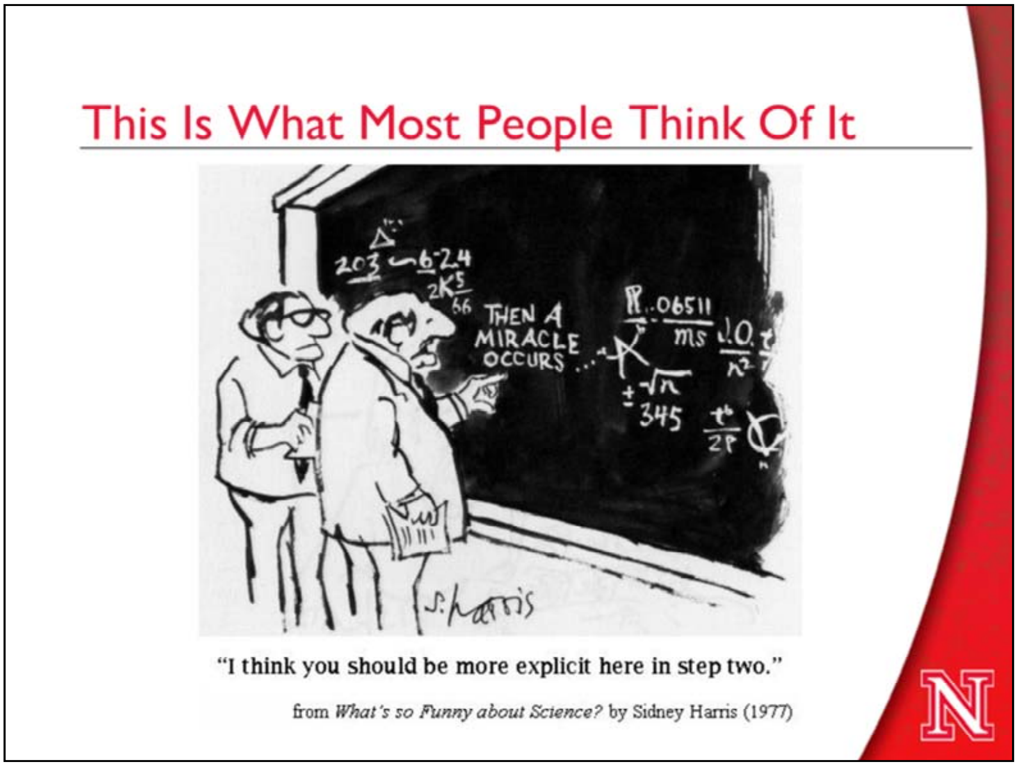
This presentation is targeted toward everyone using chemicals.

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

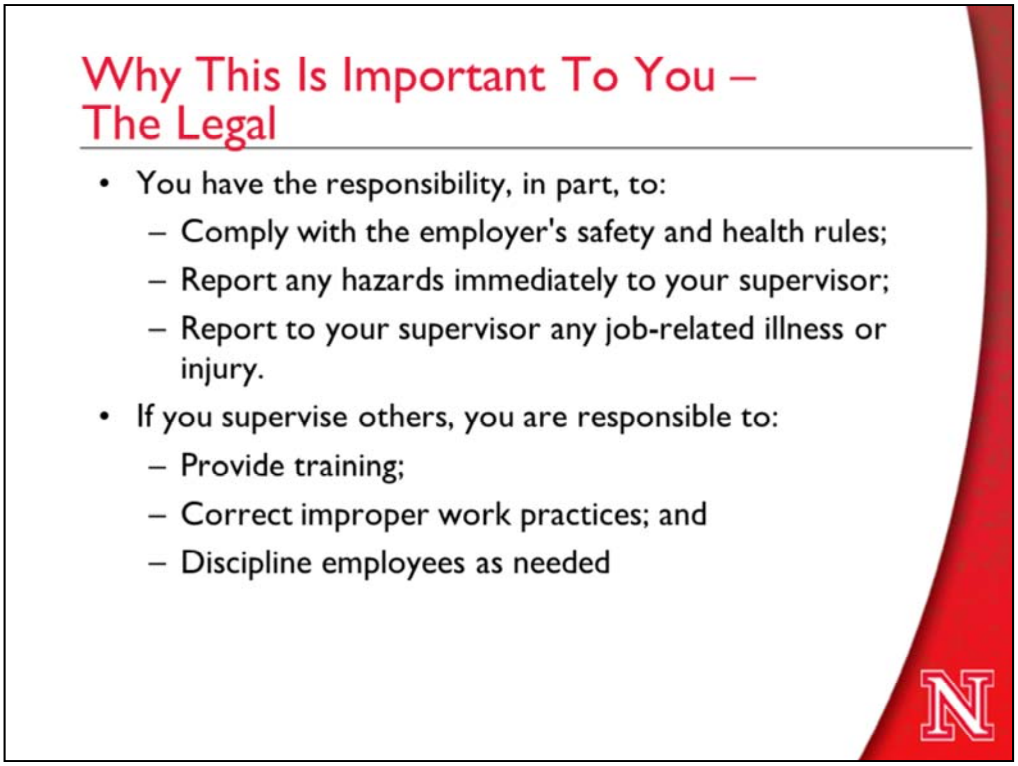
Introduction

- 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



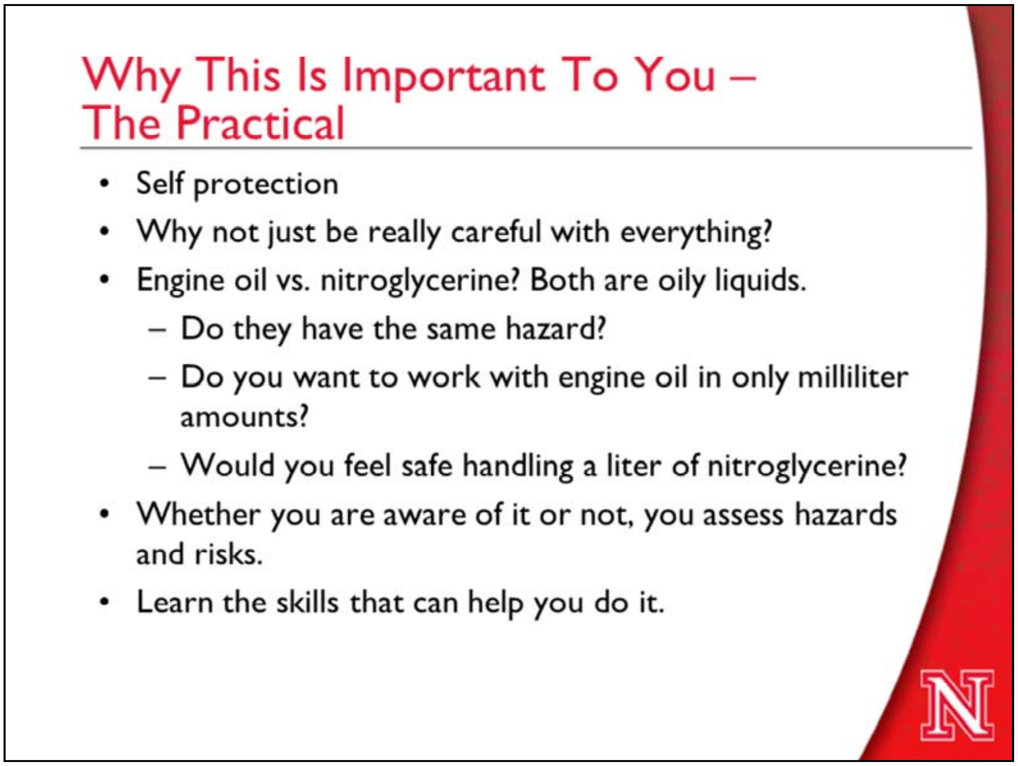
Lots of people think that hazard assessment and risk minimization is magic.

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



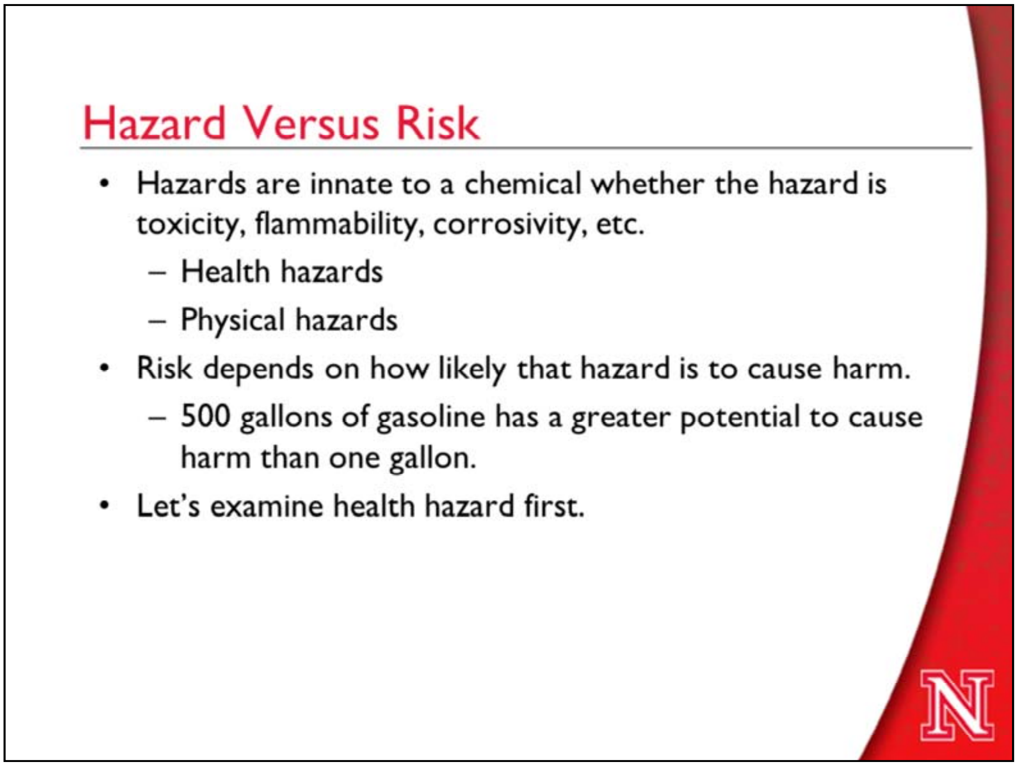
Under federal Occupational Safety and Health Administration regulations, you have the responsibility to comply with the employer's safety and health rules; report any hazards immediately to your supervisor and report to your supervisor any job-related illness or injury. With regard to reporting hazards, 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.



[Read the slide]

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



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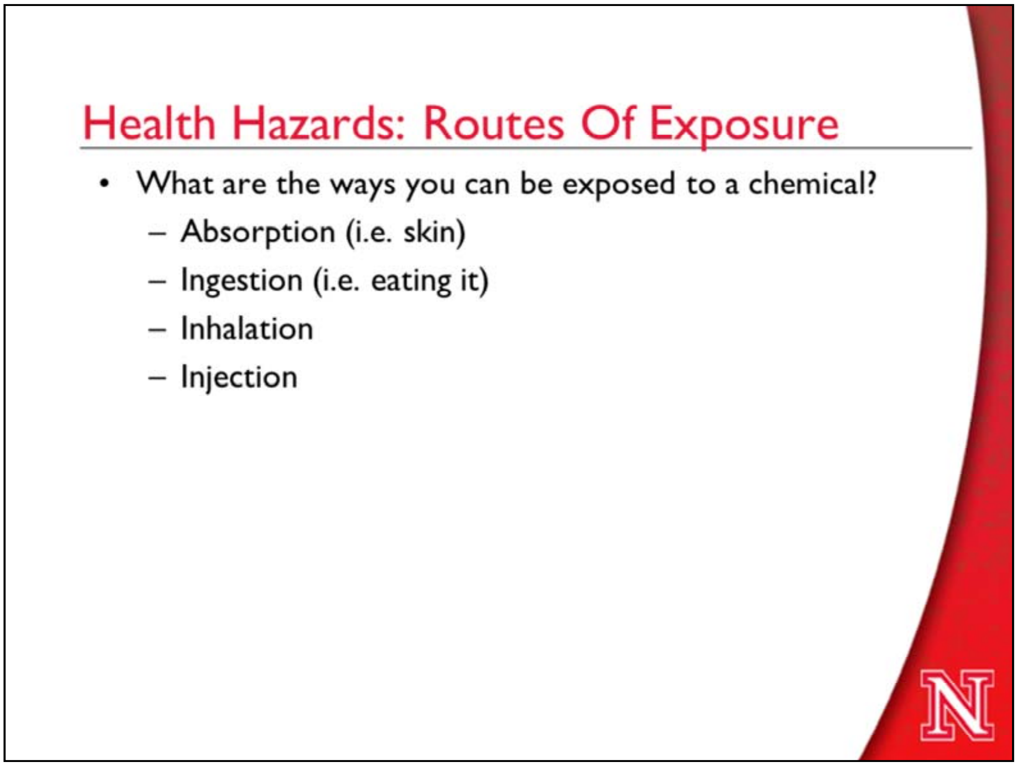


There are two different types of hazard that we'll be discussing. These are health hazards and physical hazards. We'll discuss health hazards first. For a chemical to pose a health hazard there has to be a potential for exposure.

