

Introduction

Electronic Specialty Gas (ESG) cylinders are very robust packages since they are uniquely specified and contain the top of the line valves and other components. The typical cylinder used for industrial gases such as nitrogen or helium do not have these requirements.

Background

The public has always been concerned about cylinder leaks as a result of bad handling of cylinders. Or in the worst case, can the cylinder valve be Sheared off? We all hear stories of cylinders flying through the air causing considerable damage after the valve has sheared off. This is an event that many people envision is likely. Is this true? How can it happen?

Cylinders must be handled properly to prevent leakage or damage to the cylinder valve



Figs 1 & 2 Unsafe Cylinder Handling, no cap and with cap

Cylinder Valve Protection

The transportation regulations require that the cylinder valve be robust enough to prevent it from leaking as a result of a physical impact during transportation or handling.

In Europe, industrial gas cylinders can be shipped without valve protection as long as the valve can withstand the ADR valve impact test without leakage.

Plastic valve guards are also used for many medical and calibration gas cylinders. This provides the convenience of not having to remove and reinstall the cylinder cap before and after use.

Valves had to be protected from damage.





Polycarbonate Cylinder Valve Cap

Apragaz a Belgium Testing Organization like United Laboratories (UL) conducted testing of a polycarbonate Cylinder Cap using the European National Standard, EN962 TEST PROTOCOL Drop Testing

a) 6 times at ambient temperature, rotational test at increments of 60 deg to axis of valve outlet connection

- b) 1 time at -20° C
- c) 1 time at +65°C

In each case the cylinder was dropped from a height of 1.2m and at 30° to the vertical. The cylinder is dropped onto a steel plate 1 m square.

Typical of 136-150 lbs with water added for a total cylinder weight of 253 lbs



Figs 3 & 4: Polycarbonate Cylinder Cap Drop test

In no case did the valve leak



Fig 5 & 6 Plastic Valve Guards

Opening a Cylinder Valve by Mistake

At Brookhaven National Laboratory, two firefighters were slightly injured when one of them accidentally discharged an 800-psi carbon dioxide (CO₂) cylinder. The discharge propelled the cylinder from a cart, and it spun out of control and struck one of the firefighters. The other firefighter fell while trying to avoid the spinning cylinder. (ORPS Report CH-BH-BNL-BNL- 1998-0041)

A similar event occurred at the Oak Ridge Y-12 Site, where a fire department worker narrowly escaped injury when he accidentally actuated a CO₂ cylinder. The discharge propelled the cylinder from a storage building, spinning it 30 feet into a parking area before it came to rest against a concrete ramp. (ORPS Report ORO--MMES-Y12SITE-1995-0025)

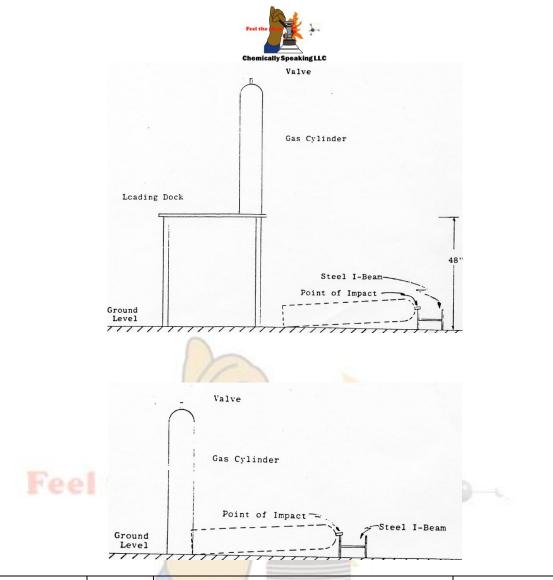
How Easy Is It to Shear a Cylinder Valve?

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Limited data from valve companies and others were also reviewed. In one case, a report indicated that the valve loosened from the cylinder and discharged its contents but did not shear. Numerous Youtube videos demonstrate valve shear of brass valves impacted by a sledgehammer.

Bell Communications Testing

In 1985 Bell Communications Research contracted Hazards Research Inc. to conduct a study on gas cylinder valve impact.



