Ken Smith is the Executive Director for Environmental Health and Safety for the University of California. In this position with the UC Office of the President, he provides systemwide direction, guidance and expertise on matters of Environmental Health and Safety to all ten UC campuses, five UC Health Medical Centers that encompass eleven hospitals, as well as Agricultural and Natural Resources and three UC managed National Laboratories.

Ken has served the UC system for 24 years in the areas of Radiation Safety and Research Safety. An alumnus of UC Santa Cruz, He received his degree in Biochemistry and Molecular Biology and holds board certifications in both Industrial Hygiene and Health Physics.

Ken is a nationally recognized expert in Health and Safety in complex research environments. He has been an invited speaker for organizations such as the American Chemical Society, American Industrial Hygiene Association, the California State University System, the California Industrial Hygiene Council, and the Campus Safety Environmental Health and Management Association. Ken also serves on the boards of the Laboratory Safety Institute and the UC Center for Laboratory Safety.

WHA International

WHA International, located in Las Cruces New Mexico, helps clients understand, evaluate, and mitigate hazards and fire risks associated with oxygen and other hazardous fluids and gases through engineering analysis, testing, training and forensic investigations. Its core business includes root-cause analysis of high pressure gas systems, fire hazards training, and oxygen compatibility testing of materials and components. WHA has been recognized since the early 1990s as a preeminent engineering firm with engineers and experts who have extensive experience across a wide range of scientific disciplines. Its engineers have formal training, including advanced degrees and licensures. WHA was founded by an engineering professor in 1987 and its focus has always been to provide just resolution of forensic engineering disputes, using the scientific method for testing and evaluation. The current leadership team is capitalizing on the industry niche services that have taken WHA from a local to an international company. WHA advances the technologies of oxygen safety, forensic engineering and fire sciences throughout the world. With the advantageous synergy that is created from WHA's industry experience, innovative drive and custom designed testing facilities, the WHA team is known worldwide for expertise in oxygen and fire-safety technologies, and aims to develop innovative solutions for clients' complex problems.