Electronic Specialty Gas Cylinder Safety

April 2022

Packages used to contain and ship Electronic Specialty Gases (ESG) are very robust. For purity and safety reasons the cylinders are typically high pressure seamless 4130 alloy carbon steel and the valves are stainless steel

Package

Most ESG packages follow the US Dept of Transportation Regulations prescribed for highly toxic gases, 49CFR173.192 Packaging for certain toxic gases in Hazard Zone A which further prescribe the requirements of 49CFR173.40

- Use of a vapor-tight cap on the valve outlet connection as a secondary seal.
- Use of a cylinder valve protection cap (Cylinder Cap) design that has passed a drop test of seven feet with a 44 liter carbon steel cylinder filled 40% full of water. It must impact a concrete surface at a 60^0 angle and the valve must not suffer significant damage and cannot leak.
- Use of a metal diaphragm packless valve.
- No pressure relief device (highly toxic only).
- No intermediate piping between the cylinder valve and the cylinder such as a reducing bushing and the thread must be tapered.

In addition to the US Transportation Regulations, many gas suppliers as a Best Practice:

- Wire the cylinder valve handle shut.
- Leak tested using a sensitive electronic leak detector.
- Valve is sealed with a plastic bag.
- For purity and safety reasons only a Stainless Steel or Hastelloy Valve is used.
- Cylinders are never shipped loose unless they are shipped on a company-owned cylinder truck in which case they are strapped and secured to the sides of the vehicle and segregated from incompatible products as prescribed under DOT Special Permit #7835. For shipment on Common Carriers, they are secured onto a cylinder pallet or enclosed in a crate.

Fill Capacity

The maximum amount of an ESG that can be filled into a cylinder is defined by DOT. Those limits being the pressure in a cylinder may not exceed 5/4 the stamped service pressure of the cylinder at 131°F (55°C) degrees. (See Cylinder Maximum Fill for details). For more hazardous products classified as Hazard Zone A and Hazard Zone B, the pressure may not exceed the stamped service pressure of the cylinder. Typically ,ESG cylinders are filled to lower amounts

Review of Possible Leak Scenarios

Cylinder Rupture

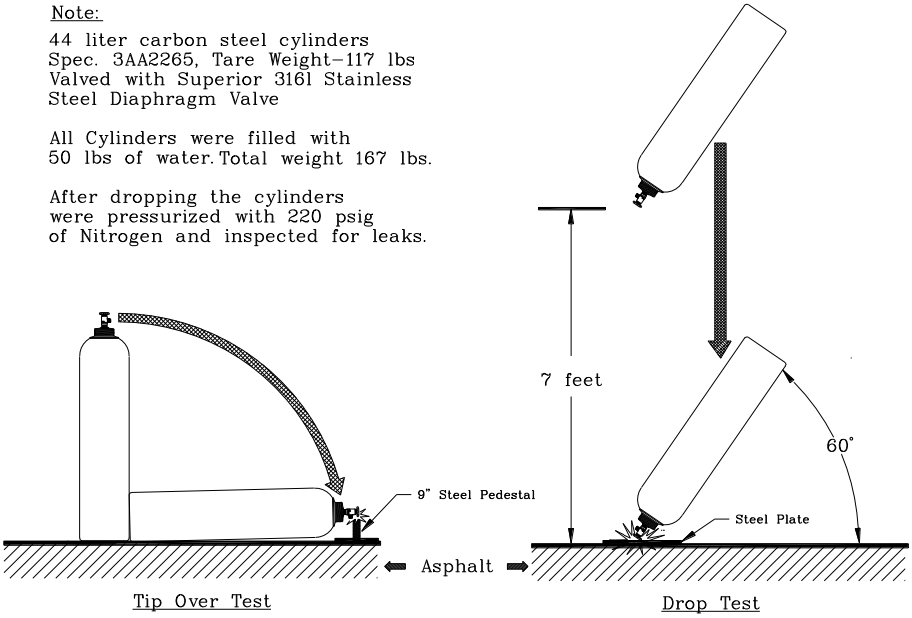
The 3AA specification cylinder is a seamless chrome/molybdenum carbon steel cylinder that has had a long history of reliability. The minimum burst pressure is 6,000 psig. With the exception of action from a fire, puncture, back-contamination causing internal corrosion or overfilling, there have been no known cases of premature cylinder rupture in one gas suppliers database of over 2 million cylinders, which include cylinders with a lesser specification. Statistically the occurrence of such an event has been reported by the gas supplier to be as low as 4.2×10^{-8} others have reported it to be 5×10^{-7} or 1×10^{-7} event [1,2].