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

Absorption (i.e. skin)

Ingestion (i.e. eating it)

Inhalation

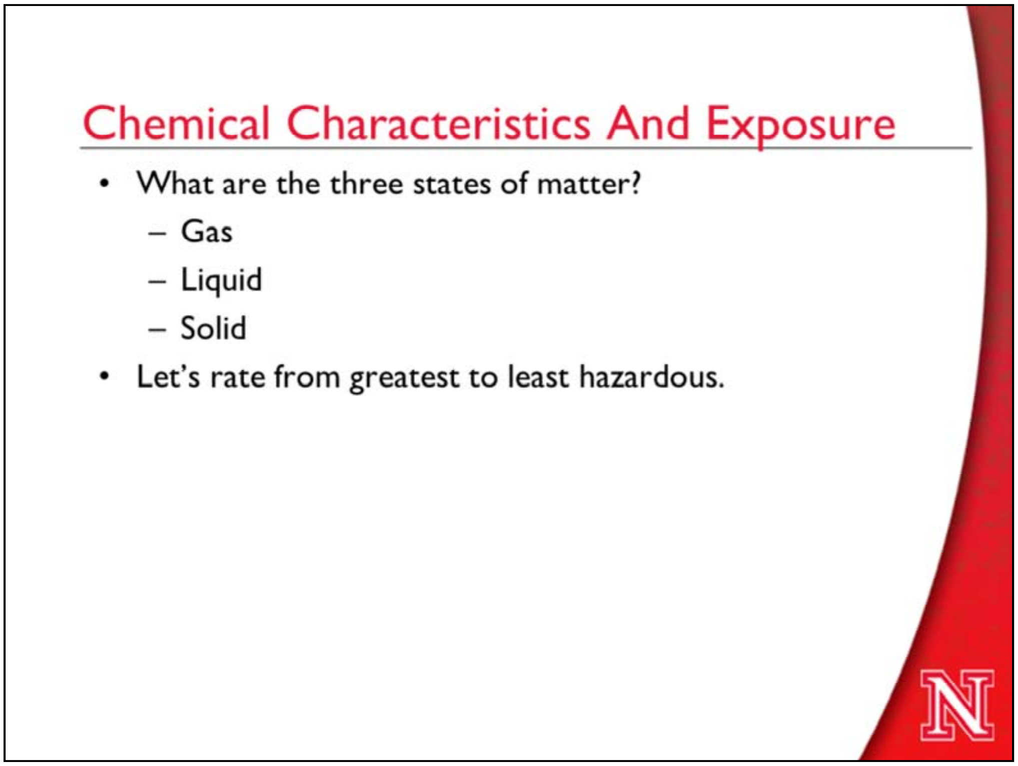
Injection

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.



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.

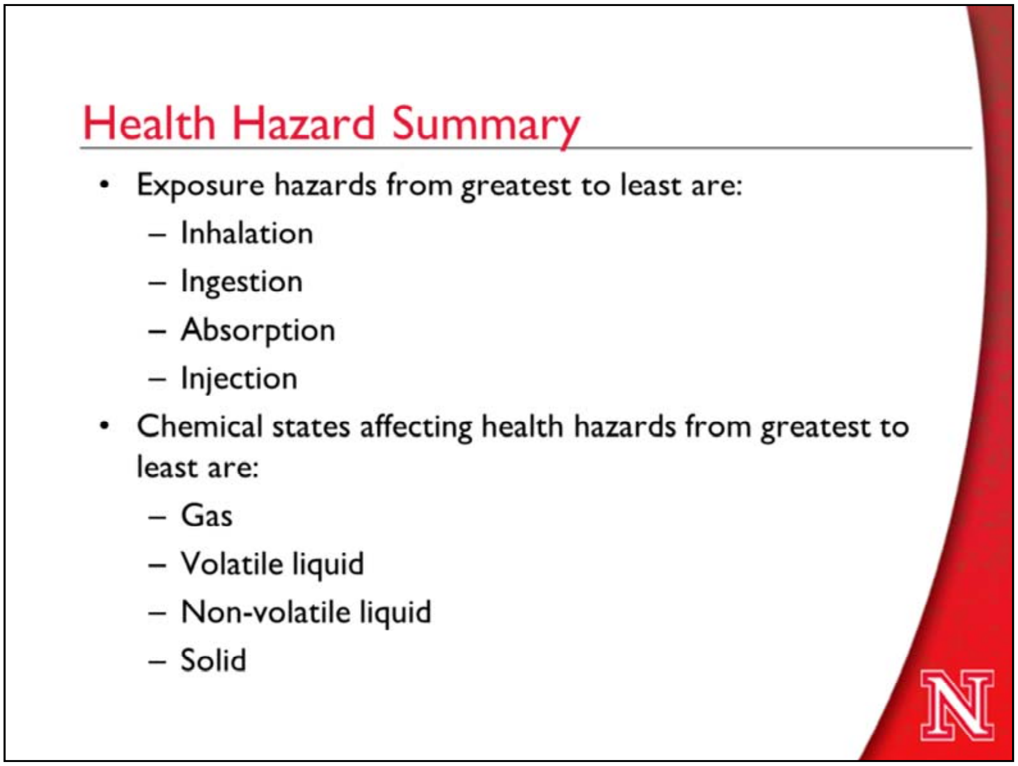
When can solids be hazardous?

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]

This is the internationally recognized Globally Harmonized System (GHS) classes of health hazards of chemcials. 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

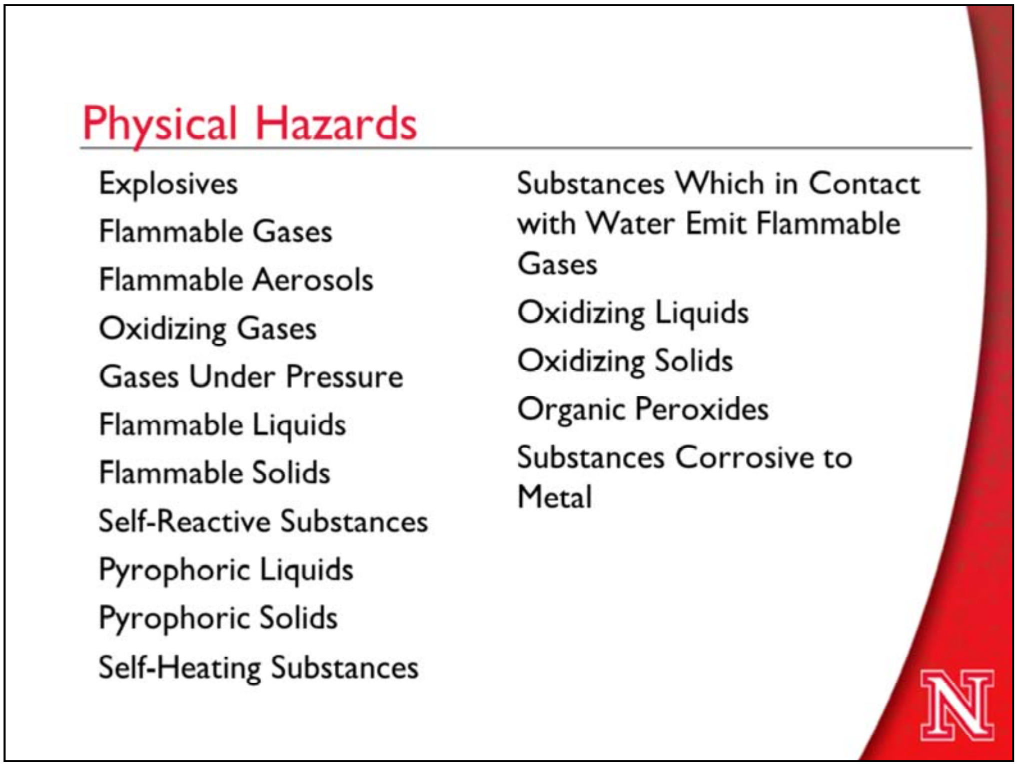
Why?

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.



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

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

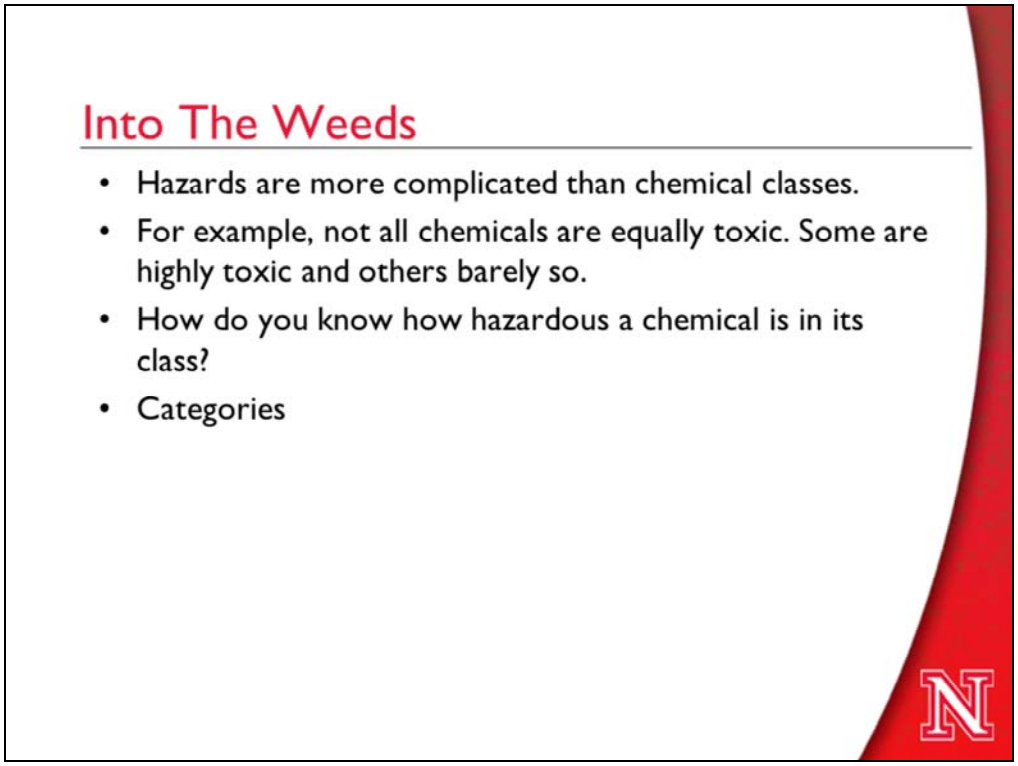
What other class(es) have high hazards?

Answer: Pyrophorics

Note that the ‘substances which in contact wth 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

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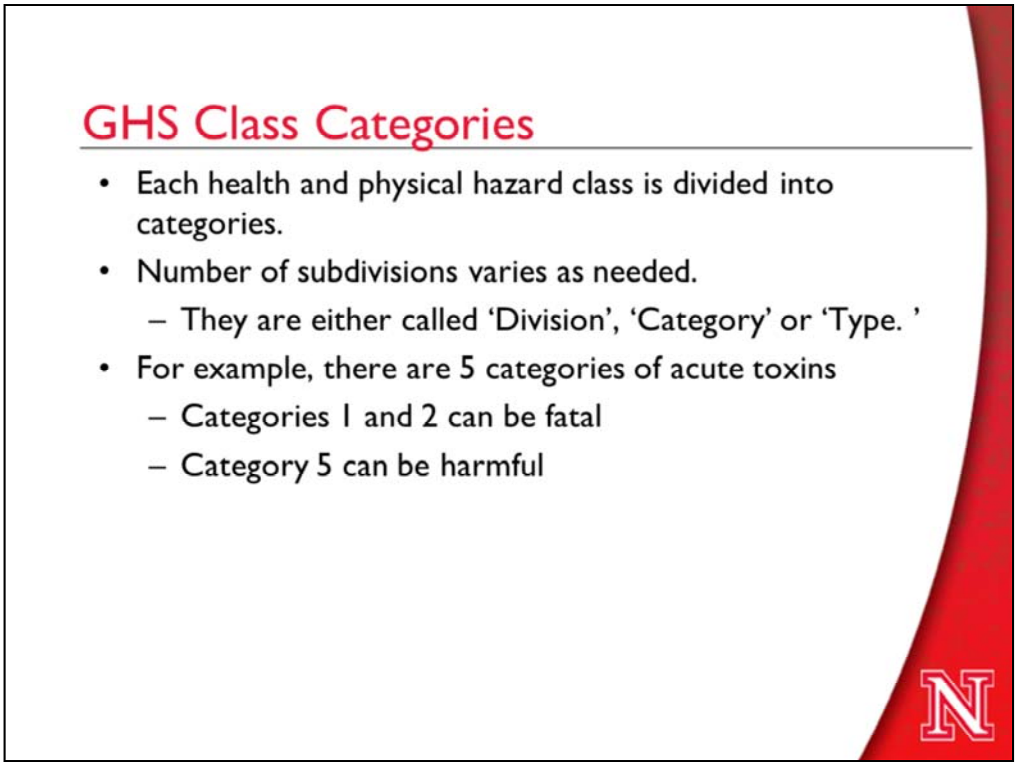

