(Photo courtesy R. Stilp)

Dangerous Gas Mixtures: Avoiding Cylinder Accidents

By Eugene Ngai

In the last 10 years a number of serious incidents have occurred as a result of inexperienced individuals filling high pressure gas cylinders with gas mixtures that caused the cylinders to rupture unexpectedly. When this happens it can not only cause serious injury and/or physical damage, it creates a significant hazard to the first responders to the incident.

Some of these incidents occurred at companies producing "green" gas mixtures. These mixtures are advertised as being environmentally friendly and energy efficient, but the companies filling these cylinders are frequently not aware of the many hazards associated with these types of mixtures.

Whenever and wherever cylinder filling, storage, and handling occurs, the safety of the handlers and the surrounding public is paramount. It is important that handlers know the inherent potential risks and the errors that caused previous unexpected incidents in order to prevent the same types of disasters from being repeated.

Carbon Monoxide Stress Corrosion Cracking

Inventors and entrepreneurs have been selling a proprietary gas mixture known by many different names: Brown Gas, Hydrillium, Aqua-Fuel, MagneGas, Carbohydrillium, and others. These are marketed as environmentally friendly (green) fuel gas purportedly more energy efficient than hydrocarbon-based fuels. This gas mixture is also used as a fuel for barbeque grills with a flame temperature hotter than propane.

One method of making this mixture is by electrolytically decomposing water using a carbon electrode. It typically forms a gas mixture of hydrogen (60–70%) and carbon monoxide (25–30%) with a low concentration of methane (1–2%). There is also some carbon dioxide, nitrogen, and oxygen. This is compressed into high pressure cylinders to pressures over 2,000 psig (13.89 mPa). When this mixture is packaged at high pressures in a carbon steel cylinder, it forms the ideal environment for carbon monoxide Stress Corrosion Cracking (SCC).

What You Don't Know Can Hurt

The SCC was involved in a case of a violent cylinder explosion involving a gas mixture in an Orlando, Florida industrial building in September 2013. The fire department response to this, recorded in an excellent *Fire Engineering* article, "The Dangers of Hydrogen Based Experimental Fuels: Public Life and Health Is at Stake," was written by two retired officers from the Orlando Fire Department involved in the investigation.

In this incident, the cylinder containing the mixture suddenly ruptured, blowing out an adjacent exterior wall and destroying the building interior. Fortunately, the building was not occupied at the time. (See Figure 1.)

When examined, the jagged edges of the cylinder tear as well as the longitudinal cracks in the cylinder interior indicated significant SCC. The cracks became apparent because the cylinder walls peeled back, stretching the interior wall backward, creating long cracks along the horizontal axis.

The Orlando inventor had experienced a number of cylinder leaks and valve failures, yet continued to produce this mixture. He erroneously concluded that the leaks were due to cylinder or valve defects rather than SCC, and exchanged the cylinders for new ones at the local gas supplier.

Four Factors for SCC

Carbon monoxide (CO) SCC is a problem that is well known within the compressed gas industry. The industry experienced a number of pure carbon monoxide cylinder ruptures in the 1950s when the fill pressures for the gas were increased above 1,000 psig (7.0 mPa) to 2,000 psig (13.89 mPa). This led to a number of studies on the problem that came to the same conclusion: in order for SCC to occur, carbon monoxide, carbon dioxide, liquid water, and carbon steel under stress (pressure) all had to be present.(1)

Having only three of these factors will not cause SCC to occur. SCC is the combined action of corrosion and tensile stress (applied or residual). These cracks form throughout the cylinder interior, and continue to grow when all four ingredients are present. The trigger is thought to be local dissolution of iron due to the carbonic acid formed between water and carbon dioxide, with general corrosion being inhibited by carbon monoxide. This phenomenon leads normally to transgranular cracks with branching, as is illustrated in Figure 2.

Transgranular Cracking of Carbon Steel

CO SCC will create numerous microscopic cracks throughout the cylinder. A singular crack due to a manufacturing defect would not cause a catastrophic failure of the cylinder, it would only produce a gas leak through the crack.

The SCC reaction will occur at room temperature with the rate increasing with increasing temperatures and/or pressure. The presence of oxygen or sulfur compounds will also increase the rate of SCC.

CO SCC is not a problem with aluminum or stainless steel cylinders. This could be the reason why some of the "green" gas producers are now using these types of cylinders; they might have experienced cylinder leaks when using carbon steel.

After the incidents in the 1950s, DOT limited the fill pressure for carbon monoxide and carbon monoxide mixtures of greater than one percent (49CFR173.302a(c)) to 2,000 psig (13.89 mPa) or 5/6 of the working pressure of the cylinder, whichever is less. This reduced one of the four components, stress. The cylinders in the Orlando incident were filled to pressures well above this.

