



This presentation is targeted toward everyone using chemicals.

About Dan Olsen

- Grew up as a pig farmer
- Graduated from ISU in Biochemistry
- Worked for the Iowa DNR in Underground Storage Tanks and Emergency Response
 - ER training anecdotes
- Started at UNL in 1990
 - Hazardous waste
 - Lab safety
 - Water quality (discharges; not drinking)
 - Air quality
 - Emergency response

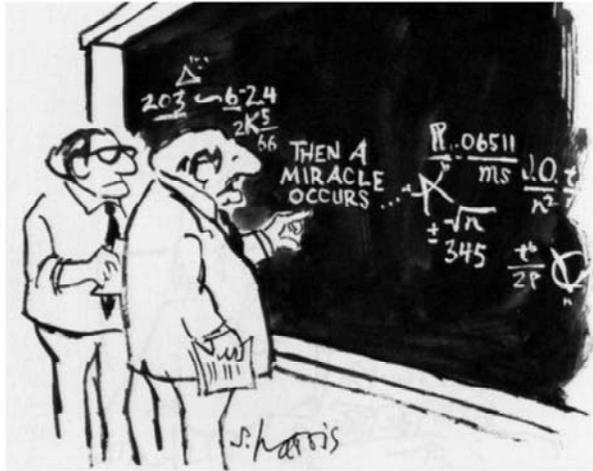


Introduction

- This talk will cover:
 - Why this is important to you
 - The concept of “hazard”
 - How to do a hazard assessment
 - Examples
 - How to assess risk and minimize it
 - Examples
 - Case Study
 - Conclusions



This Is What Most People Think Of It



"I think you should be more explicit here in step two."

from *What's so Funny about Science?* by Sidney Harris (1977)



Lots of people think that hazard assessment and risk minimization is magic.

Fortunately, what you need to know about hazard assessments and risk minimization is not that difficult to learn.

Why This Is Important To You – The Legal

- You have the responsibility, in part, to:
 - Comply with the employer's safety and health rules;
 - Report any hazards immediately to your supervisor;
 - Report to your supervisor any job-related illness or injury.
- If you supervise others, you are responsible to:
 - Provide training;
 - Correct improper work practices; and
 - Discipline employees as needed



Under federal Occupational Safety and Health Administration regulations, you have the responsibility to comply with the employer's safety and health rules; report any hazards immediately to your supervisor and report to your supervisor any job-related illness or injury. With regard to reporting hazards, this includes actions taken by others if it appears to create a hazard.

If you supervise others, you will be responsible to provide training; correct improper work practices; and discipline employees as needed.

Why This Is Important To You – The Practical

- Self protection
- Why not just be really careful with everything?
- Engine oil vs. nitroglycerine? Both are oily liquids.
 - Do they have the same hazard?
 - Do you want to work with engine oil in only milliliter amounts?
 - Would you feel safe handling a liter of nitroglycerine?
- Whether you are aware of it or not, you assess hazards and risks.
- Learn the skills that can help you do it.



[Read the slide]

Now let's define some terms we'll be using as we go forward.

Hazard Versus Risk

- Hazards are innate to a chemical whether the hazard is toxicity, flammability, corrosivity, etc.
 - Health hazards
 - Physical hazards
- Risk depends on how likely that hazard is to cause harm.
 - 500 gallons of gasoline has a greater potential to cause harm than one gallon.
- Let's examine health hazard first.



[Read the slide]

Health Hazards: Routes Of Exposure

- What are the ways you can be exposed to a chemical?
 - Absorption (i.e. skin)
 - Ingestion (i.e. eating it)
 - Inhalation
 - Injection



There are two different types of hazard that we'll be discussing. These are health hazards and physical hazards. We'll discuss health hazards first. For a chemical to pose a health hazard there has to be a potential for exposure.

What are the ways you can be exposed to a chemical?

Absorption (i.e. skin)

Ingestion (i.e. eating it)

Inhalation

Injection

Inhalation is the greatest risk because the lungs are designed to exchange vapors, gases etc.

Ingestion is next because it is also an exposure by exchange.

Absorption is typically a lower likelihood as skin is intended to be a barrier.

Injection is most commonly related to infectious needle sticks but can result

from other things such as puncture with broken glass.