The Building and Fire Codes require the use of a gas cabinet and sprinkler for storage and use, which will protect a cylinder from any external events such as a fire.

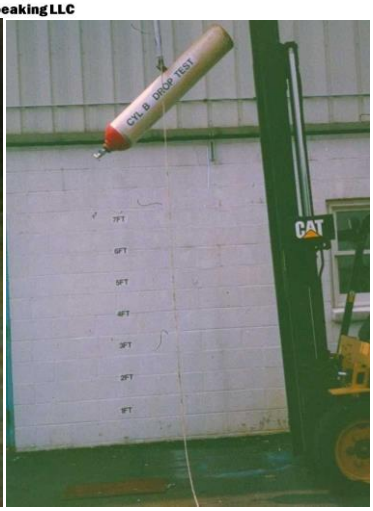
Physical Impact

A 3AA Specification cylinder with an approved cylinder cap is a very rugged package. A cylinder with the cylinder cap on, even if dropped during storage or transportation, will not leak even when dropped from a height of seven feet as required by the DOT regulations.

Even in the case of an operator forgetting to put on a cylinder cap, testing at Solkatronic Chemicals has demonstrated that a 44 liter cylinder filled with 50 pounds of water and dropped from a height of seven feet directly onto the stainless steel diaphragm valve has not leaked when pressurized with Nitrogen to 220 psig [3]. This is due to the use of a stainless steel valve, which has greater than twice the tensile strength of brass. In 1995, four cylinders were tested in this manner with the same results.

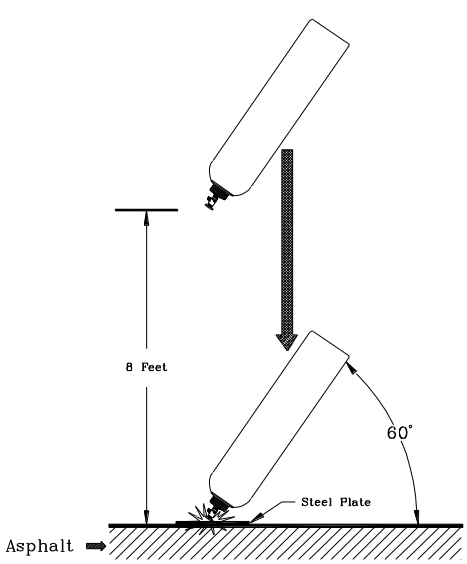


DROPTEST WITHOUT CYLINDER CAP



Valve Damage After Drop **Drop Test**

Further testing was done in May and June 2000. In this case the height of the drop was increased to 8’ and the total cylinder weight was a minimum of 250 lbs to reflect the new CGA cylinder cap testing guidelines. This resulted in a final impact force of two times that of the earlier drop testing. To fill a cylinder to this weight, steel shot was placed in the cylinder since water alone could not fill a cylinder to the desired weight.



New Drop Test

The test results confirmed the earlier testing and highlighted the differences between stainless alloys. The weaker 303 Stainless cracked at the thread interface in one of the two cylinders dropped while the 316 Stainless both had small leakers (<10 cc/min) [(4)]

Spontaneous Leak Development

Under normal storage and transit conditions, without an abnormal external event (e.g. exterior corrosion, fire, etc.) a cylinder in rare cases may develop a small leak at the Valve (<<0.1 cc/min.).

Complete failure of the cylinder valve is also a remote event and its' potential occurrence is estimated to be 3.55×10^{-6} **(5)**.