Cylinder Size	Valve		
44 liter	Brass	Dropped with cylinder cap on from the dock,	Decided it was not safe to
		no damage to valve	do leaktest
		Dropped 2 times from dock without cap, valve	
100	100	hit ground, no damage	
cne	m_{10}	The 3 rd drop it hit the I beam and the bonnet	
		nut cracked, valve was bent ¾"	
44 liter	Stainless	Dropped 2 times from dock without cap, valve	Slight leak at valve threads
		hit ground and then hit I beam, no visible	into cylinder visible with
		damage	soap solution
		The 3 rd drop it hit the I beam and, valve was	
		bent ½"	
44 liter	Stainless	Tipped over without cap, hit I beam. No visible	No leaks observed
		damage	
16 liter	Stainless	Tipped over without cap, hit I beam. No visible	No leaks observed
		damage	



onomouny spouking LEO							
16 liter	Stainless	Cylinder was dropped from dock twice with cap	No leaks observed				
		on, hit the ground first and the I beam second.					
		No visible damage to cap or valve.					
		Dropped twice without cap, both times hit I					
		beam. No visible damage to valve					

Linde (Praxair)

In the 1960's Linde (Union Carbide) conducted a series of tests in a company parking lot to determine what could happen if a valve on a high-pressure cylinder was sheared. The testing was done with a high-pressure cylinder with a brass valve pressurized with nitrogen. It was lying horizontal on the asphalt surface and the valve was sheared with a guillotine device by dropping a weight onto the valve from 6'. The results were based on visual observations of the video:

Press "') 2 "') 2 "') 2 "') 2 "') 2	Cylinder ure, psig 2560 2530 1620 2550 1620	Cylinder,MPH (ft/sec) 16 (23.5) 15 (22) 11 (16) 31 (45.5) 31 (45.5)	of Cylinder, MPH (ft/sec) 13 12 10 25 20	Total Travel Time, sec 26 21 11 15 11	Distance Traveled, ft 302 natural stop 279 hit fence 110 450 275
") : ") : ") :	2560 2530 1620 2550	16 (23.5) 15 (22) 11 (16) 31 (45.5)	13 12 10 25	26 21 11 15	302 natural stop 279 hit fence 110 450
") : ") : ") :	2530 1620 2550	15 (22) 11 (16) 31 (45.5)	12 10 25	21 11 15	279 hit fence 110 450
(") (")	1620 2550	11 (16) 31 (45.5)	10 25	11 15	110 450
;") :	2550	31 (45.5)	25	15	450
1") ·	1620	31 (45.5)	20	11	275
Thrust Test					
der		Time to Empty	,		
sig Thr	ust, Ibs	sec			
	113	15-20			
		15			
2		113	113 15-20		113 15-20

They never became air borne as many believed it would.

Ghostbusters

The first time they tried they only cracked the valve, They had to build a more robust guillotine.

- 140 lb cylinder
- **Brass Valve**
- >>40 lb weight dropped from 10'
- Concrete block wall, 8", 20 ft from cylinder
- Greased metal channel
- Cylinder impacted at 40 mph
- Moved Concrete Block wall 1/2" back



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Fig 7 -10: Cylinder Impact of Concrete Block Wall



Cylinder Excess Flow Valve

Periodically excess flow valves for cylinders have been introduced as a must have safety device due to the fear many have of. These are activated if a cylinder valve is sheared off in an accident. An inventor in New York State 25+ years ago had his good friend a NY state Senator propose a bill mandating the use of one for all compressed gas cylinders. The Brit Valve was debated for a over a year but the bill never got passed.

A second valve like this was made by Whalen Corp also 25+ years ago. He advertised this at many trade shows, SESHA (Semiconductor Environmental Safety and Health Association) as well as SEMICON West and the Compressed Gas Association. He lobbied the Fire Code officials to mandate the use for pyrophoric and highly toxic gases. It should be noted that they demonstrated the valve using a brass cylinder valve that they easily sheared.



Fig11: Whalen Valve

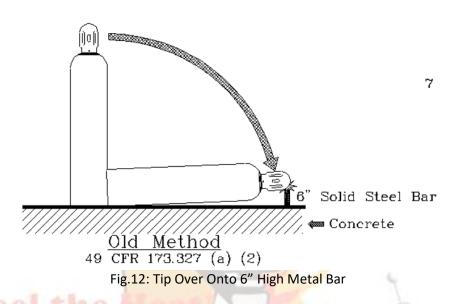
Due to the expense the only gas cylinders that could justify its use were expensive Electronic Specialty Gases such as silane or arsine. As a test a US gas company installed a dozen of them in silane cylinders and shipped them across the country. 2-3 of them activated I assume due to vibration or impact. Now they were stuck having to drill into the cylinder to remove the silane. A second test had a similar problem. They abandoned the program after that. The Whalen Valve was not adopted.