Chemical Characteristics And Exposure

- What are the three states of matter?
 - Gas
 - Liquid
 - Solid
- Let's rate from greatest to least hazardous.



Gas can fill the air and its route of exposure is the most dangerous one (i.e. the lungs). Even a small/slow release can migrate by convection currents in the room. If the gas is corrosive, it can damage mucus membranes, like the eyes and even the skin.

Liquids can flow across a room or a countertop and contact the skin.

If a chemical is volatile, it can evaporate, creating a vapor that can migrate by convection currents.

When can solids be hazardous?

Answer: Air borne dusts can be inhaled.

What about ingestion?

Answer: Contaminants on the hands can be transferred to food.

And airborne dusts can be trapped by mucus in the throat then swallowed.

Health Hazard Summary

- Exposure hazards from greatest to least are:
 - Inhalation
 - Ingestion
 - Absorption
 - Injection
- Chemical states affecting health hazards from greatest to least are:
 - Gas
 - Volatile liquid
 - Non-volatile liquid
 - Solid



[Read slide]

Health Hazard By Class

Acute Toxicity
Skin Corrosion
Skin Irritation
Eye Effects
Sensitization
Germ Cell Mutagenicity
Carcinogenicity
Reproductive Toxicity
Target Organ Systemic Toxicity: Single Exposure &
Repeated Exposure
Aspiration Toxicity



This is the internationally recognized Globally Harmonized System (GHS) classes of health hazards of chemicals. As part of the online EHS **Chemical Safety** training, you should be familiar with the definitions of these terms so I won't go into detail on them here.

Of these classes, which poses the greatest health hazard?

Answer: Acute toxicity

Why?

Answer: This is the class of chemicals that can kill you right now.

Which class poses the second greatest hazard?

Answer: Corrosives. Again, it is an exposure that can cause permanent injury almost immediately.

Now let us examine physical hazards.

Physical Hazards

Explosives	Substances Which in Contact with Water Emit Flammable Gases
Flammable Gases	Oxidizing Liquids
Flammable Aerosols	Oxidizing Solids
Oxidizing Gases	Organic Peroxides
Gases Under Pressure	Substances Corrosive to Metal
Flammable Liquids	
Flammable Solids	
Self-Reactive Substances	
Pyrophoric Liquids	
Pyrophoric Solids	
Self-Heating Substances	



These are the GHS internationally recognized classes of physical hazards of chemicals.

Of these classes, which class poses the greatest hazard?

Answer: Explosives

Why?

Answer: ;The effects of an explosion are immediate and dramatic and are not localized. A beaker containing a flammable liquid can burn but a beaker containing an explosive will send shrapnel across the room.

Is there another class(es) that are also recognized as having the potential to explode?

Answer: Organic peroxides; self-reactive substances

What other class(es) have high hazards?

Answer: Pyrophorics

Note that the 'substances which in contact with water emit flammable gases' include chemicals that will emit flammable gases when exposed to moist air

and then ignite spontaneously. Sodium hydride is an example.

All of these classes need little to nothing to initiate them to react. This is not to disregard the hazards of the other classes but to put them into perspective.

And generally speaking, I rate physical hazards above health hazards. Health exposures tend to be incidents where the person makes a full recovery in a short period of time.

Into The Weeds

- Hazards are more complicated than chemical classes.
- For example, not all chemicals are equally toxic. Some are highly toxic and others barely so.
- How do you know how hazardous a chemical is in its class?
- Categories



[Read slide]

GHS Class Categories

- Each health and physical hazard class is divided into categories.
- Number of subdivisions varies as needed.
 - They are either called 'Division', 'Category' or 'Type.'
- For example, there are 5 categories of acute toxins
 - Categories 1 and 2 can be fatal
 - Category 5 can be harmful



[Read slide]

Provided is the EHS Safe Operating Procedure, **Chemical Hazard Assessment and Risk Minimization**, as a resource.

With regard to health hazards, there is a complex interplay between the toxicity of a chemical, its route of exposure, how and if the body can metabolize/transform it and how rapidly the body can excrete it. As a result, sometimes the categories between different chemicals might not seem right based on your experience.

