



CleanHarbor's
ENVIRONMENTAL SERVICES

Over-Pressurization of Compressed Gas Cylinders

People and Technology
Creating a Better Environment

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HMP
ALLIANCE OF HAZARDOUS MATERIAL PROFESSIONALS
ORLANDO 2013

Topics Covered

- Causes of Over-Pressurization
- Hydrogen Cyanide Incident Review
- Hydrogen Fluoride Incident Review
- Matheson Tri-Gas Response
- Engineering Controls
- Safe Work Practices

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Causes of Over-Pressurization

- Incompatible Mixture (Typically Oxy-Fuel Mix)
 - Oxygen / Hydrogen Mix
 - Bromine / Hexane Mix

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Causes of Over-Pressurization

- Thermally Impacted (Fire)

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Causes of Over-Pressurization

- Self Reacting / Dissociation
 - Hydrogen Fluoride & Hydrogen Bromide**
 - The slow corrosion reaction of Hydrogen Fluoride (HF) and Hydrogen Bromide (HBr) with iron in the steel contributes to the separation / dissociation of the respective compounds. As a result of this dissociation, Hydrogen (H₂) collects in the vapor space and builds pressure.
 - The expected vapor pressure of the gases @ 21C are 15psia (HF) and 335psia (HBr). The vapor pressure of HF and HBr are within the limitations of standard (DOT 3E 1800) lecture bottle containers. Upon prolonged storage the internal cylinder pressures may reach 4,000 – 10,000psig causing the cylinder to violently rupture.
 - Hydrogen Cyanide**
 - The depletion of the acid stabilizer / inhibitor that occurs after 30-90 days causes rapid polymerization and Hydrogen (H₂) generation. The reaction is speculated to be instantaneous causing a violent "detonation" of the cylinder. This reaction can be triggered by movement of the cylinder.

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Requirements For Dissociation

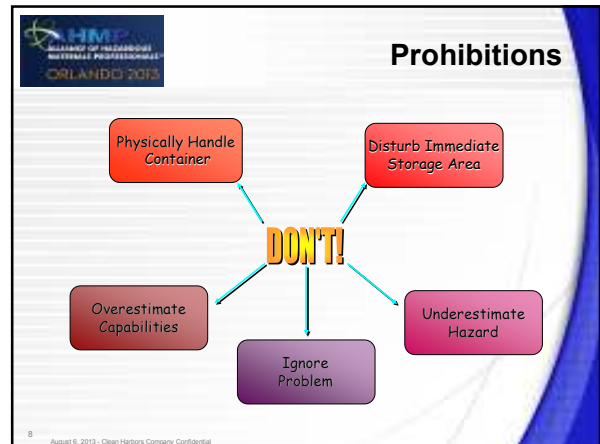
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Indicators Of A High-Hazard Condition

- Visible Distortion of Cylinder Wall
- Visible Distortion of Cylinder Valve
- Non Conforming Vapor Pressure
- High-Pressure Vibration
- Unknown Cylinder Age

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Hydrogen Cyanide Explosion

- On April 16, 2005 a nearly empty cylinder of Hydrogen Cyanide (HCN) spontaneously ruptured. The explosion occurred in the Chemical Weapons Research building (E5100) at the U.S. Army Aberdeen Proving Ground in Maryland.

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Hydrogen Cyanide Facts

- **Extremely Toxic (Zone A)**
Hydrogen Cyanide, Stabilized 6.1 UN1051 PG I
- **Requires A Stabilizer**
0.6% Sulfuric Or Phosphoric Acid (Good For 30 Days)
- **Forms Unstable Polymer**
Capable Of Auto-Catalytic Explosive Reaction