In 2019 another company designed a similar type of excess flow valve. He did not market it after I recapped the history in a letter to them on the Brit and Whalen Valve history.

DOT Cylinder Cap Impact Testing Requirements'

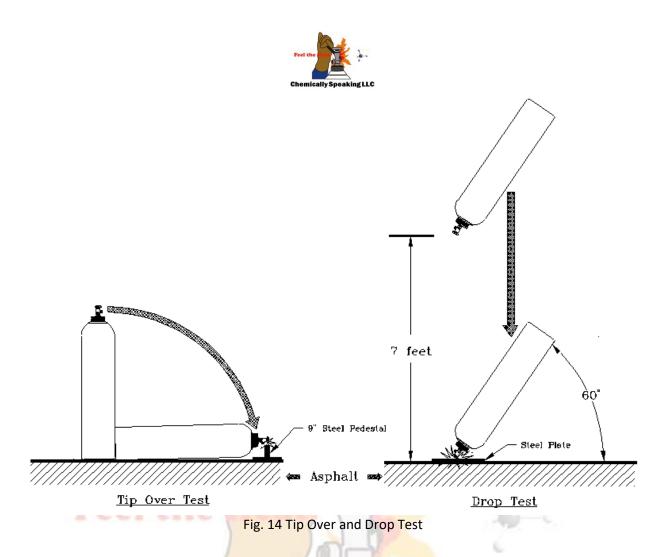
Prior to 1990



Normal impact testing American Cap Corp from 7'. One dropped per batch. Cap must be easily removed, valve must be able to work and not leak.



Fig.13: American Cylinder Cap Testing, One per batch is Dropped



Testing Without Cylinder Cap

In 1995 as a result of a Process Hazards Analysis conducted for the Solkatronic Chemicals Arsine process, it was concluded that the most likely problem at the facility would be an Operator forgetting to place a cylinder cap on the cylinder while it was being moved. In July, 1995, four cylinders were tested with a cylinder cap and cylinder simulating the DOT drop test conditions. This limited testing revealed that no leakage occurred and in May, 2000, additional tests were conducted to better understand how rugged a valve is.

emically Speaking LLC Testing, July, 1995

Four, 49 liter carbon steel seamless 3AA cylinders were tested each filled with 50 lb of water to simulate the weight of Arsine under normal conditions. These were valved with a 316L SS Manually operated spring-diaphragm valve from Superior Valve and leak tested. These were dropped using a special bracket that positioned the cylinder at a 60° angle to the ground which is estimated to create the maximum possible impact force. Impact was onto a ½ inch, carbon steel plate laid flat onto a aspahalt surface. The drop test simulated the DOT requirement, which is from 7 ft between the ground and the valve.



Immediately after the drop, the valves were visually inspected for evidence of damage. These were then pressurized to 200 psig with Nitrogen while positioned over a bucket on a scale, this would measure the leak rate as the water dripped out of the cylinder.