Exceptional Hazards

- In general, some classes/categories pose exceptional hazards:
 - Explosives – Unstable & Divisions 1.1 through 1.3
 - Organic Peroxides – Type A through C
 - Any Pyrophoric
 - Substances in Contact with Water Emit Flammable Gases – Type I
 - Self-Reactives – Type A through C
 - Acute Toxicity – Category I



The following hazards require additional oversight:

Explosives – Unstable & Divisions 1.1 through 1.3

Organic Peroxides – Type A through C

Any Pyrophoric

Substances in Contact with Water Emit Flammable Gases – Type 1

Self-Reactives – Type A through C

Acute Toxicity – Category 1

Notice that five classes of physical hazards are on the list but only one category for health hazards. Again this reflects those chemicals that can cause immediate and severe harm.

Now let's move on to risk minimization.

Risk Minimization



[Let attendees read the slide]

Risk minimization can seem this complicated. Let's see if we can simplify it some.



Risk Minimization In General

- This is the order of preference:
 1. Don't use the chemical.
 2. Substitute it with something less hazardous.
 3. Isolate the chemical from people.
 4. Add engineering controls, such as safety barriers or exhaust ventilation.
 5. Adopt safe work procedures, training and supervision to minimize the risk.
 6. Where other means are not sufficient or practicable, provide personal protective equipment.



[Read the slide]

1. Don't use the chemical.
 - Sand/buff parts instead of using solvent-based stripper
2. Substitute it with something less hazardous.
3. Isolate the chemical from people.
 - Radioactive sources that have built-in shielding
4. Add engineering controls, such as safety barriers or exhaust ventilation.
 - Fume hoods
5. Adopt safe work procedures, training and supervision to minimize the risk.
 - Like this presentation
6. Where other means are not sufficient or practicable, provide personal protective equipment.

We'll review some specific examples of this later.

Where To Find Hazard & Risk Minimization Information

- Safety Data Sheet (SDS)
- Replaces the MSDS (Material Safety Data Sheet)
- In effect as of December 1, 2015
- Pesticides subject to FIFRA, not OSHA for labelling
- SDSs for pesticides often still available



A good source for this information is the Safety Data Sheet (SDS). Under the Globally Harmonized System of classification, all chemical manufacturers to be in compliance with the GHS standard by December 1, 2015. This includes container labelling as well.

Note that pesticides are subject to FIFRA (Federal Insecticide, Fungicide, and Rodenticide Act) ,not OSHA (Occupational Health and Safety Administration) for labeling. Lots of pesticide manufacturers will also still prepare SDSs.

SIGMA-ALDRICH

SIGMA-ALDRICH.COM
SAFETY DATA SHEET
 VERSION 5.2
 REVISION DATE 02/24/2014
 PRINT DATE 06/20/2014

1. PRODUCT AND COMPANY IDENTIFICATION

1.1 PRODUCT IDENTIFIERS
 PRODUCT NAME : WATER

PRODUCT NUMBER : W4502
 BRAND : SIGMA

REACH No. : A REGISTRATION NUMBER IS NOT AVAILABLE FOR THIS SUBSTANCE AS THE SUBSTANCE OR ITS USES ARE EXEMPTED FROM REGISTRATION, THE ANNUAL TONNAGE DOES NOT REQUIRE A REGISTRATION OR THE REGISTRATION IS ENVISAGED FOR A LATER REGISTRATION

DEADLINE, CAS-No. : 7732-18-5

1.2 RELEVANT IDENTIFIED USES OF THE SUBSTANCE OR MIXTURE AND USES ADVISED AGAINST
 IDENTIFIED USES : LABORATORY CHEMICALS, MANUFACTURE OF SUBSTANCES

1.3 DETAILS OF THE SUPPLIER OF THE SAFETY DATA SHEET
 COMPANY : SIGMA-ALDRICH
 3050 SPRUCE STREET
 SAINT LOUIS MO 63103
 USA

TELEPHONE : +1 800-325-5832
 FAX : +1 800-325-5052

1.4 EMERGENCY TELEPHONE NUMBER
 EMERGENCY PHONE # : (314) 776-6555

2. HAZARDS IDENTIFICATION

2.1 THIS STUFF WILL KILL YOU.



This is how some folks view SDSs.

[Allow the staff to read the slide.]

Everything is over the top in alarm. Then again if your ship sank in the middle of the ocean, could water kill you?