Liquid water within cylinders, which is one of the factors for SCC, caused another set of serious issues. The gas industry experienced a number of cylinder failures in the 1980s, with disposable cylinders filled with an automotive exhaust gas calibration mixture containing carbon monoxide, carbon dioxide, and other gases. These mixtures were filled into low grade, low pressure carbon steel cylinders. The moisture was not adequately removed from new cylinders due to improper conditioning of the cylinders, and this oversight caused the cylinders to fail when liquid water formed.

Liquid water can also easily form in cylinders if ambient temperatures that the cylinders are normally exposed to are not taken into account and the dewpoint of the moisture is not low enough. For example a typical green gas mixture of 60 percent hydrogen, 35 percent carbon monoxide, two percent carbon dioxide, and three percent nitrogen filled to 2,400 psig (16.65 mPa) will start to condense liquid water at 100 percent relative humidity at the dewpoint temperatures, shown in Figure 3. To ensure liquid water is not formed, the gas supplier must consider the coldest temperature the cylinder can be exposed to.

Capillary condensation of water, however, can occur in cracks or surface scale at a relative humidity as low as 60 percent.(3) To be conservative one must consider a relative humidity of 70 percent. Since SCC will not occur while the water is frozen, the freezing point temperature of 32°F (0°C) will be used. At this temperature and relative humidity, a dewpoint temperature of 23.3°F (-4.8°C) is estimated. This has a water vapor pressure of 3.2 mm Hg. Once the condensation and freezing occurs, it will take a much higher temperature than the dewpoint to revaporize the water.

Figure 1: Exterior Wall Damage
(Photo courtesy R. Stip)

Figure 2: Transgranular cracks in a branching pattern
Source: (1) Martich, R.

Dewpoint	H_2O Partial Press
°F (°C)	mm Hg
70 (21)	46.53
32 (0)	14.04
-20 (-29)	1.95

Figure 3: Liquid water saturated vapor pressure and their dewpoints in a 2,400 psig gas mixture.

Cylinders containing pure carbon monoxide with a moisture dewpoint of -125°F (-87.2°C) and no sulfur have been stored for many years with no problems, even at pressures of 4,000-5,000 psig (27.68–34.58 mPa). Similarly, there have been cylinders with pressures of 2,300 psig (15.96 mPa) stored at temperatures of 212°F (100°C) that have not experienced problems. High purity CO cylinders with moisture dewpoints and high pressures, and even heated to high temps, have been fine. The danger of explosion due to SCC occurs only when all four factors are present. To be safe, the gas industry recommends a moisture level of 20 ppm, dewpoint -65°F (-54°C) or less. Some gas companies require moisture level of 16.5ppm (dewpoint -70°F, -57°C) or less.

The compressed gas industry has published safety alerts on this problem. The European Industrial Gas Association (EIGA) Doc 95/12/E, "Avoidance of Failure of Carbon Monoxide and of Carbon Monoxide/Carbon Dioxide Mixtures Cylinders," was adopted by the Compressed Gas Association (CGA) as CGA standard P-57. In "ISO 11114 Gas cylinders — Compatibility of cylinder and valve materials with gas contents — Part 1: Metallic Materials Gas, 2010 edition," it states for carbon monoxide:

> "... Highly sensitive to any traces of moisture (> 5 ppmV at 20 MPa (200 bar)), in the presence of CO_2 (> 5 ppmV). Industrial grades of carbon monoxide normally contain traces of CO_2. This can result in risk of stress corrosion, in the case of QTS, CS, and NS cylinders if used at the normal service stress levels. Experience shows that this risk is eliminated if the fill pressure at 15°C is less than ½ of the cylinder working pressure." (4)

There is not a good method to detect whether SCC has occurred with a cylinder. EIGA pamphlet 95 indicates that hydrotesting, acoustic emission, or ultrasonic testing will detect these cracks. Cylinder testers in the US are divided on whether these methods will find SCC. The other methods such as microscopic or dye penetrant inspection requires the destruction of the cylinder. Unless there are proven test methods, it is best practice to condemn carbon monoxide or carbon monoxide mixture cylinders that have been pressured at the normal steel stress levels and contained high dewpoint levels.

Explosive Gas Mixtures

A cylinder containing a flammable gas and an oxidizer gas mixture can be extremely dangerous if it is in the flammable range and at high pressure. This mixture can exist indefinitely in the cylinder until a source of energy ignites it; routine handling and transportation of the cylinder do not in themselves ignite these mixtures.