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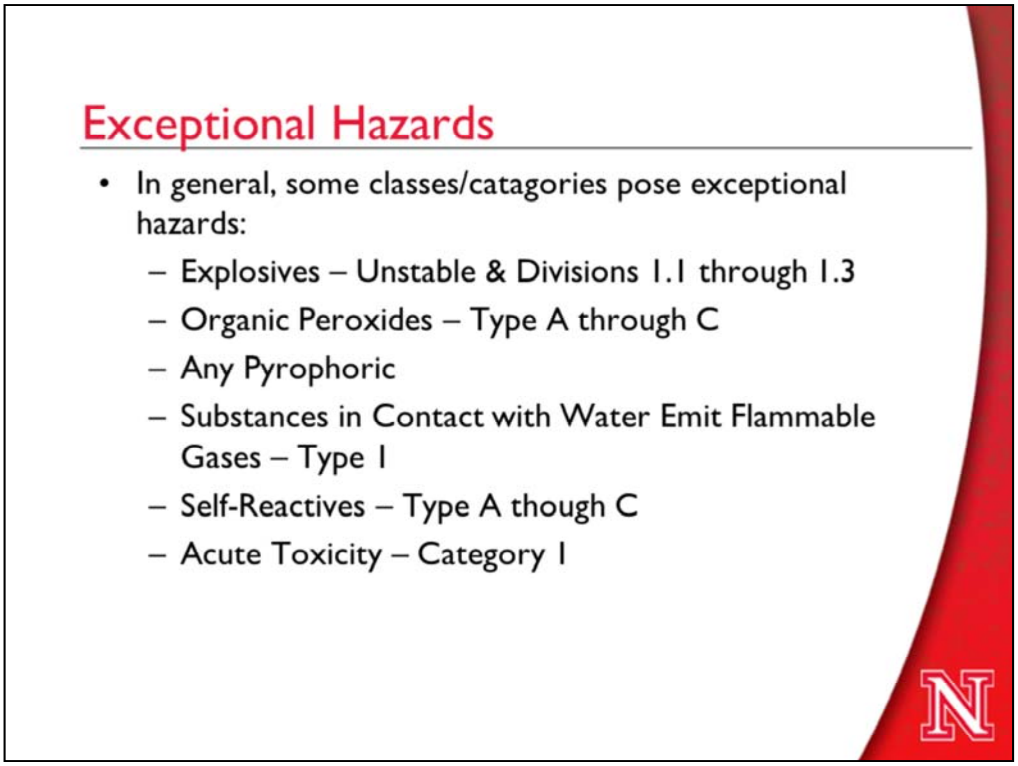
Provided is the EHS Safe Operating Procedure, ***Chemical Hazard Assessment and Risk Minimization***, as a resource.

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 metabilize/transform it and how rapidly the body can exrete it. As a result, sometimes the categories between different chemicals might not seem right based on your experience.



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 though 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 lets move on to risk minimization.

Risk Minimization

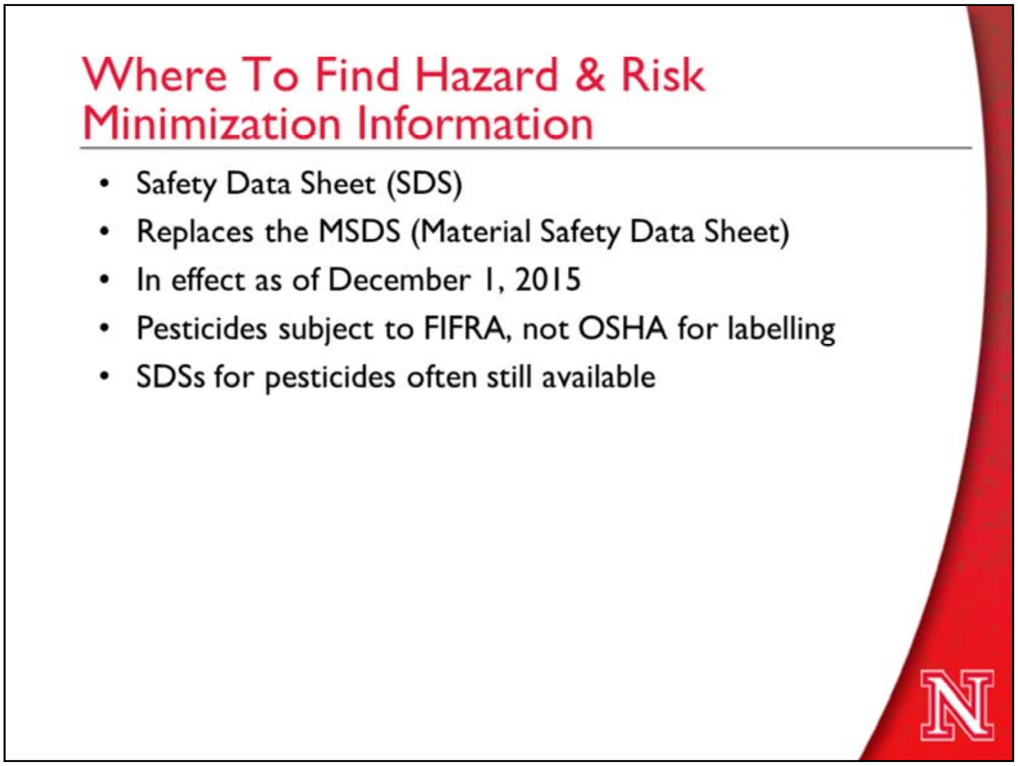
[Let attendees read the slide]

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

[Read the slide]

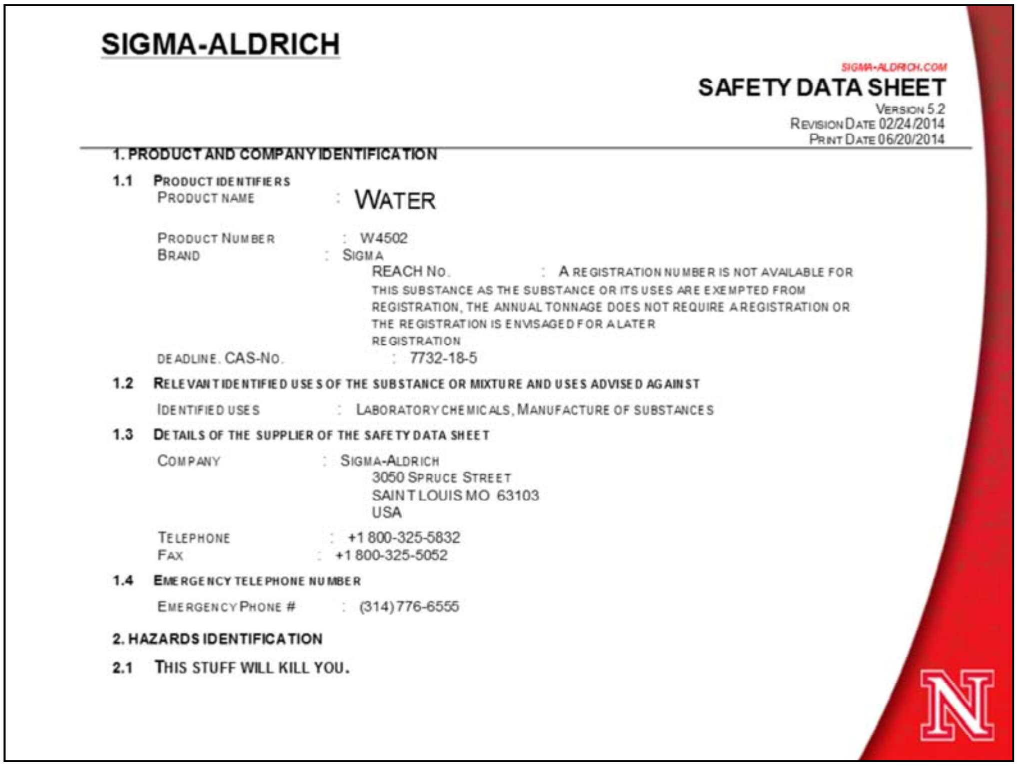
1. Don't use the chemical.
    - Sand/buff parts instead of using solvent-based stripper
2. Substitute it with something less hazardous.
3. Isolate the chemical from people.
    - Radioactive sources that have built-in shielding
4. Add engineering controls, such as safety barriers or exhaust ventilation.
    - 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.



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.



This is how some folks view SDSs.

[Allow the staff to read the slide.]

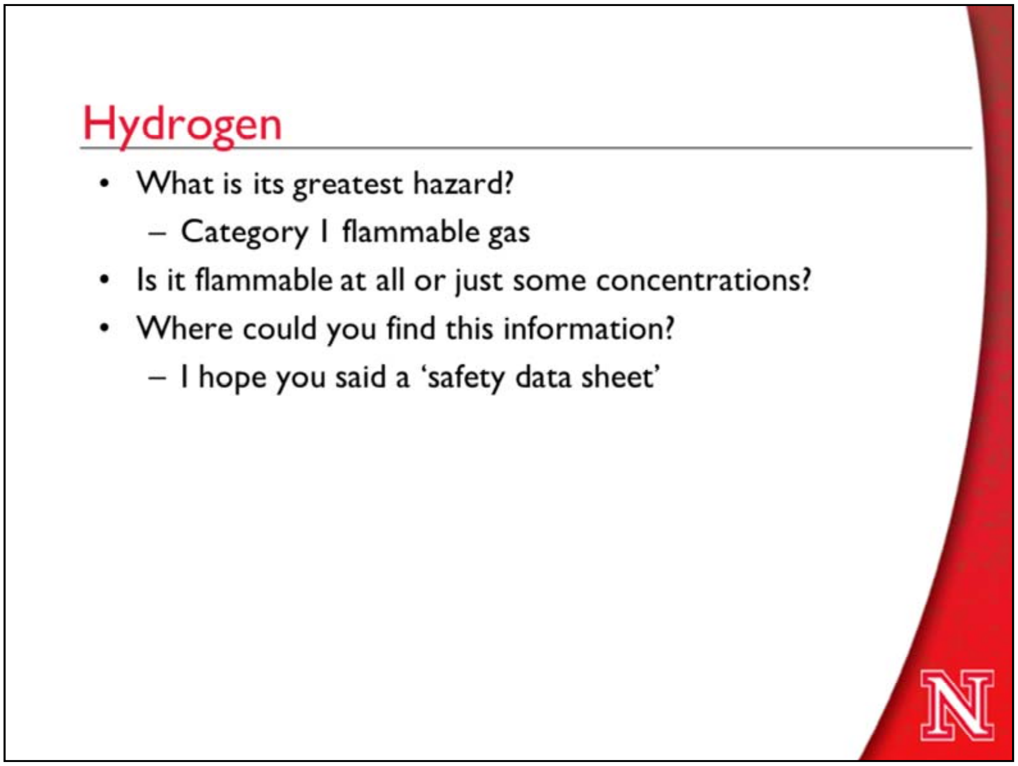
Everything is over the top in alarm. Then again if your ship sank in the middle of the ocean, could water kill you?