Context is everything.

SDSs are not perfect but they are the best first source for hazard information on chemicals that I know of. Even for the guidance in a SDS that I think is overboard, like intrinsically safe equipment for flammable liquids, I find some value. The hazard is that the chemical is flammable and that electrical and other equipment could be a source of electrical arcs, etc. and could result in a fire. Now what am I going to do about it?

The same is true of PPE. Lots of SDSs will call for full body protection. They cite worst-case scenarios because those who wrote the SDS don't know the circumstances under which the chemical will be used. They don't know the context.

As part of our case scenario let's look at specific examples of hazard assessment and risk minimization. First, let's begin with some background information.

Hydrogen

- What is its greatest hazard?
 - Category I flammable gas
- Is it flammable at all or just some concentrations?
- Where could you find this information?
 - I hope you said a 'safety data sheet'



[Read slide]

Hydrogen SDS

- From the SDS
 - Lower explosion limit (LEL) 4%
 - Upper explosion limit (UEL) 75%
 - Lower and upper flammable range also used
 - VERY IMPORTANT
 - 4% TO 75% IN AIR!
- What does that mean?
 - It can burn at any concentration in that range
 - Called a 'flammable range'
- Compare to gasoline with a range of 1.4% to 7.6%



From the SDS

Lower explosion limit (LEL) 4%

Upper explosion limit (UEL) 75%

Lower and upper flammable range also used

VERY IMPORTANT

4% TO 75% IN AIR! Air is about 78% nitrogen and 21% oxygen. So what is the hydrogen really burning with? Answer: Oxygen

What does that mean?

It can burn at any concentration in that range.

Called a 'flammability range'

Compare this to gasoline with a range of 1.4% to 7.6%.

Hydrogen SDS

- What other hazards does hydrogen have?
 - From the SDS it is also:
 - A gas under pressure
 - A simple asphyxiant
- What is a 'simple asphyxiant'?
 - Can suffocate by displacing oxygen
- Incompatibilities
 - Oxidizers



[Read slide]

Hydrogen Risk Minimization

- So we know the hazards, how do we minimize the risks?
- Gas under pressure
 - Secure cylinder
 - Keep valve cover on when not in use
- Asphyxiation
 - Keep cylinder closed
 - Use in well ventilated areas



[Read slide]

Can you identify what type of control each of these is:

Gas under pressure answers:

Secure cylinder (engineering control)

Keep valve cover on when not in use (procedure)

Asphyxiation answers:

Keep cylinder closed (procedure)

Use in well ventilated areas (engineering control)

Hydrogen Risk Minimization

- Flammability
 - Keep away from sources of ignition.
 - What can they be?
 - Flames
 - Hot surfaces/equipment
 - Sparks
 - Sources of sparks?
 - Electrical switches
 - Electrical motors
 - Tools
 - Static



[Read slide]

There can be both engineering and procedural risk minimization strategies. For example, using spark-proof tools is an engineering control. Grounding against static is an engineering control as well. A sign declaring that all ignition sources be kept away is a procedural control.

Let's talk a little more about static and fire.

Hydrogen Example



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What is this a picture of?

Answer: The Hindenburg passenger airship
Lakehurst, NJ May 6, 1937

What caused the fire/explosion?

Answer: Probably a static discharge...a spark.

Something that is not well known is that hydrogen needs very little energy to ignite...0.02 mJ (millijoule).

For reference, a 1 mJ spark is barely perceptible to people and it takes 30 mJ for people to feel a sharp prick.

Is the Hindenburg exploding or burning?

Answer: Burning

The news report was that it took 30 seconds for the airship to be

consumed.

Remember hydrogen needs air to burn. The front part of the ship won't burn until the fire gets there, burns through the gas bags, releases the hydrogen and the hydrogen is exposed to air/oxygen.

This concept will become very important later.

Oxygen SDS

- What is its greatest hazard?
 - SDS shows it as a Category I oxidizing gas.
- What is an oxidizer; what does it do?
 - There are several ways to define it.
 - That it can initiate and/or accelerate the combustion of other materials is what is important to us.
- It is also a gas under pressure.
- Incompatibilities
 - Combustible materials



[Read slide]

Oxygen-Enhanced Combustion



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Here is an example of oxygen-enhanced combustion.