Ignition is typically due to adiabatic compression heat when the cylinder valve is opened and the gas is compressed suddenly. Pressure increases as low as 150 psig (1.14 kPa) can cause the gas to heat to 576°F (302°C), which is approaching the autoignition temperature for a hydrogen balance air mixture of 752°F (400°C). A 750 psig (5.28 kPa) increase will heat to 1,182°F (639°C) while 1,500 (10.45 mPa) psig will be 1,540°F (838°C); both are well above the autoignition temperature for most hydrocarbon/air mixtures. Once ignited the reaction wavefront propagates back into the cylinder causing the rest of the mixture to react. Depending on the mixture concentration it will deflagrate or detonate. In extreme cases the cylinder will violently shatter into many small pieces.

Accidental Mixtures

Explosive gas mixtures can be made due to mistakes or created by accident as a result of: equipment failure; operator error; calculation error; procedure sequence not followed; or in gas mixture disposal activities.

The 1988 Gollub Analytical Services incident in Berkeley Heights, NJ is a tragic example of an accidental mixture causing an explosion. A silane (pyrophoric gas) cylinder was somehow contaminated with nitrous oxide (oxidizer). This cylinder was shipped and handled for more than 3,000 miles around the US without incident.

Gollub was contracted to analyze the cylinder that a user was having process problems with. They were horrified to find the silane to be contaminated with a high concentration of nitrous oxide. They were attempting to vent the cylinder when it suddenly exploded, killing three people and severely injuring a fourth person.

A similar type of incident occurred in 1991 at Osaka University, Japan, killing two graduate students. Nitrous oxide backflowed into a silane cylinder through a shared inert gas purge line and a damaged checkvalve. After these incidents, the CGA Semiconductor Gas Committee developed a Safety Alert, "Dangerous Combinations of Flammable and Oxidizing Gases." The Fire Codes were also changed to require separate high pressure purge gas systems dedicated for silane.

On October 23, 1963, a violent cylinder explosion occurred in Corpus Christi, Texas. The explosion caused four fatalities and 30 injuries when a cylinder shattered into 200 pieces. The explosion force was so violent that the thin metal rupture disk in the Pressure Relief Device (PRD) punched a hole through the 1/8" thick metal housing.

Afterward, an attempt was made to reconstruct what may have been in the cylinder. Over 40 tests with cylinders filled with various flammable gases and liquids mixed with oxygen were conducted. According to the findings, a stoichiometric mixture of 67 percent hydrogen/33 percent oxygen, filled into a high pressure cylinder and ignited by a blasting cap, yielded the results shown in Figure 4. (5)

CORPUS CHRISTIE CYLINDER INVESTIGATION

Pressure, psig (mPa)	Outcome
500 (3.55)	Cylinder bulged slightly
750 (5.27)	Cylinder shattered into 20+ pieces
1,000 (13.89)	Cylinder shattered into 40+ pieces
1,750 (12.17)	Cylinder shattered into 100+ pieces

Figure 4: Results of testing Source: (5) Matthews

Increasing pressures caused the cylinder to shatter into more pieces. The results of this investigation have become a valuable reference for people involved in explosive gas mixture cylinder investigations.

In another tragic 1998 incident, a hydrogen cylinder that was returned by a local gas distributor to a gas supplier detonated at the gas filling facility after the operator topped it off with hydrogen, not realizing that it had been used for oxygen service by the distributor. The cylinder fragmented into over 200 pieces killing the operator and destroying the building. Only 45 percent of the cylinder mass was recovered. During disposal operations of five other cylinders a second cylinder with an explosive gas mixture was also found.

Dr. Chester Grelecki of Hazards Research Corp. reported a stoichiometric mixture of hydrogen (66.6%) and oxygen (33.4%) in a 44-liter cylinder filled to 2,000 psig (13.89 mPa) to be equivalent to 10 lbs (4.53 kg) of TNT. A mixture with excess oxygen is more energetic than a stoichiometric or hydrogen rich mixture.(6) The Corpus Christi explosion was estimated to have been equivalent to 15–30 lbs (6.80-13.60 kg) of TNT. (5)

Deliberate Mixtures

Gas suppliers routinely prepare gas mixtures containing both a flammable gas and oxidizing gas for instrument calibration (lean, 2.5% CH_4/Air) or for deep sea diving (rich, 2% O_2/H_2) using formal protocols and dedicated mixing systems.(7) These mixtures have flammable or oxidizer gas concentrations low enough to not propagate a reaction. At some point during the preparation of the mixture, however, the concentrations could be at levels that could cause a reaction. CGA Standard P-58, "Safe Preparation of Compressed Oxidant-Fuel Gas Mixtures in Cylinders" recommends guidelines on how these gas mixtures can be made safely.