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 1 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'

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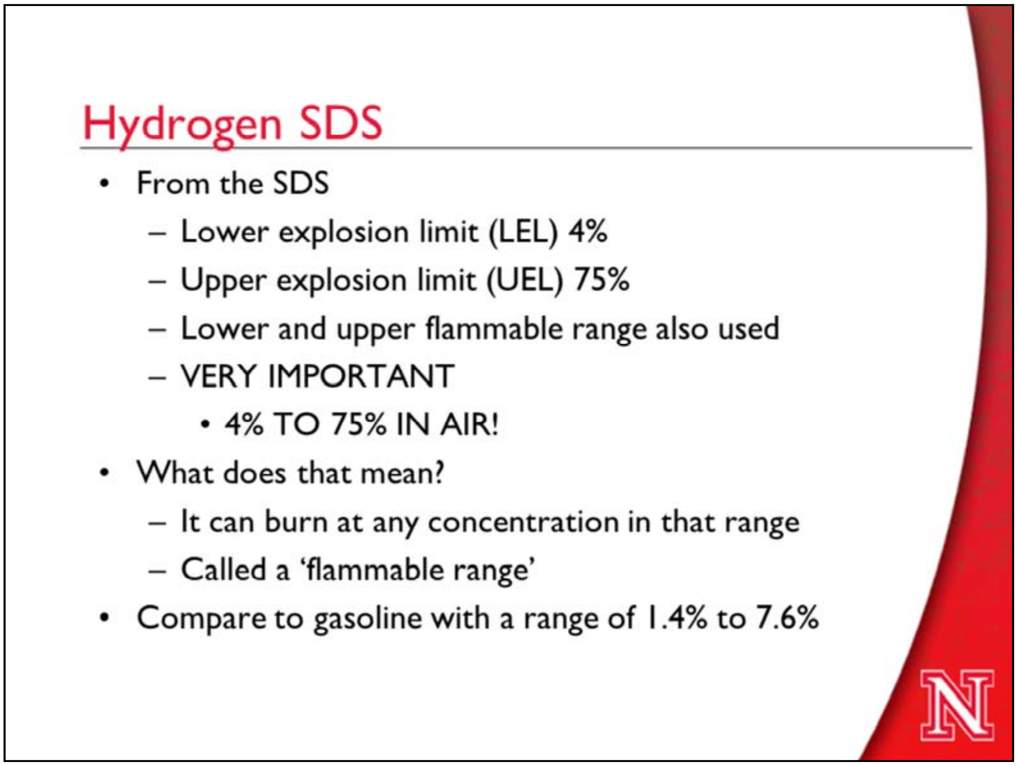


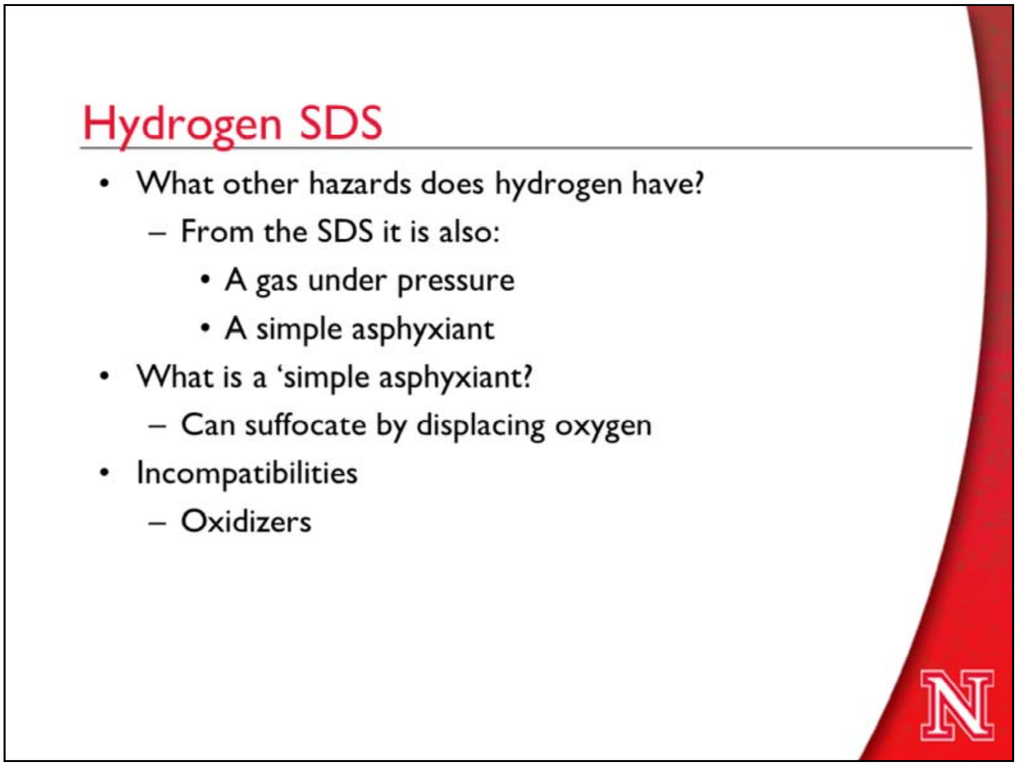
From the SDS

- 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

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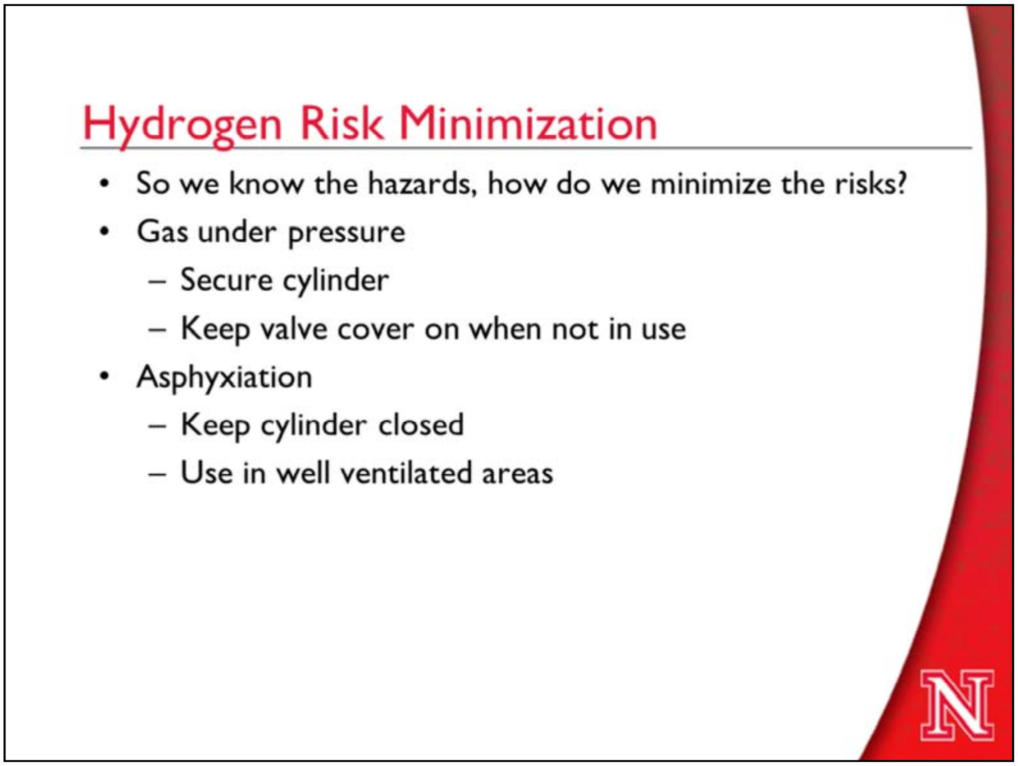

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Can you identify what type of control each of these is:

Gas under pressure answers:

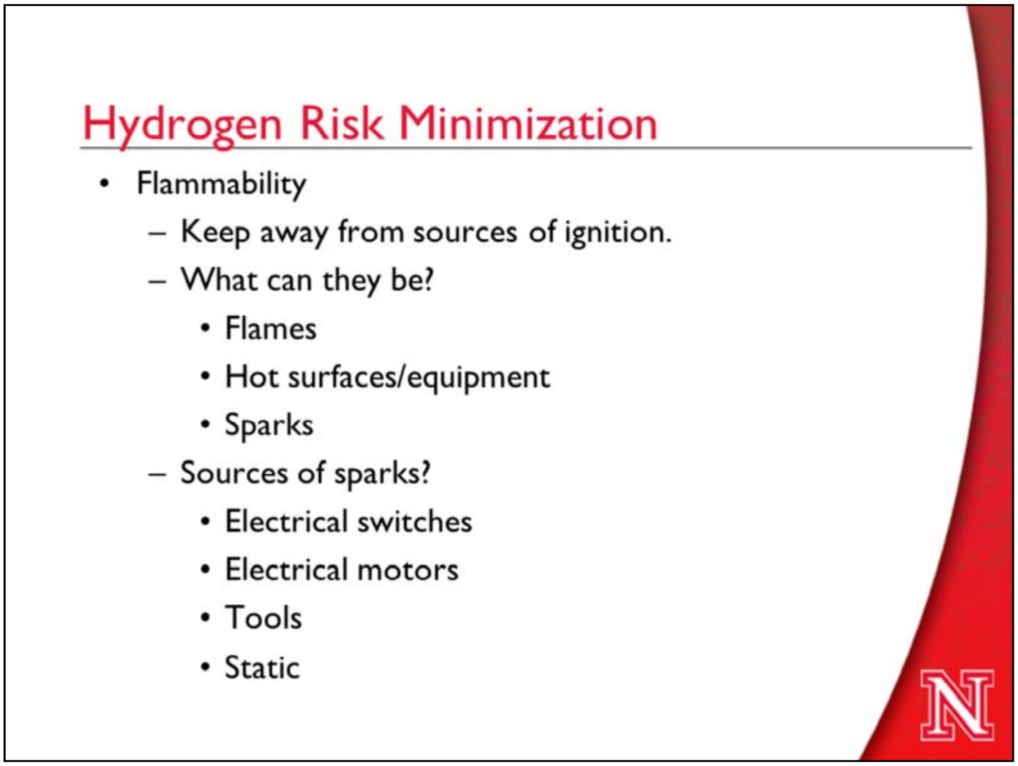
Secure cylinder (engineering control)

Keep valve cover on when not in use (procedure)

Asphyxiation answers:

Keep cylinder closed (procedure)

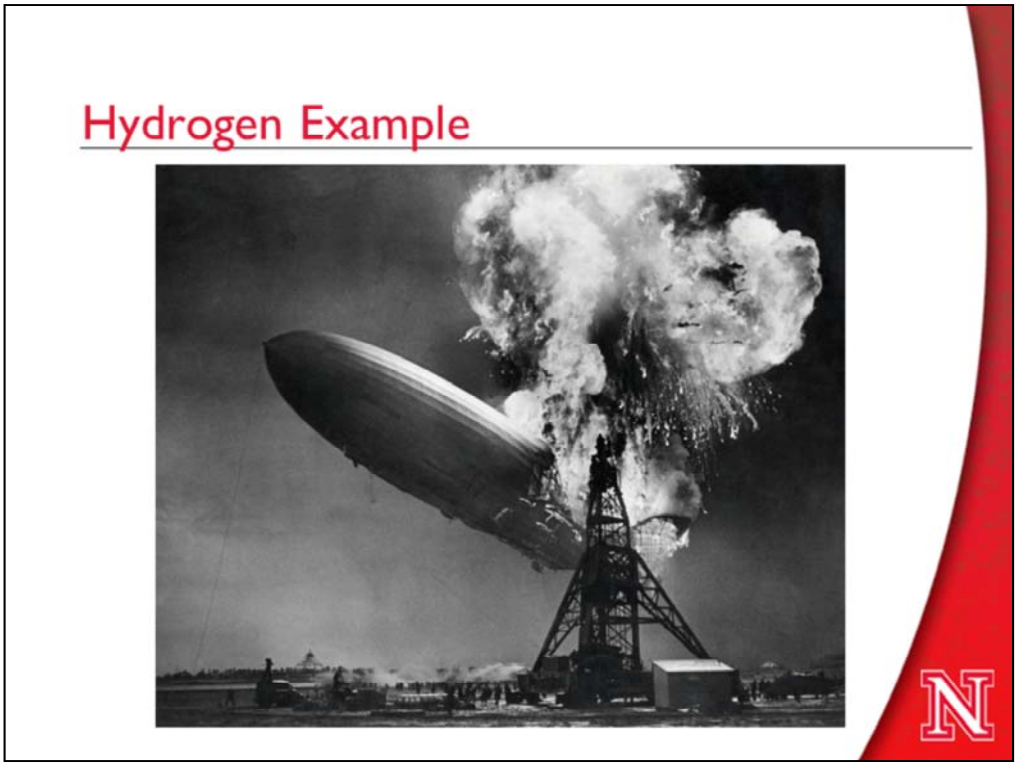
Use in well ventilated areas (engineering control)



[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.



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.