Oxygen Risk Minimization

- So we know the hazards, how do we minimize the risks?
- Gas under pressure
 - Secure cylinder.
 - Keep valve cover on when not in use.
- Oxidizer
 - Keep away from combustible/oxidizable materials:
 - Organics
 - Grease
 - Oil
 - Flammable gases



[Read slide]

Keep these things in mind as we move on.

Review

- We've talked about the hazards of hydrogen and oxygen.
- We've talked about risk minimization.
- All of this information came from SDSs.
- Are any of these concepts complicated?
- Now lets apply this to a case study: a research project.



[Read slide]

Research Project

- Goal: To study the synthesis of polyhydroxyalkonates (PHAs) by bacteria (*Cupriavidus. necator*) for use in bioplastics research
- This area of research has existed for awhile.
- Needs:
 - Growth chamber
 - Favorable growing environment which includes:
 - Hydrogen ~70%
 - Oxygen ~ 20%
 - Carbon dioxide ~10%
 - Elevated pressures



[Read slide]

Before we go any further, are there any red flags? Anything of concern?

Answer: That hydrogen and oxygen are being combined is a concern. The SDSs show them as incompatible.

A Note On Research Papers

- Research papers often do not include information on:
 - Chemical, physical or biological hazards;
 - Details on the sourcing or set up of equipment;
 - Details of process or reaction hazards;
 - Hazardous byproducts
 - Toxic gas generation
- It is up to the researcher to identify these hazards and minimize them.



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First Setup



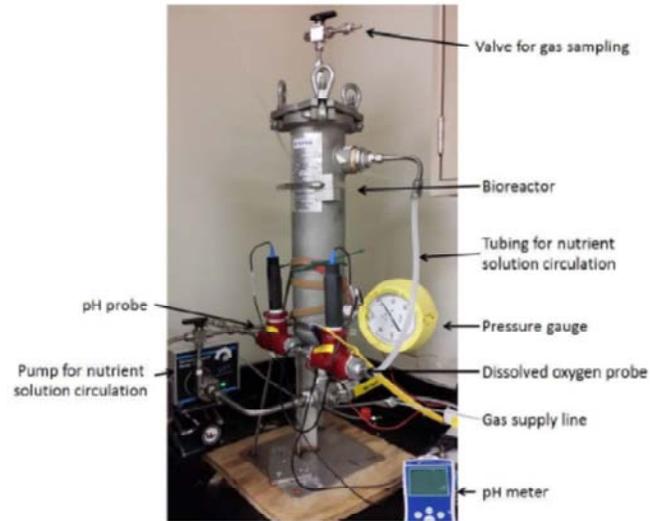
This is a growth chamber. Petri dishes with the bacteria, etc., are placed inside.

Using the pressure gauge as a guide, hydrogen, oxygen, and carbon dioxide are portioned into the vessel with the pressure reaching about 30 psig.

The vessel is incubated at 30° C and the bacteria “do their thing.”

A limitation is that the gas mixture can not be renewed.

Second Setup



[Read the slide]

Don't get too caught up in the details of this image.

What is important is that this system allowed for the gas mixture to be sparged through the bioreactor.

Where does the gas mixture come from? Let's look at that next.

Gas Mixture Source



A postdoc researcher purchased a 50-liter, low pressure tank, installed a pressure gauge, and a ball valve so that hydrogen, oxygen, and carbon dioxide could be transferred from compressed gas cylinders into the tank. The tank is then connected to the bioreactor and the gas mixture slowly sparged through it.

What again is the flammable range of hydrogen?

Answer: 4% to 75%

At approximately 70% it is within this range.

How much oxygen is present?

Answer: approximately 20%

How much oxygen is present in air?

Answer: 21%

If this mixture were to ignite, would it burn like the Hindenburg or more resemble an explosion?

Answer: Explo

What physical hazard did I say was my greatest concern?

Explosives

Ignition Sources

- How could the gas mixture in the tank ignite?
 - Static discharge
- How could that happen?
 - Transfer from someone/something to the tank
 - Transfer from the tank to someone/something
- Were there any warnings?



[Read bullet and let the audience respond]

Static is the only realistic ignition source.