The European Industrial Gas Association (EIGA) developed the standard, "Safe Preparation of Oxidant-Fuel Gas Mixtures" in February 2004, and it was adopted by CGA as CGA P-36. This guide outlines seven basic principles that must be adhered to when making these types of 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

The company TRW developed third generation car airbag technology, Hot Gas Inflator (HGI), using the explosive reaction of a stoichiometric hydrogen and oxygen gas mixture. The advantage over sodium azide technology is that the reaction byproduct (water) is not toxic and the mixture is more thermally stable.

For it to be effective as an airbag inflation device the bag must inflate within 30 milliseconds. This gas mixture is contained in a small aluminum cylinder at a pressure of 4,500 psig (31.13 mPa). The reaction is initiated by firing a squib, which penetrates a metal rupture disk. As it is propelled through the mixture it ignites it. To accommodate different size passengers a multi-stage HGI can be used where a car seat sensor can fire one or more inflators. These cylinders have undergone extensive testing for physical impact, fire, and bullet penetration to demonstrate their safety in handling and transportation. They have been assigned UN#3268 with a shipping name Air Bag Inflators, Pyrotechnic.

There are some instances, unfortunately, where safety recommendations are deliberately overlooked, most notably for terrorist purposes. It is no longer possible to bring personal cylinders of medical oxygen on a plane — these now have to be rented from or provided by the airline.

After September 11, 2001, the US Department of Transportation (DOT) conducted testing of medical E oxygen cylinders filled with explosive gas mixtures due to concerns that an explosive gas mixture can be used in a terrorist attack.(8) Cylinders and the gases used by terrorists are commonly used by consumers, and therefore can be easily obtained. These can also be stored indefinitely and transported without reaction. Of the common flammable gases tested at 2,000 psig (13.89 mPa) with pure oxygen, ethylene was the most energetic, double that of methane and even hydrogen.

Deliberate mixtures and safety precautions are not always foolproof. A Combustion Light Gas Gun (CLGG) is an experimental weapon developed for a ship, which can shoot a five-inch 2.7 cm) diameter shell at a velocity of 8,000 ft/sec (2,438 m/sec). This is a significantly higher velocity than the conventional weapon velocity of 2,650 ft/sec (808 m/sec). It has a range of 200 miles (322 km) versus the current 20 miles (32 km). An added bonus is that the cost per shell is 10 percent of the current cost.

The high pressure gas mixture of hydrogen and oxygen is blended in the weapon chamber just prior to ignition. Despite years of working with this mixture, though, the company R&D group suffered an explosion which propelled a cylinder though the roof. The cylinder then returned puncturing the roof at another location.

Green Gas Mixtures

Other types of "green" gas mixture have been prepared and marketed. In one case the inventor, Timothy A. Larson, received a US patent (#7,793,621, Alternative Fuel Engine) claiming that his method of electrolysis "modif[ies] the bond angles of water," and therefore gives it more energy. The hydrogen and oxygen produced by electrolysis is simply compressed back into high pressure cylinders as a stoichiometric mixture. This is sold as a more environmentally friendly fuel gas for research projects typically involving fuel cells.

Companies owned by Larson experienced three explosions, which caused serious injuries and physical damage. A fourth explosion injured three people including Larson's son, and destroyed the surrounding building on August 9, 2011 at Sylmar, California. The facility was shut down and multiple state and federal agencies responded.

During the cleanup the authorities found nine other cylinders containing the gas mixture, known as TyLar. To move these cylinders the EPA obtained an Emergency Special Permit #15462. They evacuated 10,000 residents and closed the adjacent interstate when they began the operation to render the filling system on-site safe.

Over a period of three months, three separate operations were conducted to vent the cylinders. Initially steel-tipped 308 caliber bullets were used to pierce the side of three small cylinders. Two flashed and one detonated, destroying the disposal area. They resorted to shaped charges at a military facility for the remaining cylinders.

On October 16, 2011, DOT issued the first-ever stop order for Strategic Sciences Inc., Realm Industries, and Rainbow of Hope, all

owned by Timothy A. Larson, which prevented him from filling any cylinder with TyLar gas and from transporting those cylinders.

Safely Disposing Explosive Gas Mixtures

As noted, opening the cylinder valve can cause an explosive mixture to ignite. In some incidents cylinders suspected of containing an explosive gas mixture have been transported to remote locations to be disposed of. In an incident in 1993, a cylinder containing an explosive mixture of hydrogen and oxygen in Colorado Springs, Colorado exploded when the valve was opened. The authorities and gas supplier identified five other cylinders made in the same batch. These were transported to a military site and disposed of by using a shaped charge to puncture a hole in the cylinder.

If a cylinder is suspected of containing an explosive gas mixture, special procedures are required to safely dispose of the mixture. One method involves the use of a custom designed remote valve opener and cylinder manifold, but other methods rely on tactics like those mentioned here. As of yet, very few gas supplier Emergency Response (ER) teams are trained or have the equipment to handle this.

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