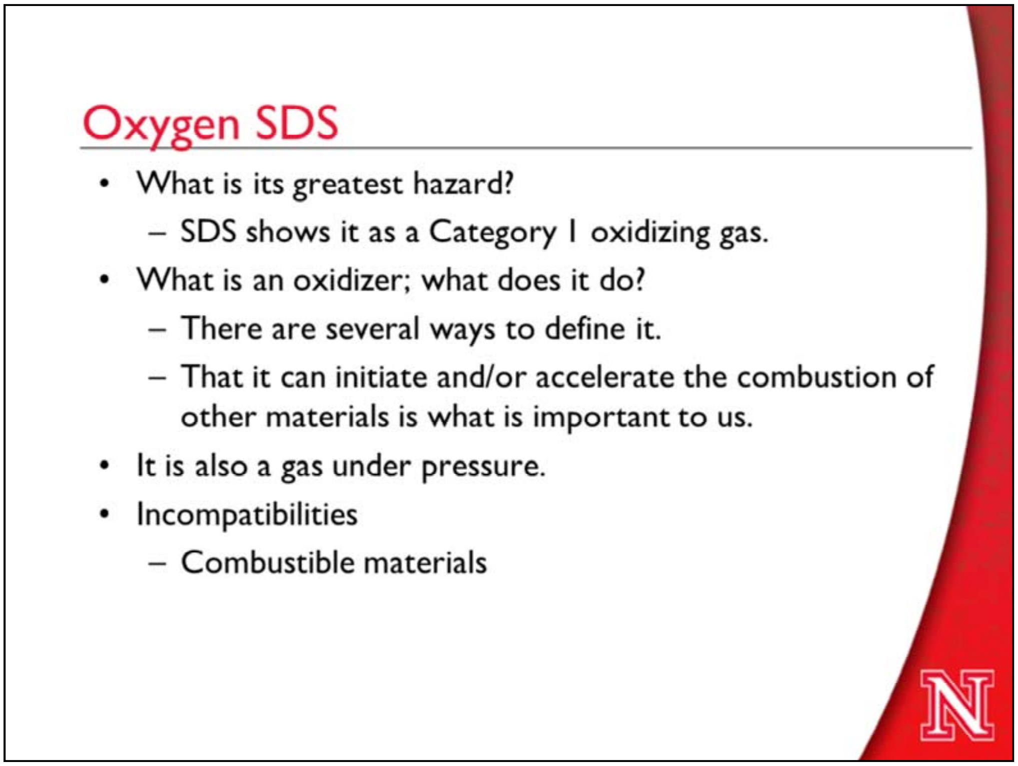
Is the Hindenburg exploding or burning?

Answer: Burning

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

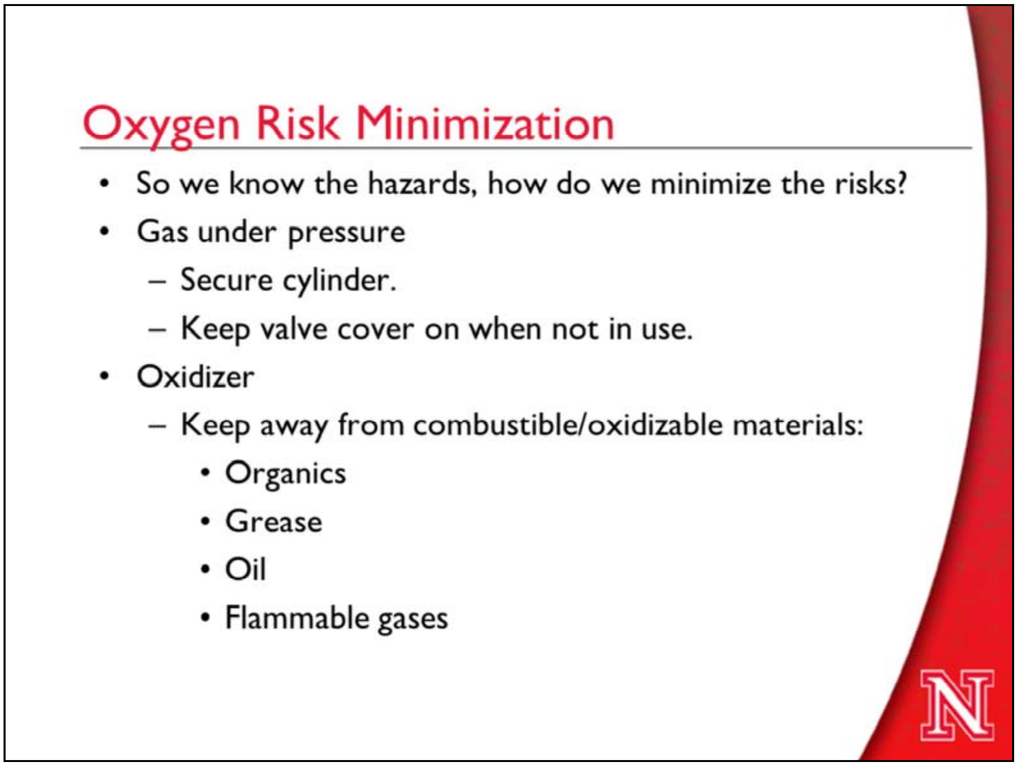
Remember hydrogen needs air to burn. The front part of the ship won't burn until the fire gets there, burns through the gas bags, releases the hydrogen and the hydrogen is exposed to air/oxygen.

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]

Here is an example of oxygen-enhanced combustion.



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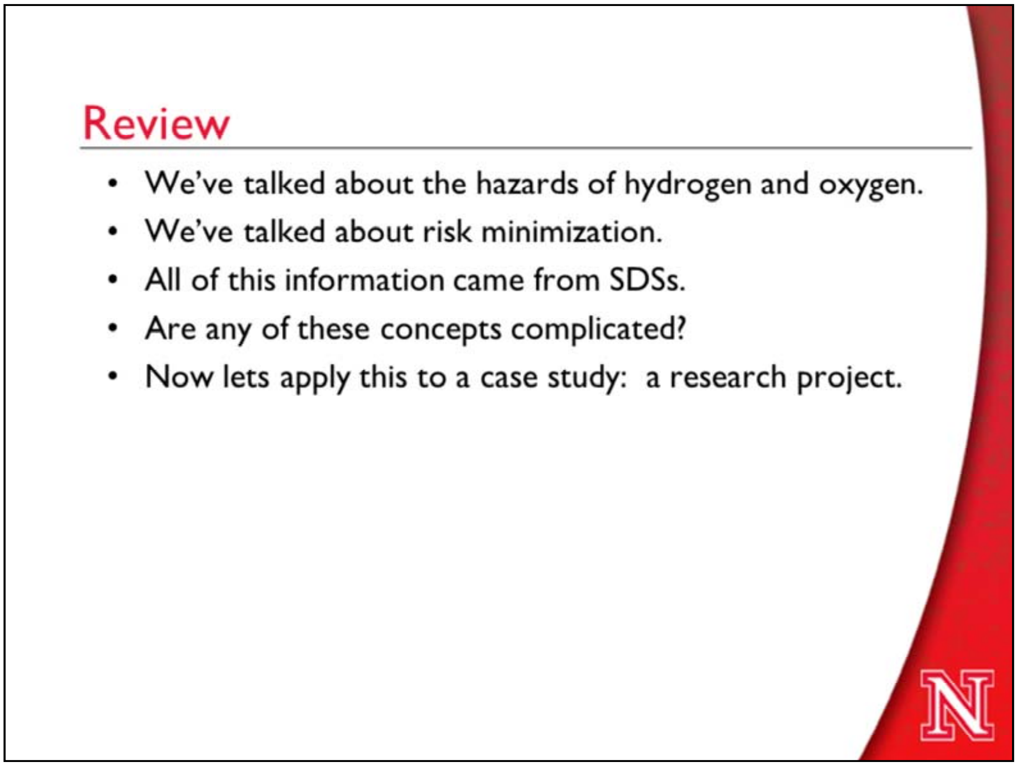
Keep these things in mind as we move on.


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.

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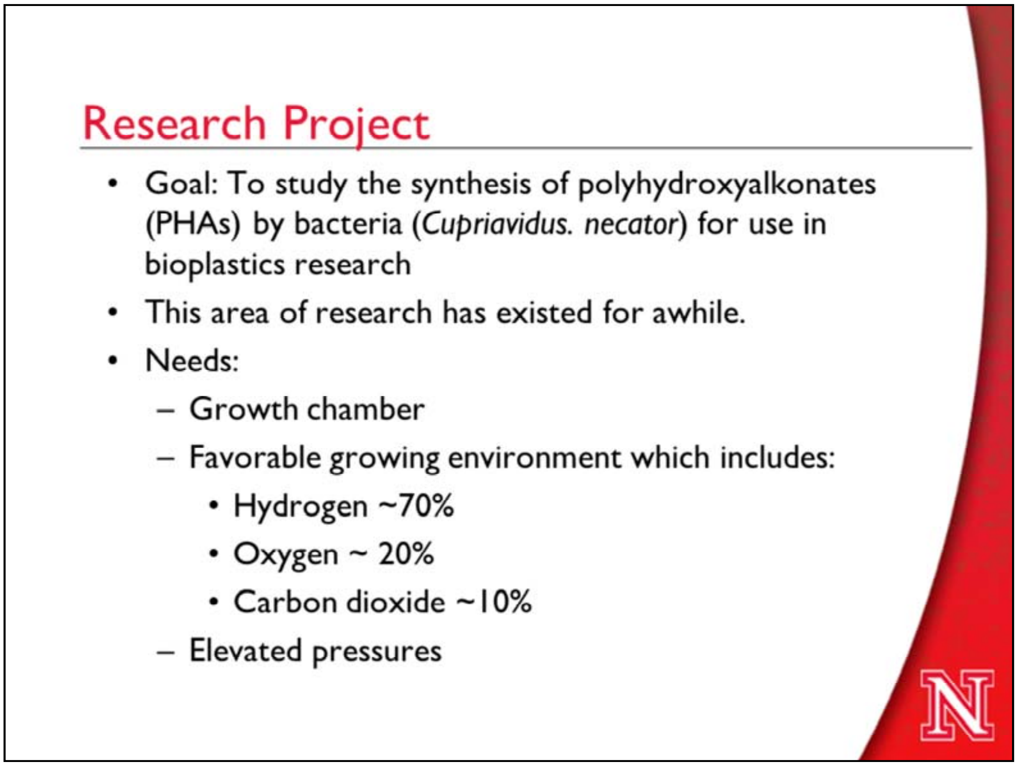

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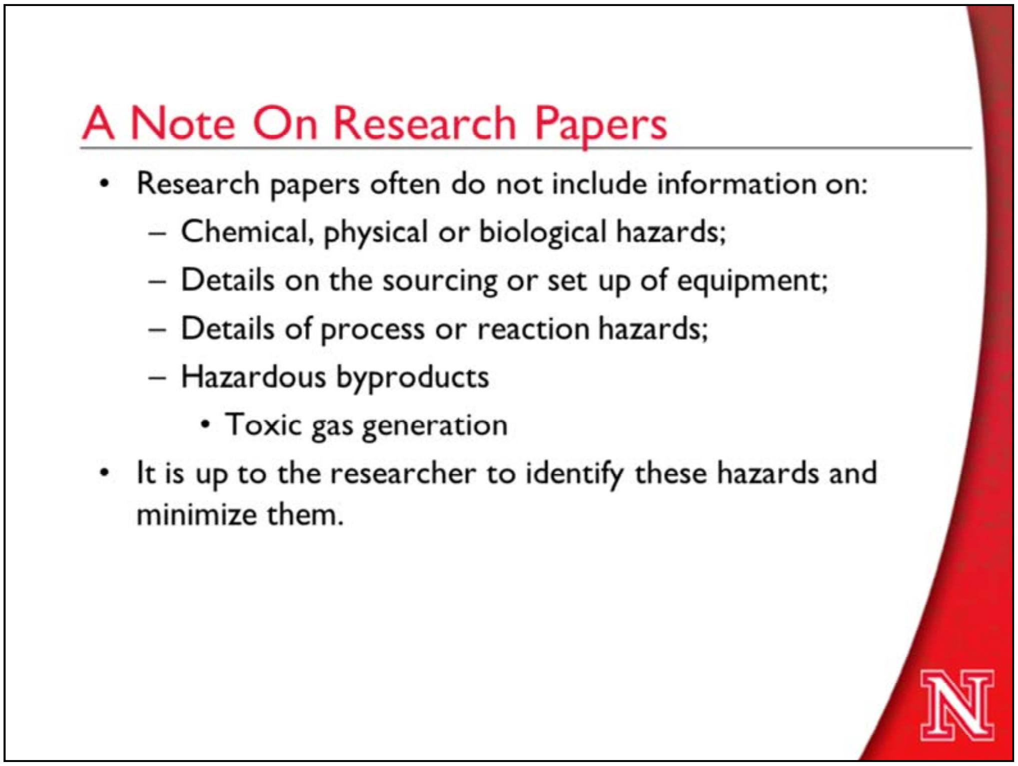
Before we go any further, are there any red flags? Anything of concern?