[Read the rest of the slide]

Warnings

- The postdoc reported getting shocked on occasion when touching the tank.
- A week before when using the first setup:
 - Had charged with the gases
 - Heard a crackling sound
 - The pressure in the gauge jumped and then dropped to well below its original pressure
 - What happened?
 - Hydrogen and oxygen reacted, became water vapor, and began to condense in the vessel



[Read slide]

The investigators hypothesized that there wasn't an explosion as the gases hadn't mixed well before they ignited.

In other works, it burned something like the Hindenburg.

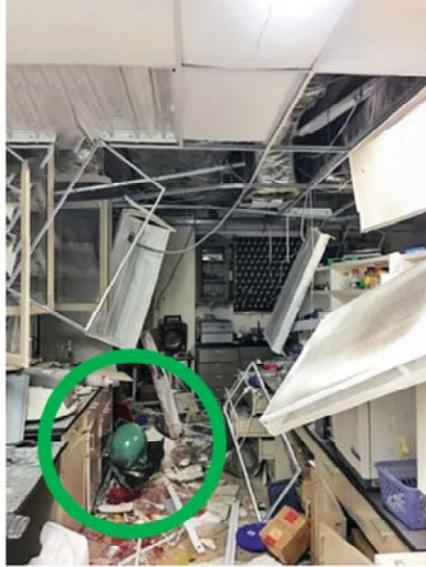
Warnings

- The postdoc opened the vessel and found the plates singed and cracked and with a burnt odor.
- Here was the near miss. **She does not heed the warning!**
- Research like this had been done for years.
- The postdoc had run the second setup safely 10 previous times.
- She ran the second setup using the 50 liter tank for the 11th time.



[Read slide]

The Explosion



See the tank or what is left of it within the lab post event?

The Explosion



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A close-up of the tank.

The Explosion



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Another picture of the lab post event.

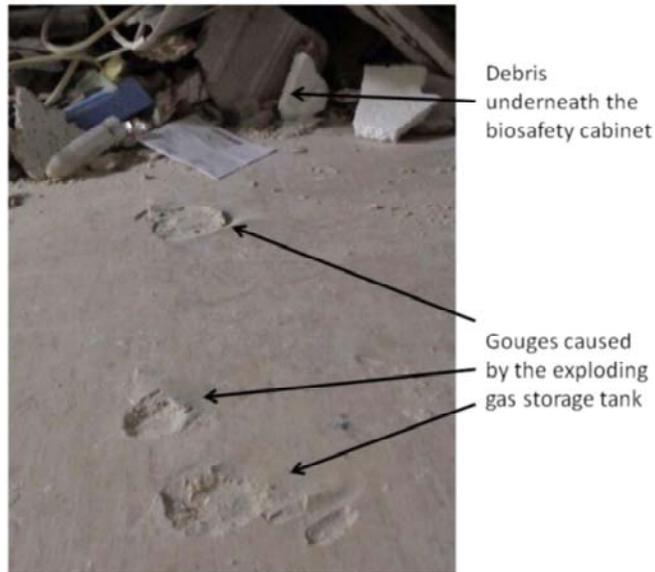
The Explosion



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Damage to the refrigerator where part of the tank hit it.

The Explosion



Gouges in the floor from the tank legs.