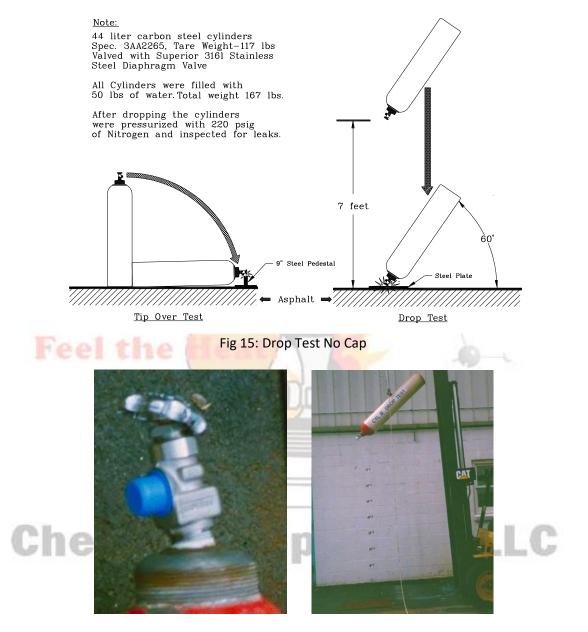


Fig 16: Drop Test No Cap



Fig 17: Tipover test

Testing, June 8, 2000

A second series of cylinder drop testing took place on 6/8/00. Two cylinders were valved with Superior tied diaphragm 316 stainless steel valves, CGA 330 with Safety. The cylinders were then leak checked to 500 psig with Nitrogen. (These were (2) previously used cylinders in the first series of drop tests). As in the first series of tests, metal shot was left in place in these cylinders. The pressure was released and each cylinder was loaded onto the lifting device and dropped from a height of 8 feet onto a 24" x 24" x ½" thick steel plate on the ground. (The 8 feet is as measured from the valve to the plate on the ground). See results of each test below.

Cylinder #1

Serial # CT-29044

Superior CGA 330 tied diaphragm, With Safety, 316 Stainless steel After pressurizing the cylinder to 250 psig, evidence of leak around the thread area was very obvious. I would classify this type of leak as a "bubbler". There was no evidence of Cross-porting or a Safety leak. In addition, there was no evidence of leakage above the diaphragms.

Cylinder #2

Serial # SKI-19199

Superior CGA 330 tied diaphragm, with Safety, 316 Stainless Steel After pressurizing the cylinder to 250 psig, evidence of leak around the thread area was very obvious. I would classify this type of leak as a "bubbler". There was no evidence of Cross-porting or a Safety leak. In addition, there was no evidence of leakage above the diaphragms.

Both cylinder valves showed no visual evidence of metal tearing, although there is definite evidence of metal pulling. Closer evaluation under a microscope should provide more detailed analysis.

Additional valves tested include Aluminum Silicon Bronze, 303 stainless, and pneumatically actuated valves. Since 1995, the DOT or CGA proscribed drop tests for cylinder caps has been modified to require a cylinder be filled to a minimum gross weight of 250 lb. The 44 liter cylinders that were being used



could not reach this gross weight full of water so steel shot was used instead to bring the total cylinder weights above 250 lb gross. In addition, we decided to increase the impact by utilizing the higher height of 8 ft as used by some cylinder cap manufacturers. This resulted in a final impact force of two times that of the earlier drop testing.

In order to understand the results of the drop testing, we have compiled relevant technical information that can be used for comparison purposes.

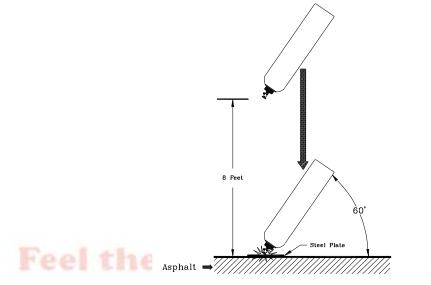


Fig. 18: Second Drop Test 2000

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⁾



Fig 19 &20: ASB and stainless steel valves



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Material	Tensile	Yield	% Elongation	Hardness,	Izod Impact	Nickel	
	Strength ,ksi	Strength, ksi		Rockwell B	Strength, ft-lb	Content, %	
ASB	79	38	30	78		Not Applicable	
303 SS	90	35	50	160	80	8-10	
316L	80	30	60	149	110	10-14	
C-22	116	59	70	95	260	55	

*the values stated above are based on the material condition that the impact strength data was found

The impact strength of a material is related to brittleness and ductility as well as % elongation. From the table above we can see that as the impact strength increases so does the nickel content. Nickel is known for its ductile characteristics. A correlation between % elongation, impact strength, and nickel can be seen.

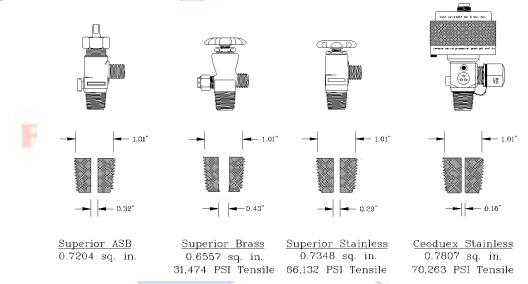


Fig. 21: Valve Cross Section and Tensile Strength

Conclusion

Both tests demonstrated the impact resistance of stainless steel valves.

