Minimum Safety Requirements for Toxic, Corrosive and Reactive Compressed Gases

EXPLAINED

CBC Lab Safety Workshop
Beyond the Basics
Wednesday, March 16, 2011
University of Arizona Student Union
Tucson Room
Overview

• Define terms in presentation
• Provide specific gas examples
• Explain need for concern
• Explain general hazard control approach
• Introduce minimum requirements checklist
• Describe an application of requirements
• Campus resources
Toxic and Highly Toxic Gases

• **Toxic:** \( LC_{50} \) between 200 and 2000 parts per million *

• **Highly toxic:** \( LC_{50} \) of less than 200 parts per million *

* when administered continuously by inhalation for one hour to albino rats
Corrosive Gases

- Gases that cause visible destruction or, or irreversible alterations in, living tissue by chemical action at the site of initial contact
• **Unstable (reactive):** Gases which in the pure state, or as produced or transported, will vigorously polymerize, decompose, condense, or will become self-reactive under conditions of shocks, pressure, or temperature.
Compressed Gases

- Gases or mixture of gases having, in a container, an absolute pressure exceeding
  - 40 psi at 70°F (21.1°C); a gas or mixture of gases having, in a container, an absolute pressure exceeding OR
  - 104 psi at 130°F (54.4°C) regardless of the pressure at 70°F,
- or a liquid having a vapor pressure exceeding 40 psi at 100°F (37.8°C).
TOXIC, CORROSIVE AND REACTIVE COMPRESSED GASES
(examples)

- **Toxic and Highly Toxic**
  - carbon monoxide
  - arsine
  - chlorine
  - cyanogen chloride
  - diborane
  - fluorine
  - germane
  - phosgene
  - hydrogen cyanide
  - hydrogen fluoride
  - hydrogen selenide
  - hydrogen sulfide
  - nitric oxide
  - nitrogen dioxide
  - phosphine

- **Carcinogenic**
  - 1,3-butadiene
  - vinyl chloride
  - ethylene oxide

- **Corrosive**
  - ammonia
  - chlorine
  - hydrogen fluoride
  - sulfur dioxide
  - silicon tetrafluoride
  - hydrogen chloride
  - hydrogen bromide

- **Reactive**
  - silane
  - germane
  - dichloroborane
  - phosphine
  - stibine
Why the Extra Concern?

• Difficult to contain
  - High vapor pressure (VP)
  - Under pressure
    • e.g., ammonia – 114 psi @ 70°F
    • e.g., nitric oxide, chlorine, hydrogen cyanide - 2000 psi

• Large quantity in a small package
  • e.g., 50” ammonia cylinder, 50 lbs liquid or 1039 ft³ gas
Why the Extra Concern?

• Low exposure limit
  – e.g., arsine, hydrogen selenide – 0.05 ppm (TWA)
  – e.g., cyanogen chloride – 0.3 ppm (Ceiling)
  – e.g., fluorine – 2 ppm (Ceiling)
  – e.g., ammonia, carbon monoxide – 25 ppm (TWA)
  – contrast e.g., acetone – 500 ppm (TWA)
Why the Extra Concern?

- High vapor hazard ratio (VHR)
  - VHR = $\left( \frac{VP \text{ @ temperature of use}}{\text{atmospheric pressure exposure limit}} \right)(10^6)$
  - e.g., arsine $\frac{114 \text{ psi} \times 10^6}{14.7 \text{ psi}} = 155 \times 10^6$
  - contrast e.g. acetone $\frac{185 \text{ mm Hg} \times 10^6}{760 \text{ mm Hg}} = 490\frac{500}{500}$
Why the Extra Concern?

• Some have history of serious incidents
  • e.g., silane

  – 6 fatalities from gas cabinet explosions where silane was released unignited into the cabinet (two most recent - Taiwan 2005, India 2007,
  – Other major incidents in China and U.S. in 2009
Why the Extra Concern?

- Some are difficult to detect (i.e., poor warning properties)
  - e.g.,:
    - carbon monoxide
    - sulfuryl fluoride
    - hydrogen sulfide
Serious Hazards Require Serious Controls

• Specified Codes and Regulations
  – International Fire Code (IFC 2006)
  – Occupational Safety & Health Administration (OSHA)
• Accepted Consensus Standards/Industry Practice
  – Compressed Gas Association (CGA)
  – Semiconductor Equipment Manufacturers Institute (SEMI)
  – Gas suppliers
• Redundant controls if a single point failure could result in a significant accident or exposure above the occupational exposure limits (OELs)
Primary Hazard Controls

• Minimizing gas quantity
• Enclosing or isolating the source, distribution system and apparatus in which the gas is used

Passive Hazard Controls (require no power or human intervention after initial installation)

• Ventilation

Active Hazard Control (rely on the presence of power or human intervention to be effective)
Passive Hazard Controls
(examples)

• Substitution with non-gaseous compounds
• Dilution in a compatible non-toxic, non-corrosive or non-reactive gas in the cylinder mixed by the vendor (i.e., reduced gas concentration)
• Onsite gas generation
• Quantity limits that can be stored at a given location and used within a reasonable time (i.e., reduced gas amount)
• Restrictive flow orifices (i.e., limited available gas)
• Use of all-welded gas delivery lines (i.e., reduced likelihood of gas leaks)
Active Hazard Controls
(examples)

- Leak testing using an inert gas
- Ventilation with airflow monitor/alarm (regular testing and calibration)
- Operating at pressures below atmospheric
- Gas monitors (regular testing and calibration)
- Process shut-off devices
Minimum Safety Requirements Checklist

(http://risk.arizona.edu/healthandsafety/labchemicalsafety/MinReqforCSL-3ToxicCorrosiveGasUse.pdf)

• Quantity limits
• Personal protection and training
• Indoor cylinder location
• Piping, tubing, valves and fittings
• Equipment maintenance
• Environmental protection
• Label, signs and material safety data sheets
• Separation from incompatible materials
• Cylinder handling and transportation
• Security
• Hazard analysis
Carbon Monoxide

- Toxic and flammable compressed gas
- Inhibits the blood from carrying oxygen (brain and heart most susceptible to effects)
- No warning properties
- 76 ft³/ cylinder, 2000 psi
- Exposure limit = 25 ppm (TWA)
- VHR = 2.3 x 10⁶
Chemical Safety Level 3 (CSL-3) Gases/Gas Activities

• The storage or use of compressed pyrophoric gases in flammable concentrations
• The storage or use of compressed highly toxic gases or compressed toxic gases with poor or no warning properties
• The storage or use of compressed gases, which are select carcinogens, reproductive toxins, toxic or corrosive:
  – in quantities greater than 20 ft³ OR
  – that are plumbed outside of the source exhausted enclosure
• Transfilling
Need Help?

- Chris Redondo, URIC Cryogenics & Gas Facility
  - credondo@email.arizona.edu or 621-2374
- Frank Demer, RM&S
  - demer@email.arizona.edu or 621-3585