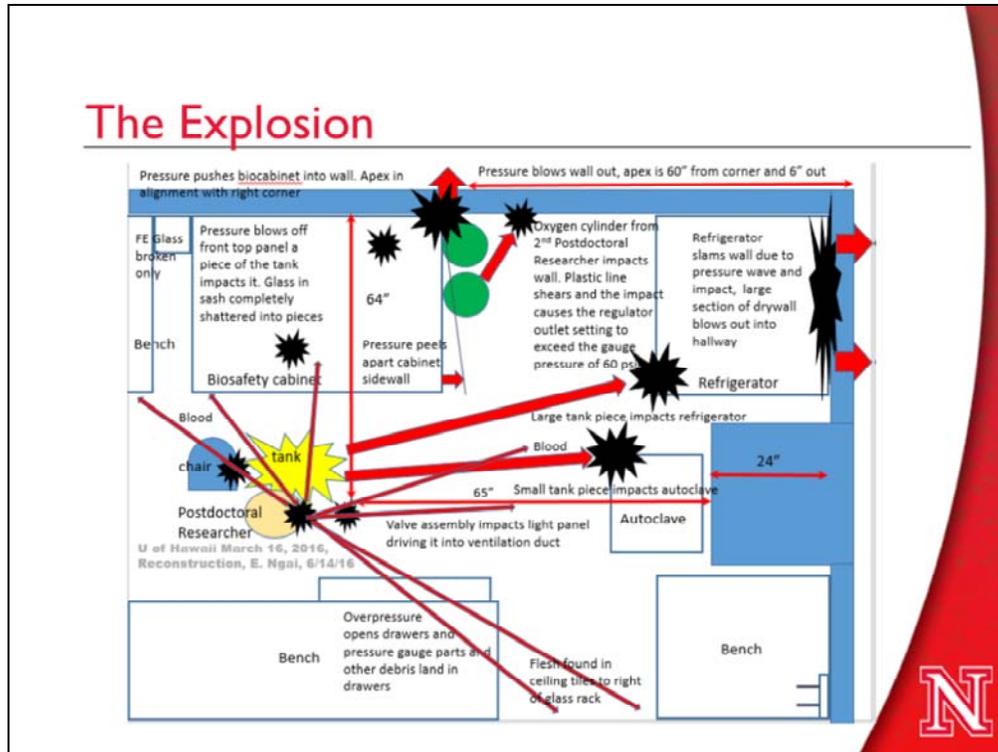
The postdoc was kneeling next to the tank when it exploded.

The explosion was equal to between 70 and 700 grams of TNT.

She suffered burns to her body and lost the lower part of one arm.
Emergency responders could find no piece of it large enough to reattach.

She is lucky to be alive.

The Explosion



Start with the postdoc and moving clockwise around the image, see the damage done to the lab.

In Hindsight

- What could have been done different?
 - Ground the tank to prevent static.
 - The pressure gauge was not intrinsically safe.
 - Fill/use the tank remotely.
 - Design a system that mixed the gases just before they entered the bioreactor; no tank.
- She could have heeded the warning of the accident in the first setup:
 - That was the near miss



Considering the tragedy, it seems inconsiderate to second-guess the postdoc.

If we are going to learn from this, we have to think of what could have been done differently.

So with this in mind, let us humbly continue.

[Read the first point and let the audience respond]

- What could have been done different?

Answers:

- Ground the tank to prevent static
- The pressure gauge was not intrinsically safe
- Filled the tank remotely
- Designed a system that mixed the gases just before they entered the bioreactor; no tank

- She could have heeded the warning of the accident in the first setup

In Hindsight

- Some of these considerations might not be obvious to a researcher.
 - She's a microbiologist.
 - Compressed gas systems were outside her expertise.
 - That is exactly the point!
- She could have enlisted gas company personnel in the design or asked EHS for guidance



[Read slide]

For me, these last points are the most obvious considerations.

The explosion happened because the postdoc was working in areas outside of her expertise.

Gas company personnel would have recognized the explosion hazard and risks from static and non-intrinsically safe equipment.

Gas company personnel would have also been a good resource for designing a system where the gases were mixed as they were being used.

She could have asked the university's Environmental Health and Safety department for guidance.

Other Ramifications

- University of Hawaii was fined \$115,500 by Hawaii OSHA.
- The explosion caused \$716,000 in damage to the lab/building.
- The building was closed for days.
- The university is being sued by the postdoc.



[Read slide]

Other Ramifications

- An official report offered 38 pages of recommendations to make research safer.
 - Investigation found failures at all levels from research, to EHS to administration.
 - The official report will affect all research done.



[Read slide]

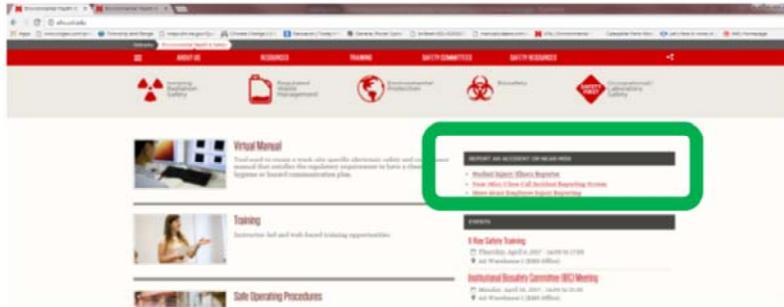
Conclusions

- Go beyond research papers/protocols when doing research.
- Read and understand the SDSs of the chemicals you are using.
- Consider chemical interactions and the potential hazards created.
- Consider equipment set up and process hazards.
- Enlist outside support for areas where you don't have expertise.