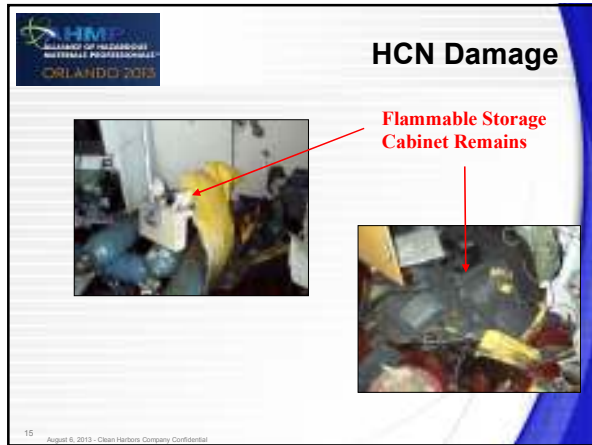
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Hydrogen Cyanide Explosion

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HCN Damage

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- ### Causes
- Age of HCN was over 1 year. HCN has a 30 day shelf life that should not be exceeded.
 - Depletion of sulfuric acid inhibitor within the cyanide.
 - Accelerated inhibitor depletion may have been caused by defects within the steel of the cylinder.
 - Increase in the rate of polymerization until the critical temperature of HCN was reached.
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Documented HF Cylinder Failures


- UK, 1984 (21 years of storage)
- Australia, 1991 (25 years of storage)
- Germany, 1992 (No details)
- Confidential University, 1997 (20+ years of storage)
- Clean Harbors, 2003 (25+ year old waste cylinder)
- Confidential University, 2008 (Age Unknown)



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Hydrogen Fluoride Explosion

- On June 19, 2003 a cylinder containing Hydrogen Fluoride (HF) spontaneously ruptured. The explosion occurred during transportation from a University in Arizona. The reaction breached the secondary container and released the entire contents of the cylinder.




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HBr & HF Facts

- **HBr Is Corrosive & Toxic**
Hydrogen Bromide, Anhydrous 2.3 UN1048 (Zone C)
- **HF Is Corrosive & Toxic**
Hydrogen Fluoride, Anhydrous 8 UN1052 PGI (Zone C)
HF Decalcifies And Will Cause Burns That May Not Be Immediately Visible Or Painful
- **Both Can Disassociate & Rupture The Cylinder Due To Hydrogen Build-up**
 $HBr \rightarrow H_2 + FeBr_2$ $HF \rightarrow H_2 + FeF_3$

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Hydrogen Fluoride Explosion



- Ruptured Container
- Ruptured Cylinder
- Packing List

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University Hydrogen Fluoride Explosion

July, 2008




Ruptured Container Damaged Fume Hood

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Hydrogen Fluoride Remediation

- **Matheson Tri-Gas**
 - October 2008
 - 4 Dissociated HF Cylinders
 - 3500+psi




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Transportation Options


High-Pressure Cylinder Recovery Vessels



Solkatronic 5502



HP-10




HP-15

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Remediation Procedures



Cylinder Rupture Vessel




Cylinder Rupture Vessel




Cylinder Rupture Vessel



Remote Drilling Machine

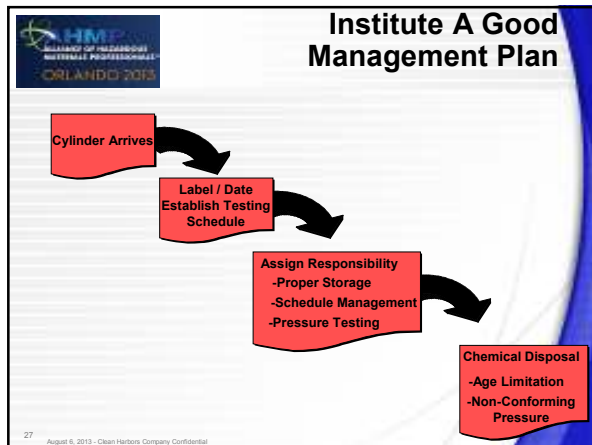


High-Pressure Tapping Ring



High-Pressure Tapping Ring

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