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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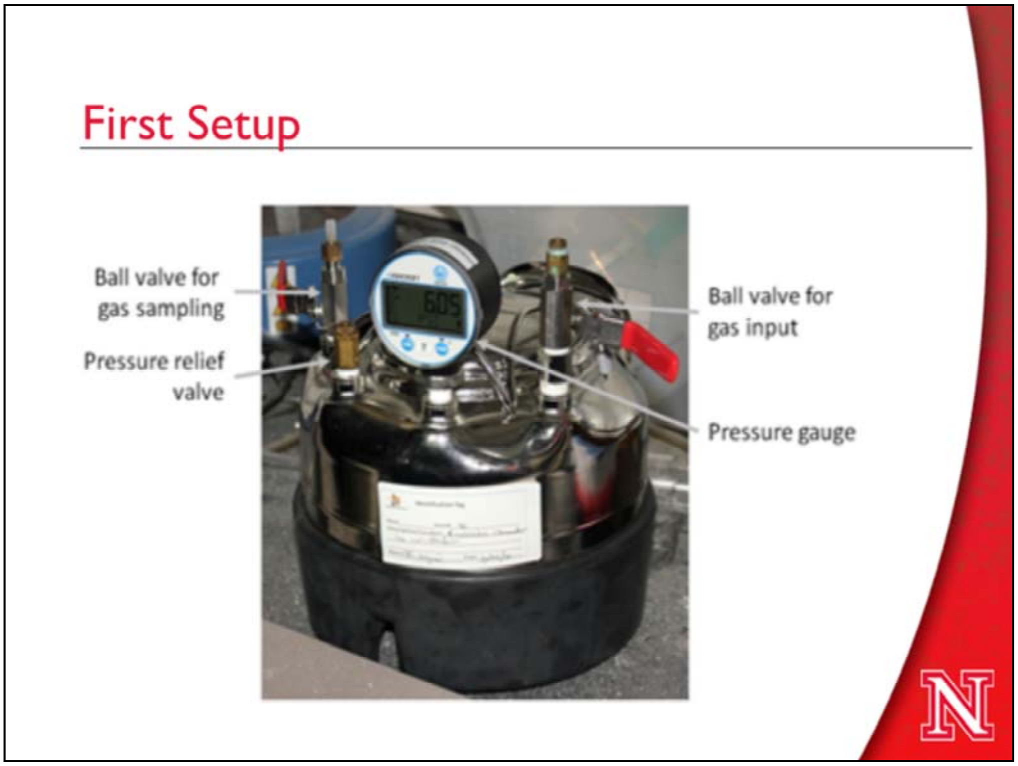
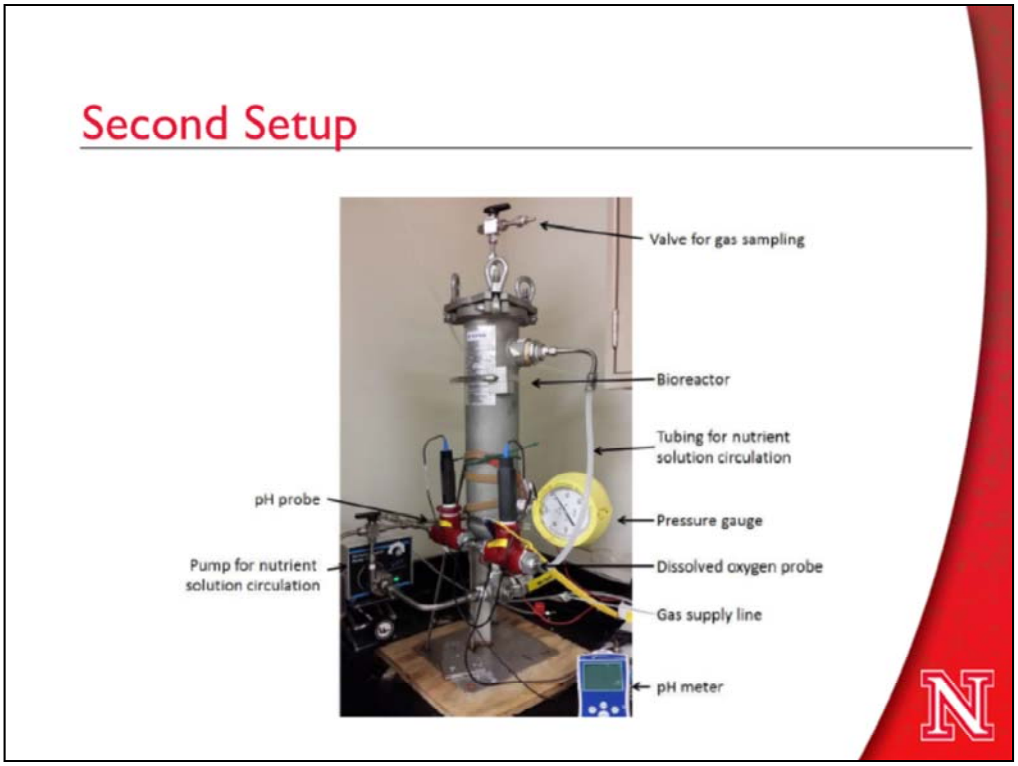


This is a growth chamber. Petri dishes with the bacteria, etc., are placed inside.

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 30º C and the bacteria “do their thing.”

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

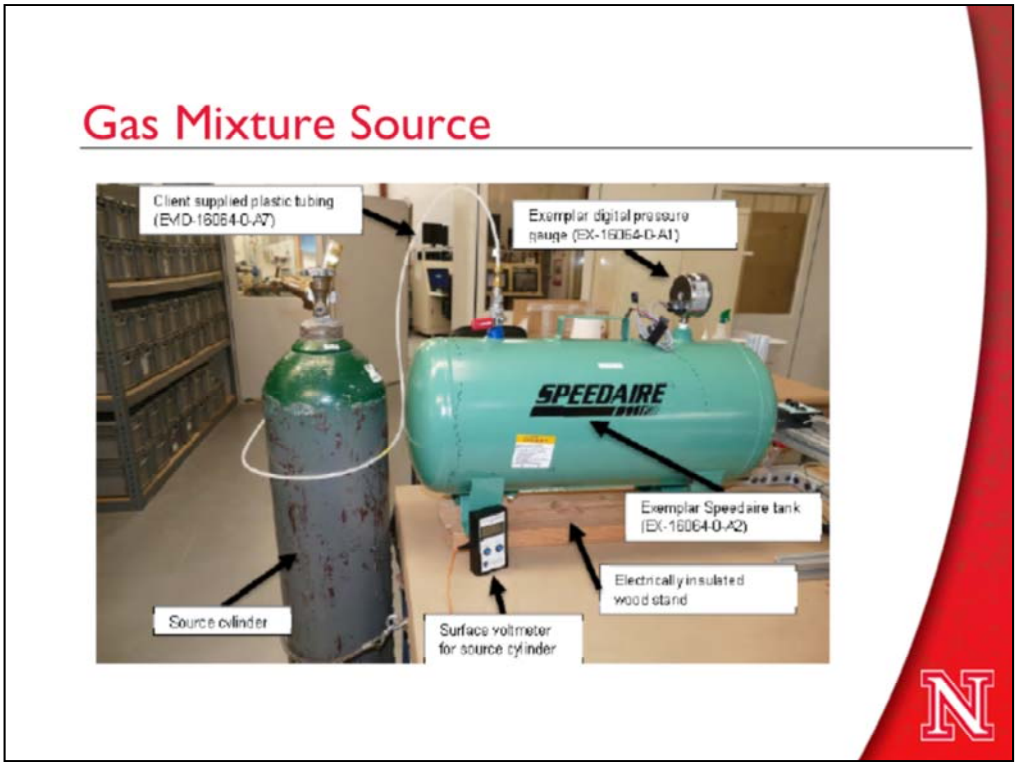


[Read the slide]

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 though the bioreactor.

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



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%

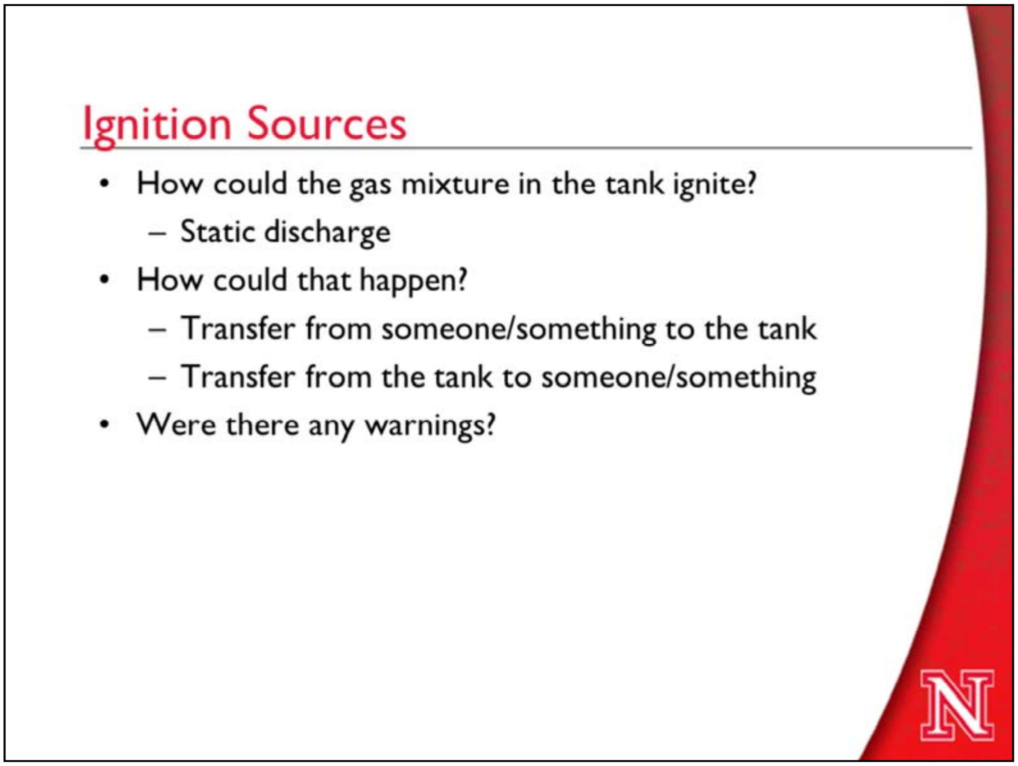
How much oxygen is present in air?

Answer: 21%

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

Answer: Explo

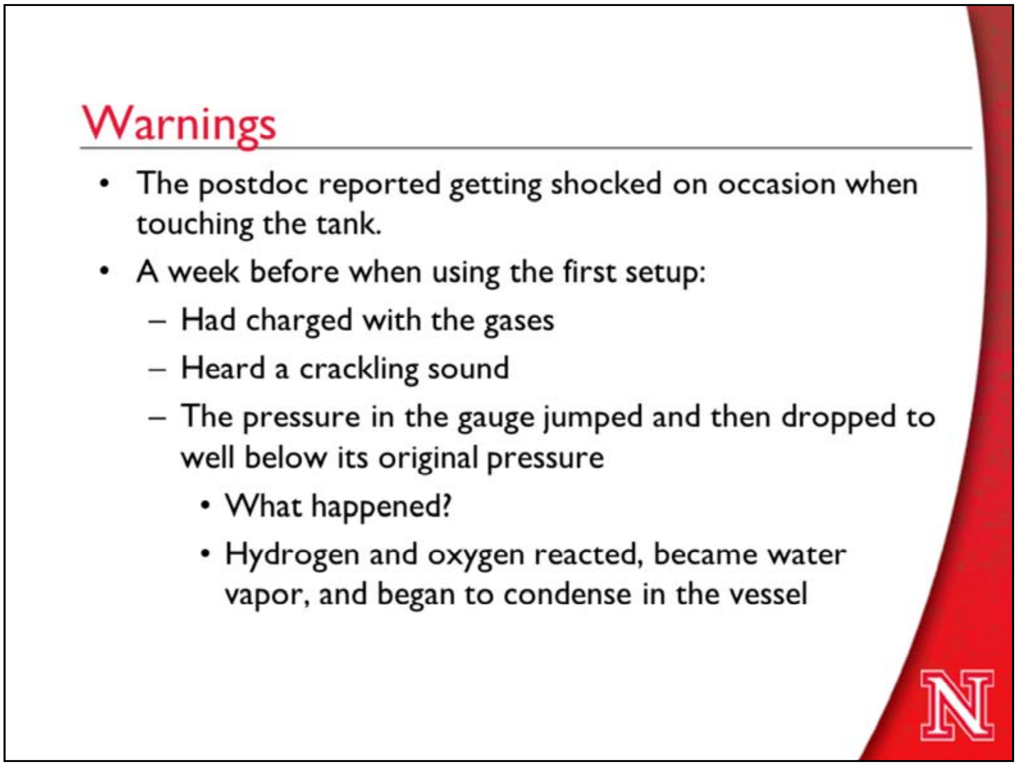
What physical hazard did I say was my greatest concern?
Explosives



[Read bullet and let the audience respond]

Static is the only realistic ignition source.