A typical ESG cylinder has three potential leak points, which all may occur at the cylinder valve.

a. Diaphragm Leak

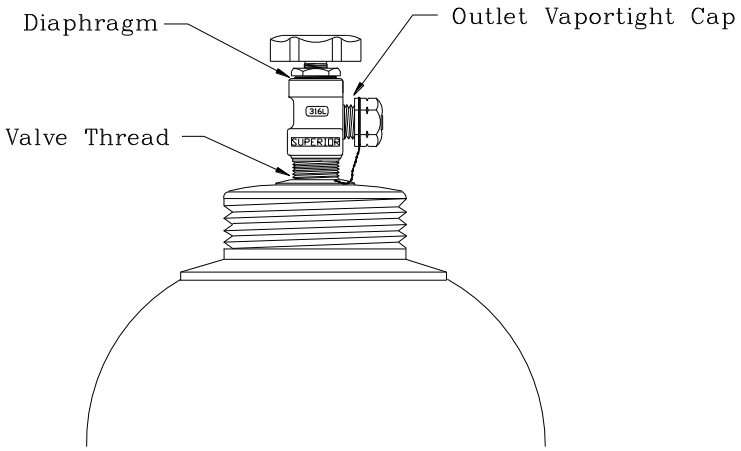
ESG cylinders typically have metal diaphragm valves, which have excellent leak integrity. For a leak to occur on the diaphragm, two failures would have to occur. The valve seat would have to fail therefore pressurizing the diaphragm with gas pressure and the diaphragm would also have to leak. ESG cylinders are leaktested with the Vaportight Cap off prior to shipment to pickup any minute seat leaker.

b. Outlet Vaportight Cap Leak

A valve outlet leak would also require that a double failure occur. The valve seat would have to fail, pressurizing the vapor-tight cap with gas pressure and the vaportight cap would also have to be loose or defective. ESG cylinders are leaktested as described in the following section with the Vaportight Cap off prior to shipment to pickup any minute seat leaker.

c. Valve Thread Leak

If a leak were to occur, this would be the most likely area. In storage and distribution, these are primarily detectable only with a electronic leak detector. In some unusual cases, a leak of <0.1 cc/min could develop.



CYLINDER LEAK POINTS

At ESG Suppliers, a newly valved cylinder is tested numerous times to insure that a mechanical defect will not cause a leak. Immediately after valving, a cylinder is leak tested by pressurizing with Nitrogen to 2000 psig for outboard leaks. During vacuum baking it is tested for inboard leakage. After filling and during analysis it is leak tested with a gas specific leak detector. Prior to shipment all ESG cylinders undergo a final custom leak check sensitive to the ppb level.

The chances of a leak occurring, is very small when the cylinder is in transit or storage. The most vulnerable point in the life cycle of the cylinder outside of the fill facility is when the customer prepares it for use. At this point the Cylinder Cap, Vaportight Valve Outlet Cap and Valve Holddown Wire are removed to connect the cylinder to a system. At most companies this is done within a ventilated and monitored gas cabinet and the Operator is protected with Personal Protective Equipment (PPE) which includes Self Contained Breathing Apparatus (SCBA). The cylinder is also tested with a leak detection device before it is connected to the system. After connection, the systems are leak tested with inert gas pressure prior to the cylinder valve being opened.

To comply with the fire regulations (e.g. NFPA 318) or Insurance requirements (e.g. Factory Mutual S7-7), many users require the cylinder valves to have a restricted-flow orifice of 0.006" or 0.010" diameter. This is inserted in the valve outlet to limit flow in the event of a downstream line failure or the accidental opening of the cylinder valve. (See Development of a Cylinder Valve Restrictive Flow Orificae)

References

1. Appendix IX of Cremer and Warner, **Risk Analysis of Six Potentially Hazardous Industrial Objects in The Rijmond Area, A Pilot Study**, Kluwer Academic Publishers, B. V. Dodrecht, The Netherlands
2. S. Atallah, **"Assessing and Managing Industrial Risk"**, (Gas Research Institute), Chemical Engineering, Sept. 9, 1980, pp 94-103
3. Ngai, E. Y. and Gerver, L, **"Arsine Worst Case Testing"**, July 1995, Internal Solkatronic Chemical Report
4. Ngai, E. Y., Loyd, M and Gerver, L., **"Cylinder Drop Testing, 2000"**, Internal Solkatronic Chemical Report, July 2000
5. **"Comparative Analysis of a Silane Cylinder Delivery System and a Bulk Silane Installation"** (ESH B001, SEMATECH, Technology Transfer #95092976A-ENG, Oct. 31, 1995