Conclusions

- Recognize near misses, learn from them and report them so that others can learn as well.
 - Department
 - EHS



Recognize near misses, learn from them and report them so that others can learn as well

Report to the department safety committee, safety chair, or department head as appropriate

At the University of Nebraska-Lincoln, report to Environmental Health and Safety via the EHS webpage.

Click on the “Near Miss/Close Call Incident Reporting System”

Resources

- The World Wide Web
- Chemical Safety Library
 - <http://www.pistoiaalliance.org/projects/chemical-safety-library/>
- Bretherick's ***Handbook of Reactive Chemical Hazards***



[Read slide]

The internet in general is a valuable resource on chemical hazards and hazards.

Sigma Aldrich and Fisher among other chemical companies have very good SDSs

A relatively new database tool scientists can use to share information about hazardous chemical reactions is the ***Chemical Safety Library*** by a non-profit development group. Google 'Chemical Safety Library' and you will find it.

Bretherick's ***Handbook of Reactive Chemical Hazards*** is an assembly of all reported risks such as explosions, fire, toxic or high-energy events that result from chemical reactions gone astray, with extensive referencing to the primary literature.

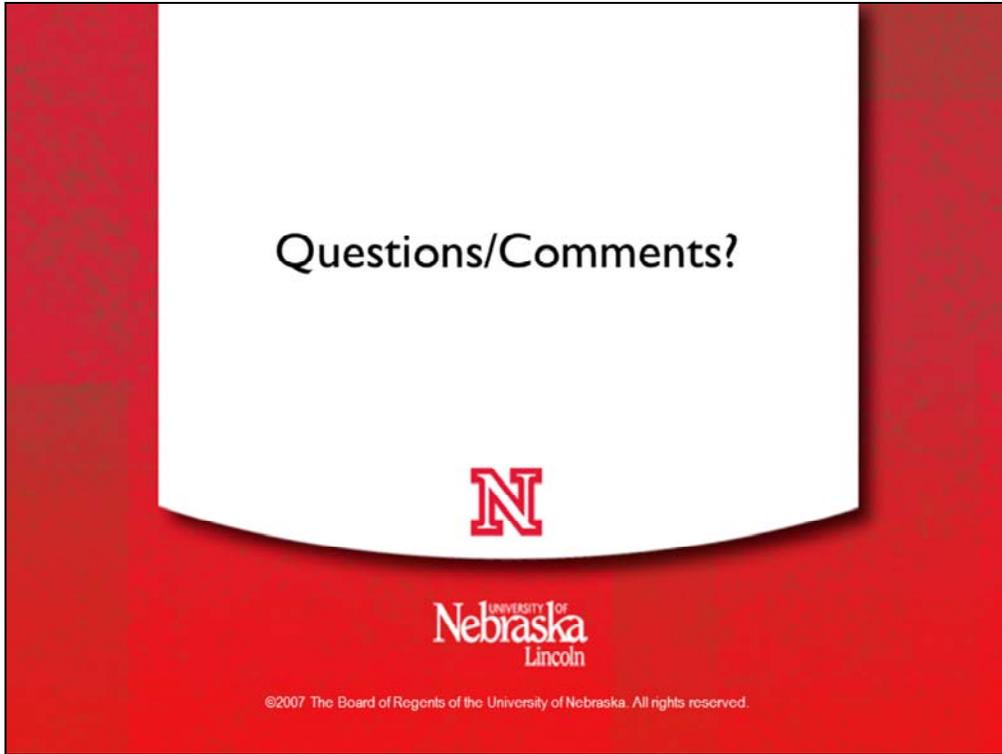
EHS Support

- Contact EHS with any questions
- Will meet with anyone on the subject



[Read slide]

Consult with Environmental Health and Safety with questions.



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The End



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And because I don't like ending on too serious a note...puppies and kittens.