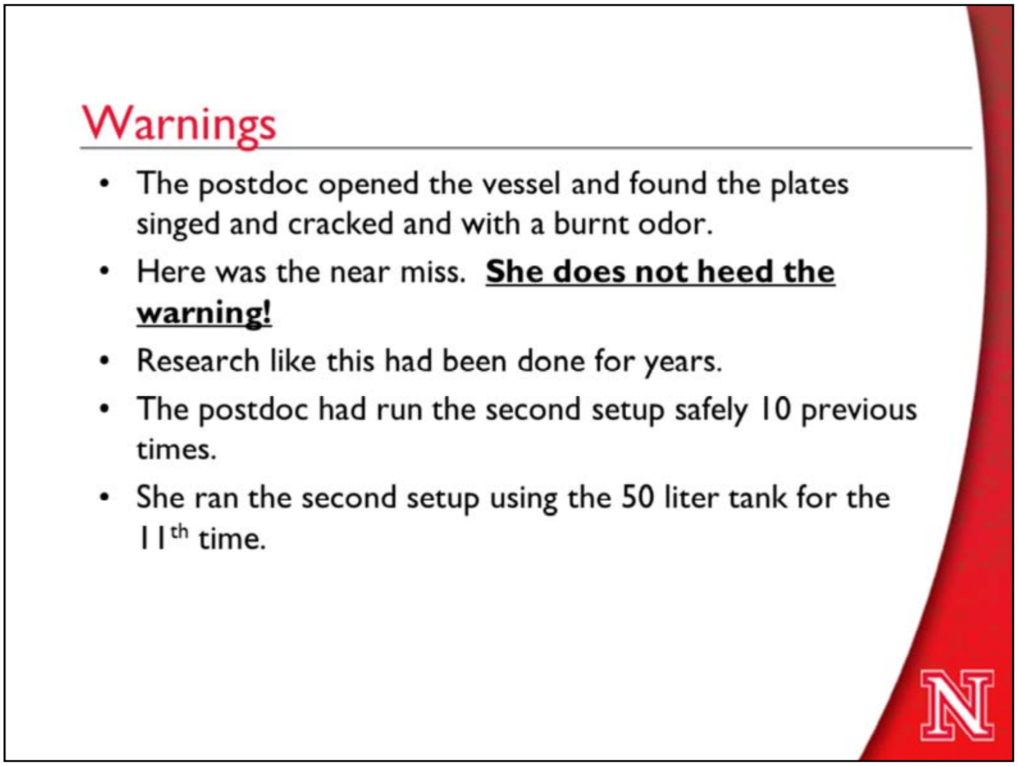
[Read the rest of the slide]



[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?

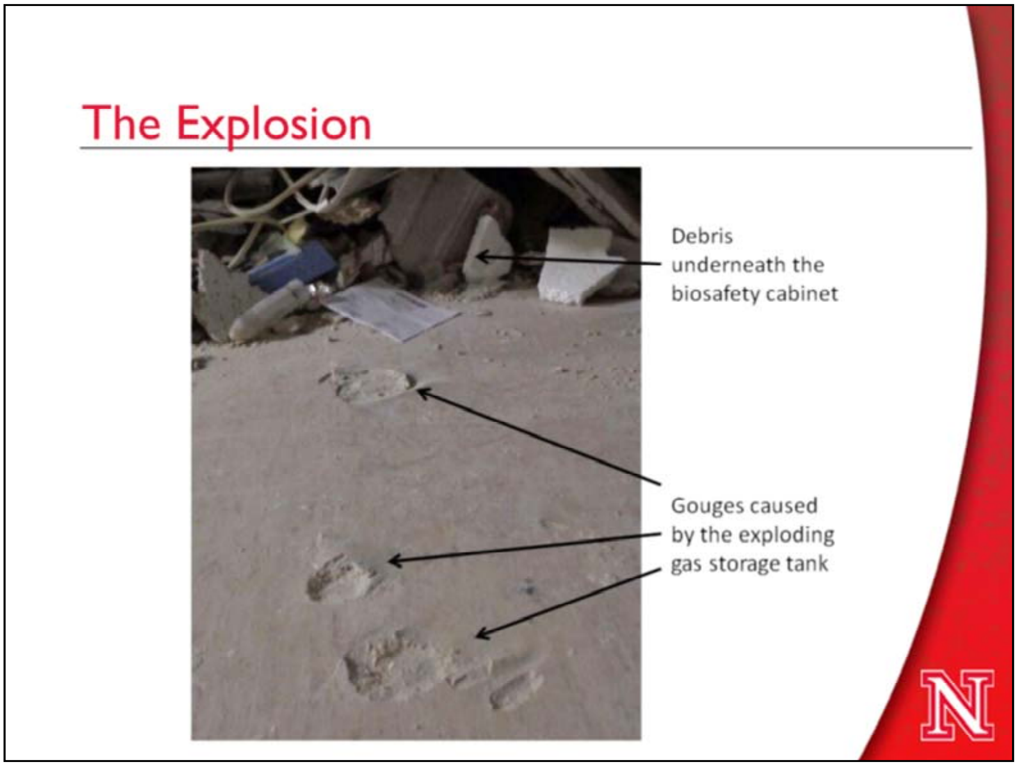
A close-up of the tank.

The Explosion

Another picture of the lab post event.

The Explosion

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



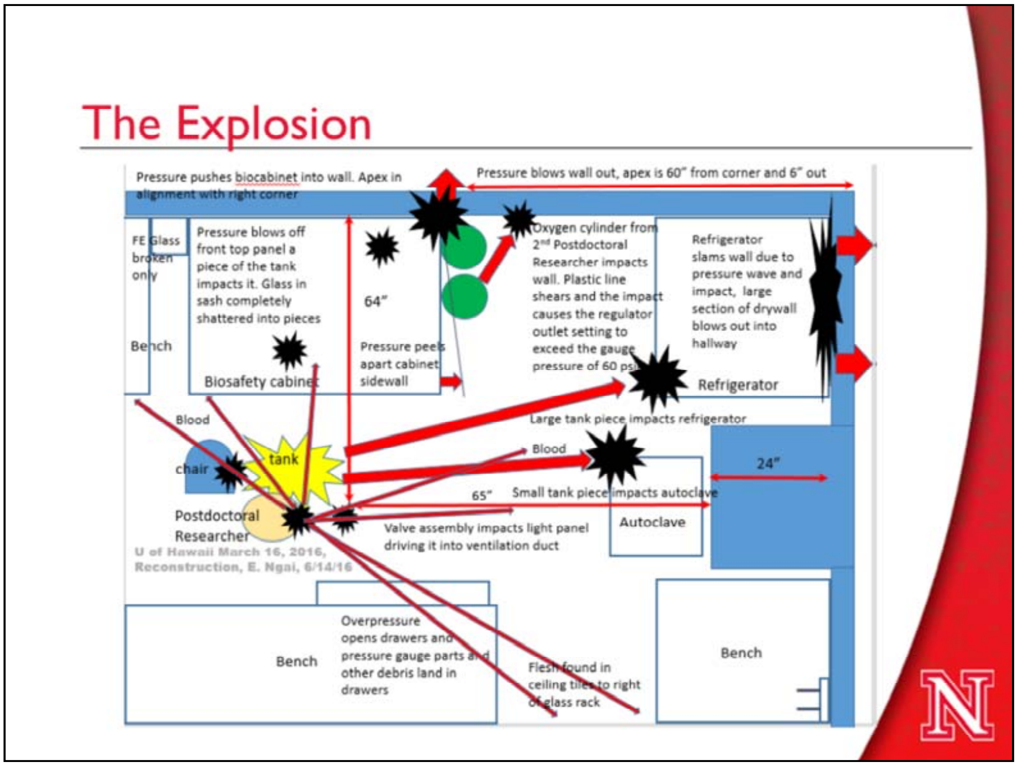
Gouges in the floor from the tank legs.

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

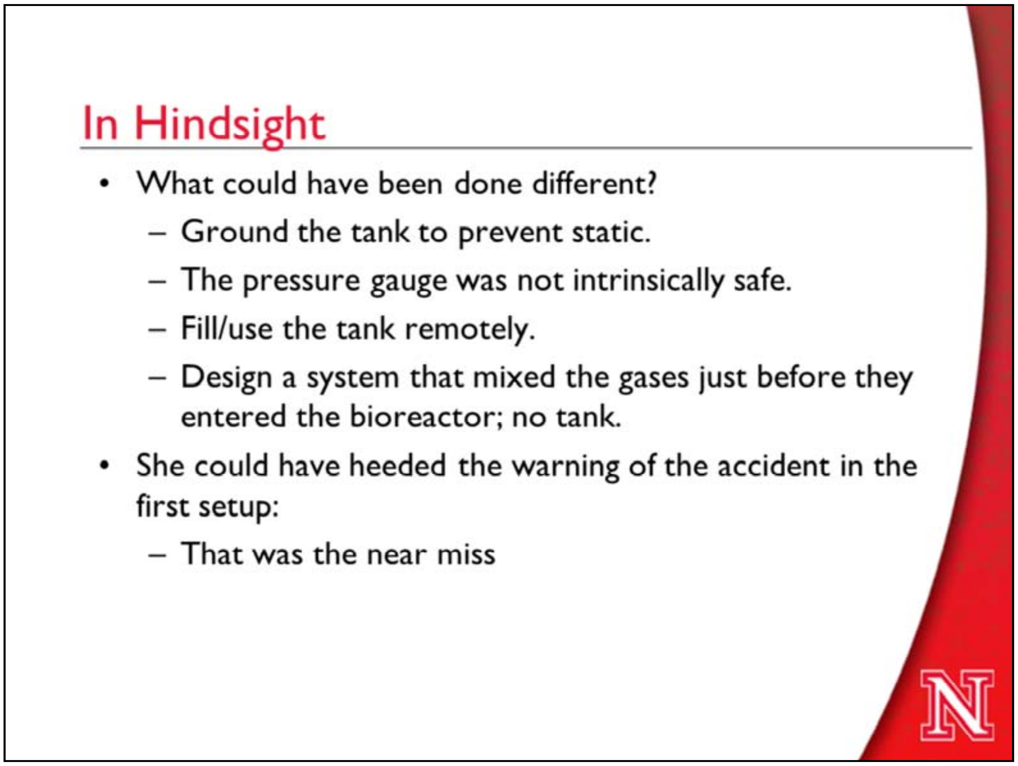
The explosion was equal to between 70 and 700 grams of TNT.

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.



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



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.

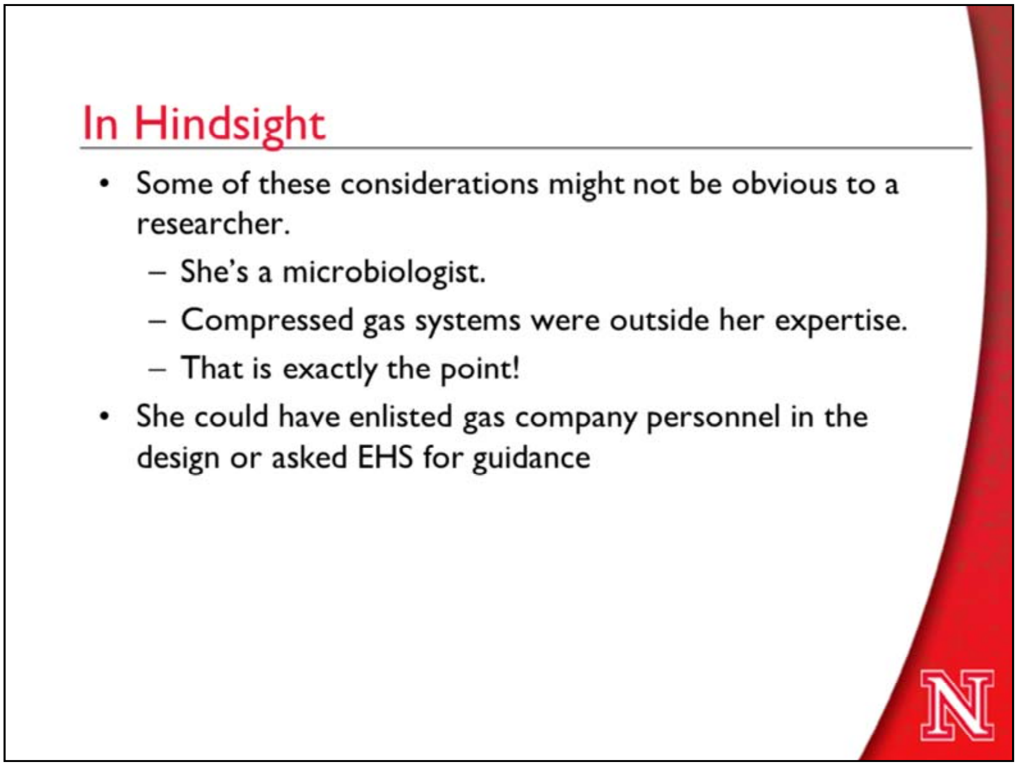
[Read the first point and let the audience respond]

- 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



[Read slide]