Current Cap Testing Requirements

DOT under 49CFR173.40 (d)

Additional handling protection. Each cylinder or cylinder overpack combination offered for transportation containing a Division 2.3 or 6.1 Hazard Zone A or B material such as

- 1. arsine,
- 2. boron trifluoride
- 3. diborane
- 4. germane
- 5. hydrogen selenide



- 6. hydrogen sulfide,
- 7. nitric oxide
- 8. phosphine
- 9. silicon tetrafluoride

must conform to the valve damage protection performance requirements of this section. In addition to the requirements of this section, overpacks must conform to the overpack provisions of § 173.25.

(1) DOT specification cylinders must conform to the following:

(i) Each cylinder with a wall thickness at any point of less than 2.03 mm (0.08 inch) and each cylinder that does not have fitted valve protection must be overpacked in a box. The box must conform to overpack provisions in § 173.25. Box and valve protection must be of sufficient strength to protect all parts of the cylinder and valve, if any, from deformation and breakage resulting from a drop of 2.0 m (7 ft) or more onto a non-yielding surface, such as concrete or steel, impacting at an orientation most likely to cause damage. "Deformation" means a cylinder or valve that is bent, distorted, mangled, misshapen, twisted, warped, or in a similar condition.

(ii) Each cylinder with a valve must be equipped with a protective metal or plastic cap, other valve protection device, or an overpack which is sufficient to protect the valve from breakage or leakage resulting from a drop of 2.0 m (7 ft) onto a non-yielding surface, such as concrete or steel. Impact must be at an orientation most likely to cause damage.

Metal Cylinder Cap

CGA V9 has defined the following criteria for toxic and corrosive gases as per 49CFR173.

Six new caps must be tested by Drop and Tipover test.

The cap must be tested with a cylinder filled to a minimum weight of 250 lbs.

Droptest is from a height of 2 meters (7') and impact at a 30° angle to vertical on a concrete surface.

Tipover test must strike a 1 inch square by 6 inch high metal anvil.

Caps must protect valve from damage and not leak after cylinder is pressurized to full pressure. Minor damage is acceptable. The cap must be removable after impact and the valve operable.

Caps must be tested and marked for maximum valve size:

A - 4.5" high x 3.25" dia. B - 5.25" high x 3.25" dia. C - 5.25" high x 4.5" dia.

D - 6" high x 4.5" dia.

Larger cap may be used for smaller cylinder valve

Caps as a minimum have to be marked with the manufacturer, weight of test, year, etc



Fig. 22: Cylinder Cap Markings

If a metal cylinder cap is not used, the cylinder must be overpacked in an overpack capable of meeting the 7' drop impact requirements.

A plastic guard can also be used if it can perform as required. Air Liquide America in 2001 obtained a DOT Exemption E-12782 authorizing their plastic valve guard design to be used for Toxic Zone A & B Gases



Fig. 23: Air Liquide Plastic Valve Gaurds



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Point of Impact in relation to axis of valve outlet connection	Ca	þ			Valve		
Ambient Temp 0degC	Deformation without rupture	Detachment from cylinder	Hand wheel Damage	Outlet connection damage	Permenant deflection of the valve	Leak Tight	Functional
0	Yes	No	No	No	No	Yes	Yes
60	Yes	No	No	No	No	Yes	Yes
120	No	No	Yes	No	Yes	Yes	Yes
180	No	Yes	Yes	No	Yes	Yes	Yes
240	Yes	No	No	No	No	Yes	Yes
300	No	No	Yes	No	Yes	Yes	Yes
-20degC	Yes	No	No	No	No	Yes	Yes
+65degC	Yes	No	Yes	No	Yes	Yes	Yes

Many reports of flying cylinders were due to them rupturing during an overfill or a fire not to a sheared valve..

References:

- 1. "Performance Criteria for Air Operated Valves, Test Requirements/Results" Internal Ceouex S.A. memo from George Bourscheid to Russ Snyder, July 9, 1990
- 2. Tunkel, Steve J. "Gas Cylinder Drop Tests and Leak Check Tests", Hazards Research Corporation Test for Bell Communications Research, #5984, April 11,1985
- 3. "Topple Test", LSN-409, Internal Superior Valve Report, May 25, 1995
- 4. "Drop Test" Superior Valve Laboratory Test, #451, July 19, 1996

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