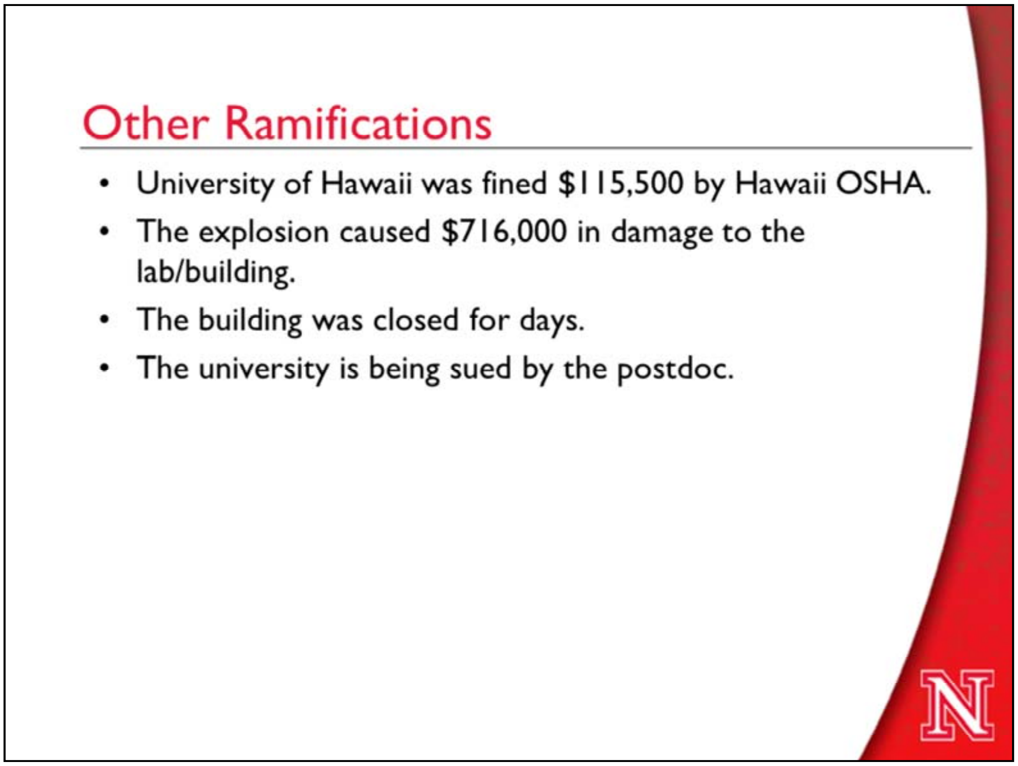
For me, these last points are the most obvious considerations.

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 as 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.

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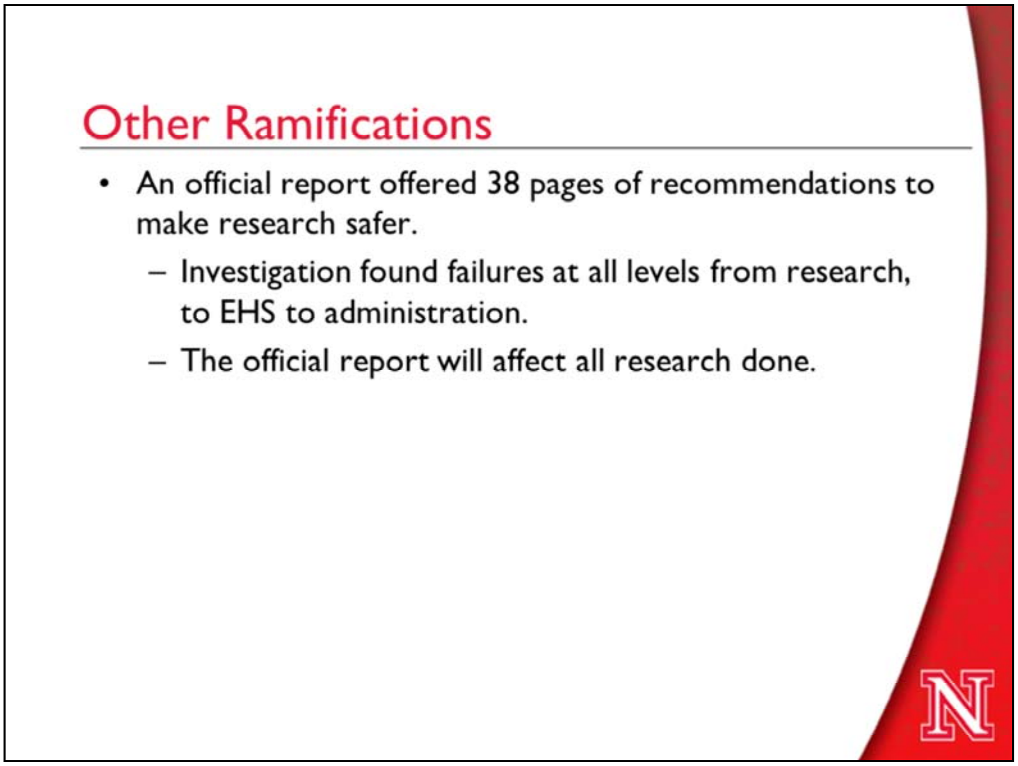
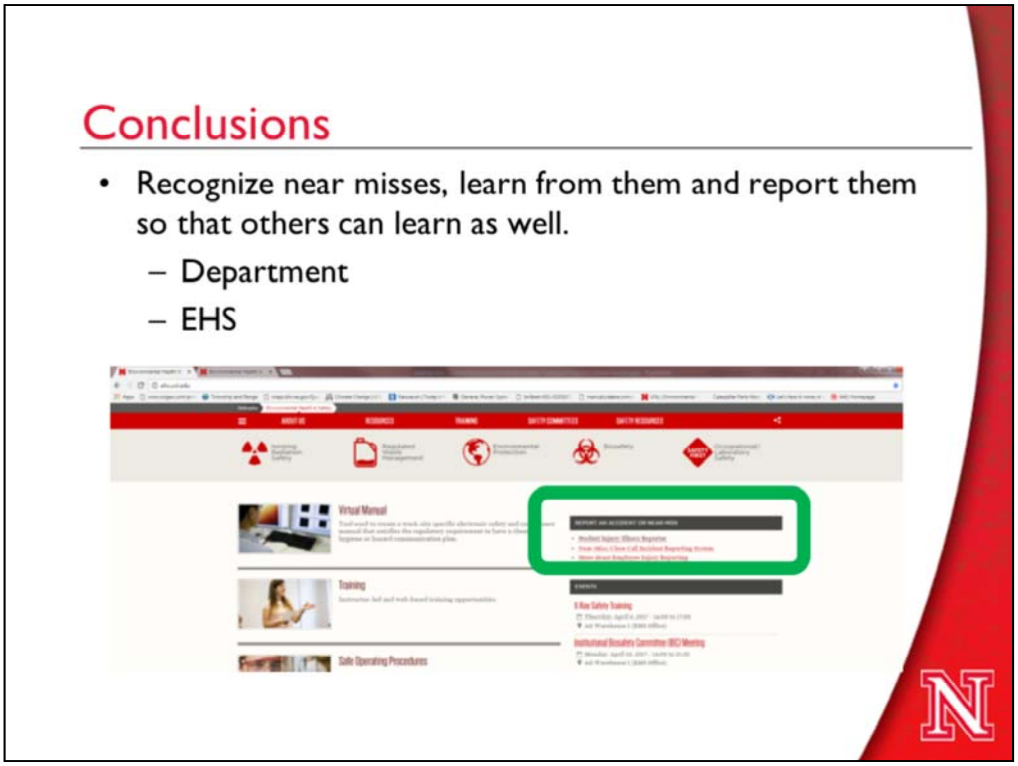

Other Ramifications
• An official report offered 38 pages of recommendations to make research safer.
– Investigation found failures at all levels from research, to EHS to administration.
– The official report will affect all research done.

[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.

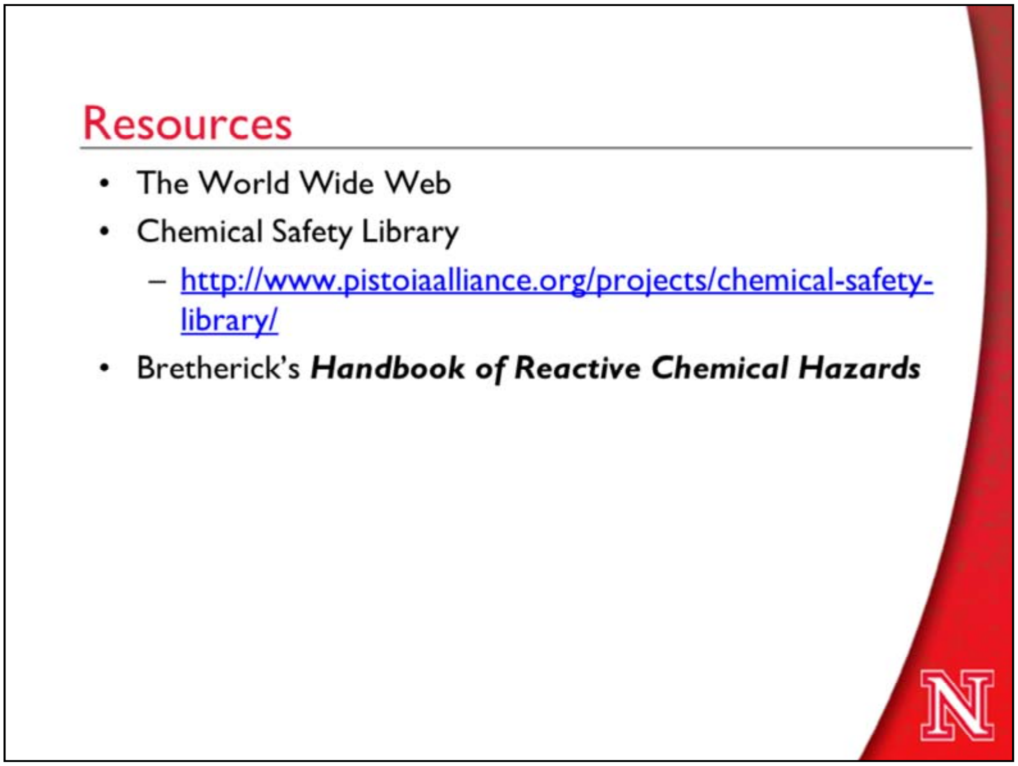


Recognize near misses, learn from them and report them so that others can learn as well

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”



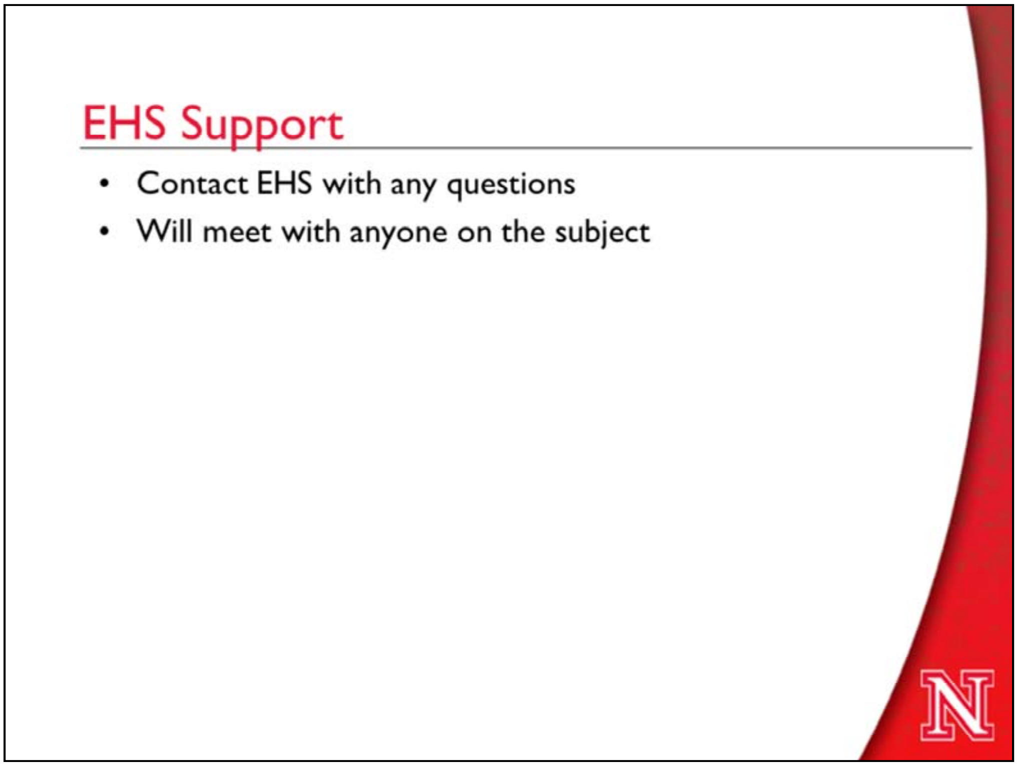
[Read slide]

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 an 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.



[Read slide]

Consult with Environmental Health and Safety with questions.

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